

COMPARATIVE PERFORMANCE OF PLA AND PET BOTTLES FOR ALCOHOL
AND SUGAR ACID SOLUTIONS

By

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ABSTRACT

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Poly (lactic acid), PLA, has gained increasing attention in the last decade as it can be obtained from renewable resources and is compostable. PLA has poor barrier properties against moisture vapor and oxygen. The barrier properties of PLA can be improved with silicon oxide (SiO_x) coating. The aim of this study was to benchmark the thermal, mechanical and barrier performance of SiO_x coated PLA bottles produced with the PlasmaxTM process against poly(ethylene terephthalate) (PET) bottles. Four different types of bottles were used: uncoated PLA (PLAU), SiO_x coated PLA (PLAC), neat PET (PETS) and 3-layer co-extruded PET (PETM) with nylon as the middle layer. Bottles containing two simulants (alcohol and sugar/acid solution) and a control (distilled water) were stored for 4 months at 37.8 °C and 70% RH. Bottles exposed to control and sugar/acidic solution showed loss of clarity in segments of the bottles, starting after 4 weeks of exposure. The heat deflection, glass transition temperature, tensile and compression strength for both PET and PLA bottles increased until week 8. After 16 weeks, coated as well as uncoated PLA containers exposed to alcohol solution became brittle. After exposure for 16 weeks, tensile strength and barrier properties decreased and showed statistically significant difference for uncoated and coated PLA bottles exposed to two simulants and the control solution. PET containers did not show any significant change as the length of exposure increased from 8 weeks to 16 weeks.

Dedicated to my family

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CHAPTER 1- INTRODUCTION

PLA belongs to the family of aliphatic polyesters, and it is a rigid thermoplastic that can be extruded as semi-crystalline or totally amorphous, depending on the architecture of the polymer backbone (i.e. the stereochemical makeup of the backbone). PLA is made by fermentation of lactic acid (LA), which can be obtained from 100 % renewable resources. Lactic acid is the basic building block for PLA and is mostly produced by carbohydrate fermentation of corn dextrose [1]. Lactic acid can exist in two optically active isomers, D-lactic acid or L-lactic acid, due to its chiral nature. High molecular weight PLA of about 100,000 Daltons can be produced using three methods: (a) direct condensation polymerization; (b) azeotropic dehydrative condensation and (c) polymerization through lactide formation. Polymerization through lactide formation was developed and patented by Cargill Inc. in 1992, and it is the most widely used method for fabricating PLA resin [1, 2]. In this method, the lactic acid is produced from fermentation of dextrose. This lactic acid is then converted into an intermediate low molecular mass poly(lactic acid) by pre-polymerization of either D-lactic acid, L-lactic acid or a mixture of the two lactic acids. Under low pressure the intermediate low molecular mass PLA is catalytically converted into a mixture of lactide stereo-isomers. The lactide mixture is then purified using vacuum distillation. Lactide is polymerized further using ring opening polymerization to obtain high molecular mass PLA [1, 3].

PLA can also be considered as a unique polymer because in many ways it acts like PET and also performs a lot more like a polyolefin [4]. Previous studies have already shown that PLA is an economically feasible polymer to be used as packaging material [1]. The amount of LA that migrates from PLA is much lower than the amount of LA found in common food ingredients [1, 5]. Therefore, PLA was recognized as GRAS for food applications [5, 6].

1.1 Applications of Polylactides

PLA was first commercially used as fibers for resorbable sutures. Then gradually many different prosthetic devices were built up from PLA. Due to the bioresorbable and biocompatible properties of PLA it has been widely studied and used in medical applications [1]. Applications of PLA can range from biomedical implants to packaging to durable consumer goods. PLA can be fabricated into various forms from fibers to films to molded components. Now-a-days, rigid PLA is also used in durable goods. For example, NEC Corporation and Unitika are manufacturing mobile phone components from kenaf fiber-reinforced PLA composites; Samsung is also planning to use PLA blends for mobile components; and Fujitsu is using PLA-based casings for laptop computers [7]. PLA can be potentially used as hollow fiber-fill for pillows, comforters, bulk continuous filament for carpets as well as yarns for apparel. PLA can be used for a broad range of applications, due to the fact that it can be stress crystallized, thermally crystallized, impact modified, filled, copolymerized and processed in most polymer processing equipment [4]. Initially, due to its high cost, PLA was only used for manufacturing high value packaging films, rigid thermoforms, food and beverage containers and coating paper. Due to recent advances in fermentation, production costs of PLA have been dramatically reduced, so now PLA is used in the arena of fresh produce, short shelf life products like fruits and vegetables [8]. Other applications include containers, drinking cups, sundae and salad cups, laminating films and blister packaging, and it is currently used for packaging mineral water [9].

1.2 Plastic Bottles

Bottles are rigid containers which consist of a body, a neck and a mouth. Normally the neck of the bottle is narrower than the body and there is an opening at the top (mouth). The mouth of the bottle is sealed often using plastic caps. Bottles can be made with glass, plastic, and

recently aluminum. They are typically used to store liquids such as water, milk, soft drinks, beer, wine, cooking oil, medicine, shampoo, inks and chemicals.

The food industry has almost completely replaced glass bottles with plastic bottles due to their light weight and relatively low production cost. Still wine, beer and other alcoholic drinks are still commonly sold in glass bottles due to the fact that they have high barrier properties as compared to plastics.

Plastic bottles can be formed using a variety of resins like high density polyethylene (HDPE), low density polyethylene (LDPE), polyethylene terephthalate (PET), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS). The choice of material varies depending upon the application. For example, HDPE is used for laundry and milk bottles; PVC for edible oil, liquor and dairy products; PP for hot fill applications like pancake syrup and PS bottles for pills, tablets and capsules [10]. PET bottles are used for packaging distilled spirits, carbonated soft drinks, and noncarbonated beverages, but the largest single application is soft drink bottles [10]. All these bottles are made from non-renewable resources.

1.3 Dissertation goal and objectives

According to some of the early theoretical studies based on solubility parameters, it has been predicted that PLA will interact with nitrogen compounds, anhydrides and some alcohols whereas it will have no reaction with aromatic hydrocarbons, ketones, esters, sulfur compounds and water [1]. Since these studies were theoretical predictions, experimental research is necessary to determine the actual compatibility of PLA with these compounds.

This study will assess the interaction of PLA with two particular solvents (alcohol and sugar solution). For this, we will compare properties of PLA with PET bottles and see whether the PLA bottles can be used for packaging alcoholic, high sugar and high acidic products for which the PET bottles are already commercially used. As previously mentioned, PLA has low water vapor and oxygen barrier properties; therefore, to overcome this drawback the PLA bottles will be coated with silicon oxide. The PLA (PLAU) and PLA silicon coated (PLAC) bottles exposed to alcoholic, high sugar/acidic and control (water) solution at 37.8 °C and 70 % RH for the duration of 4 months will be compared with PET bottles (PETS) and PET multilayer bottles (PETM) exposed to the same solutions, conditions and time.

Specifically, the optical, physical, mechanical and barrier properties of the PLA bottles and silicon oxide coated PLA bottles will be compared with commercially available PETS and PETM bottles used for beverage packaging. This objective is accomplished by conducting a four months shelf life study of the bottles under accelerated conditions (37.8 °C and 70 % RH), and comparing the properties of the bottles at weeks 0, 1, 2, 4, 8, 12 and 16. Specific goals of this thesis are:

1. To assess if a silicon oxide layer can be properly coated on PLA bottles.
2. To compare the optical properties of PLAU and PLAC bottles with commercially available

PETS and PETM bottles.

3. To determine and compare heat deflection temperature (HDT) and glass transition temperature (T_g) of PLAU and PLAC bottles with commercially available PETS and PETM bottles.
4. To assess the tensile strength and compression strength of PLAU and PLAC bottles compared with commercially available PETS and PETM bottles.
5. To compare the water vapor and oxygen transmission rate of PLAU and PLAC bottles with commercially available PETS and PETM bottles.

CHAPTER 2- LITERATURE REVIEW

2.1 Poly Lactic Acid (PLA)

Poly(lactic acid), PLA, is an aliphatic polyester, generally obtained from renewable resources such as corn [1, 11]. PLA polymers are considered environmentally friendly as they are biodegradable in composting conditions [12-14]. Biodegradable polymers like PLA are generally presumed to have inferior performance to hydrocarbon based polymers, but the mechanical performance of high molecular weight PLA is comparable to that of petroleum-based polymers such as PET and PS. PLA has a high modulus of elasticity and high stiffness. Further, PLA can also be formed into shapes with good definition like other petroleum based thermoplastics [11, 15-17]. Although PLA is at parity with conventional plastics on the aforementioned properties, some of the major drawbacks of PLA for practical applications are still significant, such as its brittleness and low toughness [11].

The building block of PLA is the lactide dimer which exists in three different forms: L-lactide, D-lactide and meso-lactide. The distinction between these forms is based upon the rotation of polarized light. The L-lactide rotates the polarized light in the clock wise direction; the D-lactide rotates the polarized light in the anti-clock wise direction, whereas the meso-lactide is optically inactive [18]. Different concentrations of these isomers yield different grades of PLA.

2.1.1 Advantages of PLA

Poly(lactic acid), PLA, polymers offer unique advantages over conventional polymers. Lactic acid is the basic building block of the polymer. It can be derived from 100% renewable resources like corn, sugar beets, etc.. PLA is compostable [1, 2, 4, 13, 19] and thus when

disposed appropriately in a composting facility will degrade. During composting, PLA mineralization releases CO₂ in the same amount as the plant feedstock used CO₂ during growth to produce the raw materials for PLA production [1, 4]. So, it can be stated that PLA is almost carbon neutral if PLA production is not included. Furthermore, currently prevalent production methods to produce PLA consume 20 to 50 % less fossil fuels compared to the processes used for production of common hydrocarbon based plastic resins [4, 20]. Thus, PLA is a relatively energy efficient polymer. All these benefits do not hinder PLA's recyclability as it can be converted back into lactic acid simply by hydrolyzing it with boiling water or steam [1, 19]. PLA, being part of the polyester family, also offers excellent flavor barrier properties, similar to those of PET [1].

2.1.2 Polylactic acid Disadvantages

Like other polymers, PLA has its limitations. One of the major limitations of PLA is poor barrier properties against gas and water vapor as compared to the petroleum based polymers presently used in the packaging industry [19]. In terms of physical properties, PLA is brittle as compared to other polymers used for packaging. This limitation, though, can be corrected and flexibility of the polymer can be increased by adding plasticizers or blending with rubbery polymers such as low modulus polymers or elastomers with low glass transition temperature (T_g). The negative impact of these additional components in the polymer matrix is that they lead to decrease in the strength and modulus of the toughened polymer. So, it is very difficult to obtain the desired stiffness-toughness balance in the final product for processing [19]. This results in PLA having a narrow processing window.

2.1.3 Manufacturing of PLA

Cargill Dow LLC has patented a method for PLA production. In this method, corn is broken down in the corn wet mill into starch and various other components like protein, fats, fibers, sugar and water. Recovered starch goes through bacterial fermentation and is converted into dextrose. Purified lactic acid is generated by processing the obtained dextrose through acidulation and many purification steps [21]. A continuous condensation polymerization technique is used to produce low molecular weight “PLA pre-polymer” using aqueous lactic acid (D-lactic acid, L-lactic acid or a mixture of the two). This pre-polymer is then converted into lactide stereo-isomers. Tin catalysis under low pressure is utilized for this purpose. The molten lactide mixture is processed through vacuum distillation and purified polymer grade lactide is obtained. Purified lactide is then converted into high molecular weight PLA with controlled optical purity by ring-opening polymerization [2, 19, 22-24]

2.1.4 Processing of PLA

PLA in its homopolymer configuration has a very narrow processing window. For example, the L-lactide homopolymer can be processed only within 12 °C of its melting point. This happens because the melting point of homopolymer is extremely high (175 °C) and close to such high temperatures, the molecular chains start to break down. This degradation behavior of PLA is similar to that of PVC [1]. To improve the processing window, the melting point is depressed by blending it with its stereo-isomer D-Lactide component in 90:10 proportions. As a result, the process window broadens to about 40 °C [6]. The main drawback of lowering of the melting point is that it also decreases the crystallization rate of the polymer to a great extent and thus affects the ultimate crystallinity achieved in the polymer [6].

2.1.5 Properties of PLA

Structure

Unmodified PLA is a linear macromolecule and its stereochemical makeup defines its molecular architecture [1]. The stereochemical composition and properties of the polymer can be controlled by polymerizing different ratios of D-lactide, L-lactide, D,L-lactide or meso-lactide during processing of the polymer [6]. PLA can be semi-crystalline or amorphous depending upon the percentage of L-lactic acid during polymerization. For example, PLA with 93% L-lactic acid is semi-crystalline while PLA produced with L-lactic acid content between 50% and 93% will be amorphous in nature [1, 25]. With currently available technology, PLA cannot be produced without meso-lactide impurities; therefore, most commercial PLAs are copolymers of L and L,D lactide [1, 26].

Thermal properties

The proportion of D-lactide in PLA affects the thermal properties of the resultant polymer. The melting temperature of pure poly(D-lactide) or poly(L-lactide) is 207°C [6, 27, 28]. During the manufacturing of the polymer, it is normal to have copolymerization, slight racemization and impurities in the polymer matrix appear. Because of these, the melting point of PLA can range between 130 and 180 °C [1, 6]. For the same reasons, the glass transition temperature can range between 55 and 65 °C [1]. Additionally, an increase in the molecular weight leads to an increase in the melting temperature of PLA and a decrease in its crystallinity [1, 29]. PLA is not thermally stable above its melting temperature, and its thermal stability is inferior to that of PS, PP, PE and PET [1]. Like other plastics, it behaves like rubber above its glass transition temperature whereas it behaves like glass between its glass transition and β transition temperatures. Below its β

transition temperature PLA is a brittle polymer [30].

According to Garlotta [6], thermal degradation of PLA starts above 200 °C and the main reasons for the degradation are hydrolysis, chain scission reactions due to oxidation, lactide reformation and inter or intramolecular transesterification reactions. On the contrary, Migliaresi et al. reported the thermal degradation of PLA was due to chain splitting and not due to hydrolysis. They did not observe any oxidation in the main chain, either. Generally the literature [1, 19, 24, 31] has identified the following main reasons for PLA's thermal instability:

- (1) Hydrolysis of polymeric chains by trace amount of water producing hydrolyzed lactic acid which works as a catalyst for further degradation,
- (2) Zipper-like depolymerization; the polymerization catalyst can initiate this degradation,
- (3) Oxidation reactions can cause chain scission in the main chain,
- (4) Intermolecular trans-esterification to monomer and oligomeric esters and,
- (5) Intramolecular trans-esterification resulting in the formation of monomer and oligomeric lactides of low molecular weight.

Mechanical Properties

Mechanical properties of all polymers depend upon factors like molecular weight, stereochemical composition, crystallinity and arrangement of crystals in the structure. For example, tensile strength increases as the molecular weight of the polymer increases [32]. When PLA is compared to commodity polymers like LDPE, HDPE, PP and PVC, PLA has higher tensile strength and flexural modulus. But when compared to PS, they both have similar properties, they are brittle, have tensile strength greater than 7000 psi, elongation at break less than 5 % and Izod impact strength less than 0.5 ft-lb/in [26]. According to Sinclair [33], tensile

strength of the PLA varies depending upon L-lactide content for example PLA having 95 % L-lactide was reported to have tensile strength of approximately 10,000 psi [26, 33]. He also suggested that the tensile strength also varies with the percentage of residual monomer present in the polymer; for example the tensile strength PLA copolymer having 5 % residual lactide is approximately 6800 psi, whereas polymer having 0 to 2 % residual lactide is around 8000 psi. Basically, residual monomer acts as a plasticizer in the polymer [33].

2.2 Polyethylene Terephthalate (PET)

PET has established itself as the plastic of choice in various applications because of a variety of advantages that it offers. PET has excellent thermal and chemical resistance, strong mechanical properties, and clarity as well as good water and gas barrier properties [10]. The combination of all these properties makes it suitable for not just packaging applications but many other applications. It is used to make fibers for apparel and to make engineering components [34, 35]. In packaging applications, it is utilized to make films, clamshell blisters for packaging fresh produce, and bottles for beverages [34]. In the USA, PET is widely used in the manufacturing of bottles for carbonated soft drinks, but in recent years, PET for non-carbonated beverage products has grown at a rapid pace [10]. PET retains good mechanical properties at elevated temperatures [34] and that makes it suitable for hot fill applications such as juice and isotonic products [36]. Because of all of its advantages over other plastic materials used for packaging, its use has become dominant. This has allowed for dedicated recycle streams and PET has become the plastic of choice when it comes to recycling. Its universal recycling symbol is “1”.

2.2.1 General Properties of PET

PET is a semi crystalline material. Total crystallinity in PET produced by solid state

polymerization can be as high as 55% [37]. The extent of crystallinity in a specific PET grade is driven by many factors such as molecular weight and its distribution, nucleating agents, chain orientation and the nature of the catalyst used in polymerization [38]. Crystallinity in PET components can be affected by processing conditions. For example rapid cooling of PET from melting temperature to below T_g produces an amorphous, transparent PET for film and clear bottle applications. A slow cooling injection process produces a PET bottle with opaque crystallized finish such as is used in hot fill applications [36]. Deformation under stress at elevated temperature is much less in semi-crystalline PET as compared to amorphous PET [10]. PET has higher tensile strength than many other general purpose packaging plastics like polyolefins, PVC, etc. For example, HDPE has a tensile strength between 31- 45 MPa while PET can have it between 48.2- 72.3 MPa [10]. Its superior clarity as compared to polyolefin materials makes it suitable for display oriented products. It has very good oxygen, CO₂ and flavor barrier [10]. Its thermal stability is well-known and it can be formed into intricate shapes with definition.

2.2.2 Manufacturing of PET

PET is a condensation polymer. The process of making the polymer is briefly described here [10, 39]. Manufacturing of PET can be divided into four steps (1) trans-esterification or direct esterification, (2) pre-polymerization, (3) melt polycondensation and (4) solid state polycondensation. PET can be manufactured through two different routes, one using dimethyl terephthalate (DMT) and the other using terephthalic acid (TPA). The basic raw materials are para-xylene and ethylene. Para-xylene is converted into either DMT or TPA. Ethylene is converted into ethylene glycol (EG). In the first step, bis(hydroxyethyl) terephthalate (BHET) is

obtained, when DMT and EG are polymerized using a trans-esterification process and methanol is generated as the by-product, which is continuously removed. In the alternate process, TPA and EG are polymerized using a direct esterification reaction and water comes out as the by-product. In the second step, BHET is pre-polymerized to a degree of polymerization (DP) of approximately 30. In the third step, the polymer is further polymerized using polycondensation reaction in order to increase DP to about 100. After this step, PET melt is solidified and formed into chips. These chips go through solid state polycondensation under vacuum and high temperature. The resulting PET has DP greater than 150, which is normally used to manufacture bottle grade resin [39]. Bottle grade PET thus has higher molecular weight, intrinsic viscosity and stronger mechanical properties compared to film grade PET.

2.3 Comparison between PET and PLA

Although PET and PLA both are polyesters, the two polymers are vastly different in structure and somewhat different in behavior. PET is aromatic polyester with a benzene ring in each of the repeating units. These benzene units make PET chains stiffer. As a result, PET chains require more energy to crystallize and to melt. On the other hand, PLA is aliphatic polyester. It has relatively small pendent methyl groups which hinder rotation, degree of order and thus, crystallization. For these reasons, the specific gravity of PLA (1.24 g/cm^3) [40] is lower than that of PET (1.34 g/cm^3) [40]. Normally PET chains are linear, while the PLA molecule tends to form a helical structure [41].

In the case of PET, the rate of crystallization can be controlled by copolymerizing it with either diethylene glycol or isophthalic acid at low levels (1-10%) [4]. Similarly in PLA the crystallization can be controlled by incorporating D-lactic acid units into L-PLA [18].

PLA has a low impact on the environment in terms of greenhouse gas emission. This is

because CO₂ generated during the biodegradation of the polymer is balanced by CO₂ consumed during the growth of plant feed stocks. LCA studies have shown that the total greenhouse gas emission over the life cycle of PLA is about 1600 Kg CO₂/ metric ton of material. This was calculated assuming that PLA will go in the compost pile. But in the case of PET incineration is considered the end of life cycle, and LCA studies have predicted that a total of 7150 Kg CO₂/ metric of greenhouse gas is emitted throughout the life cycle of PET when it is incinerated [18].

PLA is quite permeable to water, and ester linkages hydrolyze quickly along the backbone of the polymer. This is because hydrolysis is autocatalytic, and with the presence of moisture and residual monomer, it becomes even faster. For PET, the inherent rate of hydrolysis is slow and it is not autocatalytic [18]. Major properties of PLA and PET are summarized in Table 2-1.

Table 2-1. Major Properties of PLA and PET

Properties	PLA	Ref.	PET	Ref.
Melting temperature (°C)	125-178	[6]	250-265	[42]
Glass transition temperature (°C)	56-63	[6]	73-80	[10]
Heat Deflection temperature (°C)	55-65	[43]	70	[43]
Thermal conductivity x 10 ⁻⁴ (cal.cm ⁻¹ .s ⁻¹ .C ⁻¹)	2.9	[43]	5.7	[43]
Thermal expansion coefficient x 10 ⁻⁶ (°C ⁻¹)	70	[43]	70	[43]
Density (g.cm ⁻³)	1.24	[40]	1.34	[40]
Tensile strength (MPa)	68	[44]	57	[44]
Elongation at break (%)	4	[44]	30-300	[10]
Izod impact (J.m ⁻¹)	29	[44]	59	[44]
Flexural strength (MPa)	70	[43]	70	[43]
Flexural modulus (MPa)	3700	[44]	2700	[44]
Rockwell hardness	88	[43]	106	[43]
OTR (cc-mil/100 in ² day.atm) @ 20 °C, 0% RH	38-42	[45]	3.0-6.0	[46]
CO ₂ (cc-mil/100 in ² day.atm) @ 20 °C, 0% RH	170-200	[45]	15-25	[45]
WVTR (g-mil/100in ² .day)	18-22	[45]	1.0-2.08	[45]

2.4 Bottle manufacturing process

The manufacturing process for PLA bottles is essentially the same as that for PET bottles and is known as injection stretch blow molding (ISBM). ISBM can be a single-step or a two-step process. The two step process allows for better process control and more flexibility with machine efficiencies and capability. The same preform can generally be utilized with various sized

containers and varying shapes. The injection cycles are usually longer than the blow cycles and this makes the 1-step machines slower. On the other hand, 1-step machines are more energy conserving and cost efficient and justify the cost for smaller scale productions [36]. The two step ISBM process becomes prohibitively expensive for such small commercial scale activities because investment is needed for both injection machine and mold and for the blow machine and mold. Some of it is alleviated if an existing preform can be utilized for the new container.

Regardless of whether it is a one step or two step process, ISB molding allows for biaxial orientation of the polymer. The stretch rod provides orientation in the axial direction, and the compressed air that forms the container introduces orientation in the hoop direction. Higher orientation allows for better clarity and at the same time increases crystallinity, accounting for increased mechanical and barrier properties of the bottle [1, 10, 25, 30, 36, 46]. These processes are described below.

2.4.1 Single Step ISBM process

In the single-step process, the resin is melted and formed into a preform. The preform is then cooled to 100- 120 °C, well below the melting temperature of PLA but above its glass transition temperature. This is most efficiently done in the same machine and cooling is carried out at the conditioning station. Once cooled to an appropriate temperature, the preform is stretch blown at the blow molding station [30].

2.4.2 Two Step ISBM process

The two-step ISBM process, also referred to as the cold process, is essentially the same as the single step process except the preform is cooled to ambient temperature [36] before blowing and then reheated just before blowing. This allows for maximizing production capacities since it allows for concentration on individual processes or steps while the preforms are stored in the

warehouse in the interim.

In the first step, the preforms are made using an injection molding machine. These preforms are later blown in a separate stretch blow machine. In injection molding, the molds get clamped and the extruder nozzle moves forward to inject the PET or PLA melt into the mold cavity. In order to compensate for the material shrinkage during cooling in the mold, the screw is kept in the forward position by a holding pressure. After the holding phase, the nozzle shuts down and the screw begins to retreat to its original position to initiate the next cycle. The injected preform is cooled to ambient temperature [10].

In the second step, the preform is conveyed on a rotating spindle and passed through an infra-red bank oven, where it is heated to 85 – 95 °C, the optimum temperature for blow molding in a 2-step process [46]. The heated up preform is transferred to the blow mold and the blow nozzle moves down to make a seal on the preform neck. A stretch rod then moves inside the preform towards the tip of the preform at a speed of 1.2 - 2 m/s and stretches the preform towards the base in the blow mold [46]. Compressed air at relatively low air pressure of about 0.2 - 0.5 MPa is simultaneously blown into the preform to partially inflate the preform, so that it does not touch the stretch rod. Once the stretch rod has traveled to the base cup, the air pressure is increased to 3.8 – 4.0 MPa to form the preform into the desired shape with good definition [30].

2.5 Techniques to improve the barrier properties of PLA

As pointed out earlier, PLA has poor barrier properties against moisture vapor, oxygen and many other permeants. In previous studies, four main approaches to improve the barrier properties of PLA have been described. These are 1) fusing nano or micro fillers in the polymer matrix, 2) blending with polymers with better barrier properties, 3) using a multilayer structure

and 4) applying a barrier coating. Out of the four approaches, two have obtained commercial acceptance and are commonly used in the industry. One of them is using multilayer structures and the other is applying a barrier coating. When PLA is used in a multilayer structure with barrier polymers which are often conventional non-biodegradable hydrocarbon based plastics, it negatively impacts the biodegradability and compostability of PLA. This undermines the most important benefit of using PLA as a packaging material. Thus, at present, coating with barrier materials is the only practical way of enhancing barrier properties of PLA. Some of these processes are discussed and currently they are commercially available for coating PET bottles.

PLA can be coated with thin layers of organic or inorganic coatings. These coatings such as silicon oxide (SiO_x), aluminum oxide (Al_2O_3), and diamond-like coating (DLC) have been proved to improve the barrier of PET bottles against oxygen and organic vapors [36, 47, 48]. These coatings are applied either under atmospheric pressure or under vacuum.

2.5.1 Non-vacuum coating/ Liquid coating Technique

Coating carried out under atmospheric pressure includes applying a liquid phase chemical solution and curing it with ultra-violet light or thermal radiation. This technique allows for coating to be carried out without vacuum, unlike traditional chemical vapor deposition technique and thus is more energy efficient. Non-vacuum or atmospheric based coatings/ liquid coatings have many advantages over vacuum coating techniques in terms of food contact regulations, recyclability and cost. As the coating is applied on the external surface of the bottles, it does not come in contact with the food and thus does not fall under food contact regulations. The coating can be easily removed by an aqueous cleaning solution in the recycling process, so it does not affect the recyclability of the base material. This coating method is considered cheaper as compared to the vacuum deposition technique since the vacuum chamber adds cost to the bottles

[49]. One of the disadvantages of this technique is that the coating is susceptible to scratches, scuff and physical damage during transportation. A few of these techniques are detailed here.

BairocadeTM Barrier Coating

One of the first of the barrier coatings was BairocadeTM (Pittsburgh, U.S.A) gas barrier coating introduced by PPG Industries [36]. This coating consists of epoxy-amine. It is electrostatically sprayed on the external surface of PET bottles under atmospheric pressure. Organic solvents are evaporated and the polymer film is cross-linked or thermoset by curing it at 65 °C in an infrared oven [50]. The cross linked coating is about 6 to 8 microns thick, enough to offer excellent CO₂ and O₂ barrier with PET containers [36, 51]. This coating is currently used for both carbonated soft drinks (CSD) and juice applications [50]. To apply this method to coat PLA will require modification in the curing temperature. PET has a glass transition temperature close between 73- 80 °C, [10] and so it can sustain the curing temperature of 65 °C. PLA has a glass transition temperature between 56- 63 °C [6] and will have problems if cured at 65 °C.

BLOXTM

BLOXTM is a barrier coating developed by Dow Chemicals [36, 49]. It is an amorphous thermoplastic epoxy resin which is clear, tough and highly adhesive. This material could be used as a barrier layer in multilayer structures or as a coating material for the bottles. BLOXTM is claimed to provide barrier to oxygen and carbon dioxide which is 10 times better than polyethylene naphthalate (PEN). It is also claimed to be more cost competitive than the other alternative barrier polymers. Dow (Midland, MI, U.S.A) and Tetrapak (Geneva, Switzerland) collaborated to produce PET performs with a layer of BLOXTM called Sealica [36, 48, 52].

NanolakTM

An exterior coating by InMat[®] and introduced by the trade name NanolakTM is an

aqueous suspension of nano-dispersed silicates such as vermiculite and montmorillonite dispersed in a polyester matrix. The coating can be applied to the substrate by a spray or gravure coating process. There are hundreds of nano-dispersed silicate platelets per micron of coating thickness. This dispersion creates a tortuous path for the permeating molecules such as oxygen, carbon dioxide and aromatic compounds and thus improves the barrier properties of the material. InMat[®] has claimed that NanolakTM provides a very efficient barrier option which can reduce the permeability of uncoated substrate by up to 100 times. For oxygen barrier, 1-2 microns of this coating is as effective as 12 microns of EVOH film [53].

Combustion Chemical Vapor Deposition (CCVD)

Microcoating Technologies Inc., (Atlanta, GA, U.S.A) now known as nGimat also developed a nanopowder coating which employs a combustion chemical vapor deposition (CCVD) technique to coat nanopowder on polymers. The manufacturer claims that the coating provides good barrier against oxygen and carbon dioxide and can increase the shelf life of 20 oz. carbonated soft drink bottles from 10 to 30 weeks [54, 55].

2.5.2 Vacuum Based coating

In this technique the intended coating materials are heated to form gases and then deposited as a solid thin layer on the substrate. The coating can be formed by condensation i.e. physical vapor deposition (PVD), or by chemical reaction to form a new compound after volatilization, i.e. chemical vapor deposition (CVD) [56, 57]. Most of this process is completed under vacuum.

When coating with Al_2O_3 or SiO_x , thin layers of oxides are formed. Oxides are chemically inert. They are stable even at high temperatures and are resistant to oxidation. Since oxygen is the most electronegative divalent element in the periodic table, the oxides formed have

a significant degree of ionic bonding. Thus, these coatings have characteristics of ionic crystals, which means high optical transparency, high electrical resistivity, low thermal conductivity and chemical stability [56, 57]. In order to improve the gas barrier properties of the films and bottles, mostly silicon and aluminum oxide coatings have been used in the packaging industry. Silicon oxide coating has been gaining significant ground in recent times and is discussed here.

Silicon Oxide Coating

Silicon oxide, commonly known as silica is a widely used industrial coating material in the optics and microelectronics sectors. Silica has a high melting point of 1610 °C and a coefficient of thermal expansion of $0.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$. There are many reasons for the popularity of silicon oxide coating (SiO_x , $(1 < x < 2)$) in packaging applications. It has glass-like clear transparency and high barrier properties. It is microwaveable and recyclable. The most commonly used technique for depositing a thin layer of SiO_x on a substrate is chemical vapor and plasma enhanced chemical vapor deposition (PECVD). Earlier studies have already suggested that the silicon oxide coating has superior barrier properties when compared to high barrier polymers like PVDC and EVOH [47, 49]. Also these coatings are not influenced by moisture and temperature. In order to use silicon oxide coating for practical applications, it has to be laminated due to its intrinsic brittleness, and poor adhesion and mechanical properties [47]. There have been new technical developments like applying a cushion layer between the substrate and the silicon oxide coating, using a heated dry gas before coating, as well as a complicated deposition system. These have made it possible to now commercially produce PET bottles coated with a silicon oxide layer [58, 59].

Currently there are three commercially available technologies for applying SiO_x coating either to the inside or outside of PET or PLA bottles:

- 1) Glaskin (TetrapackTM)
- 2) BestPET[®] (Coca Cola/ Krones)
- 3) Plasmax[®] 12D SIG

Glaskin

This technology was developed by TetrapakTM to deposit a transparent layer of silicon oxide on the inside of the bottle. The source of SiO_x is hexamethyl disiloxane, which reacts with oxygen to provide the coating material. Microwave energy excites a gas which deposits a thin glass-like coating of around 10 – 20 nm on the interior walls of bottles [50]. TetrapakTM claims that the coating is elastic and crack-resistant and improves the oxygen barrier up to 17 times and carbon dioxide barrier up to 25 times as compared to uncoated containers [60, 61].

BestPET[®] (Coca Cola/ Krones)

This technology was developed by Krones in cooperation with Coca Cola. This is an energy intensive process that generates ions of silicon oxide and a clear coating is formed under vacuum on the external surface of bottles. This technique is used with single serve CSD bottles as well as hot-filled juice and beer containers [50].

Plasmax[®] 12D SIG

This coating technique was developed by SIG Corpoplast. This silicon oxide coating process uses a plasma impulse chemical vapor deposition (PICVD) system. In this system two layers are deposited on the inside of the container, the first is an adhesion layer which helps to bind the silicon oxide layer with the polymer layer. Then it is followed by a barrier layer, silicon oxide [62]. The bottle is placed in a vacuum chamber and a mixture of oxygen and gaseous hexamethyl disiloxane is ignited with microwave pulses. Ignition of these gases creates a cold plasma which leads to decomposition of the hexamethyl disiloxane into SiO_x, CO₂ and water.

The SiO_x forms the thin coating on the internal surface of the bottle. The by-products CO_2 and water, are removed from the system with the help of vacuum [50, 62, 63]. Oxygen barrier is claimed to be improved more than 10 fold and the carbon dioxide barrier is improved by up to 7 fold [50].

Diamond Like coating

It is basically an amorphous coating of carbon. There are two main commercially available methods, detailed below.

Actis (Amorphous Carbon Treatment on Internal Surface)

This technique was developed by Sidel [50]. Acetylene is used to generate the amorphous carbon coating. A microwave assisted process excites acetylene into the state of a cold plasma, depositing a coating of hydrogenated amorphous carbon. The thickness of the coating is around 100 nm. Oxygen barrier is claimed to be improved by up to 34 folds and carbon dioxide barrier is improved up to 7 times [50]. The applications of this system range from CSD containers to hotfilled juice bottles to beer containers.

Plasma Nano Shield (PNS)

This process has been commercialized by Kirin Brewery Company in cooperation with Mitsubishi, Japan [50, 64]. The amorphous coating of carbon is generated using plasma enhanced chemical vapor deposition (PECVD). There are internal and external electrodes that ionize acetylene gas with the help of a radiofrequency source, depositing the coating. A coating thickness of around 20-40 nm provides oxygen barrier improvement by up to 11 times and carbon dioxide barrier is improved up to 26 times [64]. Reduced flavor sorption is also claimed [50, 64].

CHAPTER 3- MATERIALS AND METHODS

3.1 Materials

The four different types of bottles used in this study were poly(lactic acid) (PLAU), PLA coated with silicon oxide (PLAC), poly(ethylene terephthalate) single layer (PETS) and PET multi-layer (PETM) bottles manufactured by AMCOR PET packaging, Ann Arbor, and silicon oxide coated by GMBH, Germany. The simulants used were ethyl alcohol (40% v/v from Pharmco-Aaper, Brookfield, CT, USA), sugar and tartaric acid obtained from Sigma-Aldrich Inc., (St Louis, MO, USA) and distilled water from Country Fresh LCC (Grand Rapids, MI, USA).

3.2 Filling operation

PLAU, PLAC, PETS and PETM bottles, the 55 gallon drums (used for preparing the solutions) and the filling machine (Pro Fill 1000 volumetric filling machine, Oden, Tonawanda, NY) were sanitized with 2% v/v chlorine solution. The bottles were sanitized by immersing them in the sanitizing solution and draining it out and then rinsing the bottles with clean tap water. The filling machine was sanitized by running with 2 % v/v chlorine solution for 30 minutes and then rinsing it with water for at least 15 minutes prior to filling the bottles. The solution was filled into the bottles with the help of the Pro Fill 1000 volumetric filling machine. In the first round 588 bottles (196 bottles each of PLA, PLAC, PETS and PETM bottles) were filled with water (control). Similarly, 588 bottles were filled with alcohol and high acidic and sugar solutions, respectively. The composition of the solutions is described in Table 3-1. After filling, the bottles were manually labeled and closed with 19 – 20 inch-pound torque using an electronic torque tester from Secure Pak, Inc., (Maumee, Ohio, USA) Then the bottles were stored in an environmental chamber at $40 \pm 1^{\circ}\text{C}$ and $70 \pm 2\% \text{RH}$

Table 3-1. Composition of solutions

	40 % ethyl alcohol solution	Acidic/Sugar solution	Control (Water)
Number of bottles	588	588	588
Total Product Needed	200L	200L	200L
Composition	Water : 120L Ethyl alcohol : 80L	Water :181.9L Tartaric acid : 1.1Kg Sugar : 17Kg	Water: 200L

3.3 Surface Analysis

3.3.1 Atomic force Microscope (AFM)

Surface roughness of the bottles was measured using an AFM-Digital Instruments Nanoscope IV. The samples were taken from the neck, shoulder and body of the bottles. The samples were mounted on a steel disc and the scanned area considered was 10 μm X 10 μm and scan angle 0 degree and resolution 512 lines per linear inch. The tapping mode was used to determine the surface roughness.

3.3.2 Optical Microscope

Samples measuring 1 x 1 cm^2 were taken from the body of the bottles placed on the microscope platform, and observed using a Keyence Digital Microscope VHX 600 (Itasca, IL, USA) at 1000x magnification.

3.4 Visual inspection

Pictures of the filled and empty bottles were taken after 1, 2, 4, 8 and 16 weeks with a

Canon EOS (SLR) camera (Canon, NY, US). In addition, the bottles were inspected for color, texture, shape, and changes in dimensions.

3.5 Physical Properties

3.5.1 Heat Deflection Temperature (HDT)

The heat deflection temperature (HDT) of the samples was measured by using a dynamic mechanical analysis DMA 2980 (TA instruments, New Castle, DE, US) according to a modified ASTM D 648 method. According to ASTM D 648, a typical test specimen must be in the form of a rectangular bar with the average size of 12 x 55 x 2 mm. However, the average bottle thickness was 0.3 mm, much thinner than the standard specimens. As a result, the bottle single specimens could not withstand the weight of the clamp when the clamp was locked. The samples bent before the test started. Figure 3-1 shows the bottle specimens before and after the clamp was locked. To solve this problem 3 rectangular specimen of average size 12 x 55 mm² were cut from the bottles and stacked together this was considered as one sample for the testing. The samples were placed on the clamp with the inside surface down. After this modification, samples kept their rigidity and did not bend after locking the clamp. The three-point bending mode was used to apply a stress level of 0.455 MPa (0.66 psi). The samples were heated at a rate of 5 °C/min from room temperature to 120 °C. The HDT was defined as the temperature at which 0.2 % strain occurred. Three replicates of each bottle set were tested.

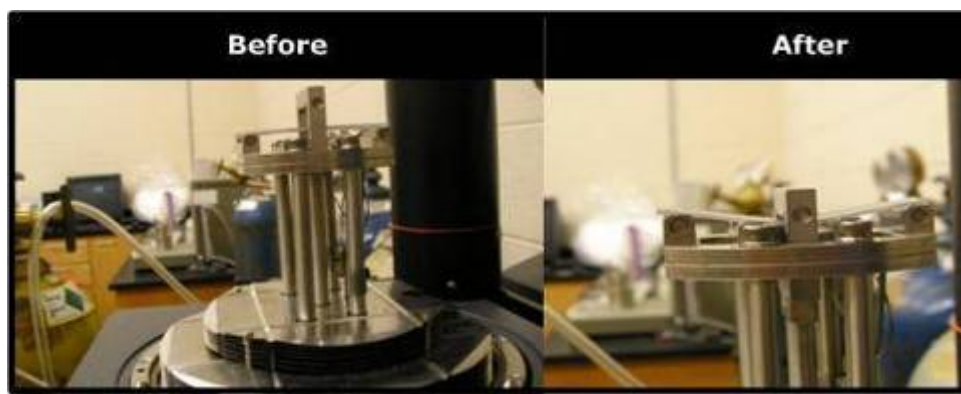


Figure 3-1. DMA samples before and after the clamp was locked.

*For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this thesis (or dissertation).

3.5.2 Glass transition temperature

The glass transition temperature (T_g) of the samples was measured by using a dynamic mechanical analysis DMA 2980 (TA instruments, New Castle, DE). The test specimen dimensions were 6 X 29 mm. The T_g was determined using the tension mode clamp. The specimen was clamped, and the temperature was increased from room temperature to 120 °C with an increment of 5 °C/ min and cooled down to room temperature.

3.6 Mechanical Properties

3.6.1 Tensile strength

Samples were conditioned according to ASTM 882-02 requirements at $23 \pm 1^\circ\text{C}$ and $50 \pm 2\%$ RH for at least 24 hr before testing. Five (1" width samples were cut along the vertical sections of the conditioned bottles and the tensile properties and elongation of the five samples from each bottle were measured on an Instron universal tensile tester model 5565 from Instron, Canton, MA according to ASTM D 882-02. The strain rate employed was 0.5 in/in.min; the initial grip separation was 1 in; and a crosshead speed (rate of grip separation) of 2 in /min was

used. The grips used were of the pneumatic type.

3.6.2 Compression Strength

The crush resistance of the bottles was measured by a compression test. The specimens tested by this technique were free of obvious defects such as rocker bottoms or bent necks. Compression strength of the PLA bottles was measured according to ASTM D2659-95 (2001). The crush resistance of the bottles was measured by a compression test. Samples were conditioned at 23 ± 1 °C and $50 \pm 2\%$ RH for at least 24 h before testing. The machine used was a compression tester from Lansmont Corporation, Lansing, MI, with a preload of 0, yield 50% and stop force of 5000 lb.

3.7 Barrier properties

3.7.1 Water vapor transmission rate (WVTR)

Water vapor transmission rate of the bottles was measured in accordance with ASTM F 1249-06 [79] using a PermatranTM 3/33 from Modern Controls Inc. (MoCon), Minneapolis, MN. The testing parameters were 37.8 ± 1 °C and 100 % RH. Two samples of each type of the bottle (PLA, PLAC, PETS and PETM) were tested. The bottles were sealed to metallic mold using a super glue epoxy adhesive. The mold was attached to the Permatran system using copper tubing to allow the carrier gas (N₂) to flow into the bottle and back to the detector. The assembly was sealed in an LDPE pouch with 2 wet sponges in order to produce 100% RH inside. The test was run until 5 steady state points were achieved. The average of the last 5 points was taken to calculate the WVTR of the bottles.

3.7.2 Oxygen transmission rate (OTR)

Oxygen transmission rate of the bottles was measured in accordance to ASTM D 3985-05 using an OxtranTM 2/22 from Modern Controls Inc. (MoCon), Minneapolis, MN, US. The testing parameters were 23 ±1 °C and 0 % RH. Two samples of each type of bottle (PLA, PLAC, PETS and PETM) were tested. The bottles were sealed to metallic mold using super glue epoxy adhesive. The mold was attached to the Oxtran system using copper tubing to allowing the carrier gas (N₂) to flow into the bottle and back to the detector. The assembly was sealed in a LDPE pouch and 100% oxygen was introduced in the pouch with the help of a Tygon[®] tube. The test was run until 5 steady state points were achieved. The average of the last 5 points was taken to calculate the oxygen transmission rate of the bottles.

3.8 Weight loss

In order to determine and compare weight loss of solution in various types of bottles during the storage, a digital weighing balance with sensitivity of 0.01g was used. Initially weights of all the bottles were taken after filling. Three bottles of each type and each solution were removed from storage after 1, 2, 4, 8 and 16 weeks and weighed again. The weight loss was calculated as:

$$\text{Weight Loss \%} = \frac{\text{Weight}_{\text{Initial}} - \text{Weight}_{\text{final}}}{\text{Weight}_{\text{Initial}}} \times 100$$

CHAPTER 4- RESULTS AND DISCUSSION

In an associated body of work completed by Azhari, change in molecular weight of the polymer was observed. In this current work and Azhari's study, samples were shared for various tests. Azhari observed that the molecular weight of PLA for both PLAU and PLAC containers exposed to sugar and control solutions as well as unexposed bottles increased throughout from week 0 to week 16. Similar results were observed for both materials in alcoholic solution until week 8 but at the week 16 mark, a significant drop in molecular weight of the polymer was observed [65]. This change in the molecular weight of PLA over time has been used to explain some of the changes in polymer properties observed as part of this study. The increment of molecular weight is attributed to the possibility of cross-linking and hydrogen bridging between the molecular chains. The reduction in molecular weight from week 8 to week 16 when exposed to alcohol solution can be explained with hydrolysis and chain scission. Below is the table of molecular weight change adapted from Azhari's work [65].

Table 4-1. Molecular weight for PLAU and PLAC

reproduced from Azhari [65].

Week	PLAC			PLAU		
	Mn (Da)	Mw (Da)	PDI	Mn (Da)	Mw (Da)	PDI
Alcohol Solution						
0	83689 ±323	144467 ±766	1.73 ±0.01	83075 ±9630	143125 ±4785	1.73 ±0.16
1	89660 ±2636	170547 ±2959	1.90 ±0.03	85332 ±1361	147352 ±1829	1.73 ±0.05
2	94246 ±5939	185778 ±1878	1.96 ±0.02	85695 ±2745	161314 ±3544	1.88 ±0.03
4	92648 ±3263	184714 ±4798	1.96 ±0.08	94982 ±6928	202392 ±6928	2.14 ±0.11
8	84853 ±1176	176984 ±3398	1.91 ±0.05	86967 ±1759	154302 ±3139	1.78 ±0.07
16	20641 ±1657	27427 ±3338	1.32 ±0.24	21328 ±1178	25865 ±1273	1.22 ±0.10
Sugar/ acidic Solution						
0	83689 ±323	144467 ±766	1.72 ±0.01	83075 ±9630	143125 ±4785	1.73 ±0.16
1	92120 ±1750	184027 ±1753	1.99 ±0.04	87820 ±1640	164972 ±4454	1.88 ±0.04
2	87348 ±4810	184027 ±3042	2.02 ±0.08	92942 ±7591	184977 ±2825	2.00 ±0.05
4	93257 ±4753	201298 ±5165	2.16 ±0.10	92031 ±3406	179935 ±7229	1.96 ±0.05
8	120780 ±8456	220496 ±1656	2.55 ±0.05	96231 ±2261	191607 ±2262	1.99 ±0.04
16	24856 ±4405	204043 ±3518	2.09 ±0.07	98946 ±1448	188075 ±2706	1.99 ±0.04
Control Solution						
0	83689 ±323	144467 ±766	1.73 ±0.01	83075 ±9630	143125 ±4785	1.73 ±0.16
1	97381 ±994	195920 ±2687	2.01 ±0.18	86475 ±4979	170840 ±6621	1.98 ±0.18
2	88594 ±2613	177257 ±2515	2.00 ±0.03	97833 ±2985	195941 ±7591	2.00 ±0.04
4	98497 ±4734	211973 ±2136	2.16 ±0.11	94841 ±1402	203929 ±4838	2.21 ±0.47
8	97813 ±6152	203771 ±1698	2.10 ±0.05	96232 ±1336	213395 ±3334	2.22 ±0.05
16	97808 ±2332	200416 ±1497	2.01 ±0.04	97051 ±2226	202284 ±2004	2.08 ±0.28
Empty Bottles						
0	83689 ±323	144467 ±766	1.73 ±0.01	83075 ±9630	143125 ±4785	1.73 ±0.16
1	85789 ±3203	152875 ±4894	1.90 ±0.09	84113 ±3505	144211 ±1587	1.89 ±0.13
2	112582 ±1118	200845 ±2337	1.78 ±0.01	110591 ±4652	196970 ±1636	1.78 ±0.01
4	97904 ±3453	196330 ±3377	2.00 ±0.04	95497 ±4231	190413 ±7823	1.99 ±0.01
8	98223 ±7000	200085 ±8997	2.04 ±0.08	106531 ±9232	212585 ±8346	2.00 ±0.02
16	96861 ±2490	192850 ±2490	1.99 ±0.04	98229 ±2216	196842 ±3175	2.00 ±0.02

Note:

Mn = Number average molecular weight (Da)

Mw = Weight average molecular weight (Da)

PDI = Polydispersity index

4.1 Visual Inspection

After weeks 1, 2, 4, 8 and 16, all four types of bottles i.e., neat PLA, PLA with coating, neat PET and multilayer PET containers that had stored alcohol, sugar/acidic and water were removed from the environmental chamber. Solutions from the bottles were removed and the bottles were stored at 23 °C and 50 % RH in the conditioning room for 24 hours. The physical state of the containers was visually recorded with pictures taken using a Canon EOS (SLR) camera, and they are shown in Figures 4-1 to 4-12. The changes in the physical appearance of PLAU and PLAC bottles were similar in the study and no change was observed in the physical appearance of PETS and PETM bottles. Therefore pictures shown below are of PLAC bottles only.



Figure 4-1. Unexposed PLAC bottles



Figure 4-2. PLAC bottles exposed to alcohol solution after 4 weeks



Figure 4-3. PLAC bottles when exposed to alcohol solution at week 8



Figure 4-4. PLAC bottles when exposed to alcohol solution at week 16



Figure 4-5. Unexposed PLAC bottles



Figure 4-6. PLAC bottles when exposed to sugar solution at week 4



Figure 4-7. PLAC bottles exposed to sugar solution at week 8



Figure 4-8. PLAC bottles when exposed to sugar solution at week 16



Figure 4-9. Unexposed PLAC bottles



Figure 4-10. PLAC bottles when exposed to control solution at week 4



Figure 4-11. PLAC bottles when exposed to control solution at week 8



Figure 4-12. PLAC bottles when exposed to control solution at week 16

Visual inspection revealed that the PLAC as well as PLAU bottles that were exposed to alcohol showed similar aging symptoms. After week 4 and 8 loss of clarity was observed in the upper most section (finish part) and the bottom section, which could be attributed to an increase in the crystallinity of PLA due to aging as previously shown by Lim et al [30]. An increase in the molecular weight, which might have been due to cross linking in the polymer may have also decreased the clarity of the bottles; and/or water sorption and swelling in the material may also have led to loss of clarity in the bottles. After 16 weeks it was observed that both PLAU and PLAC bottles stored in alcoholic solution had developed cracks throughout the bottles, as displayed in Figure 4-4. The main reason for these changes can be due to hydrolysis of the material. In table 4-1, we can see the significant decrease in the molecular weight of APLAU and

APLAC at week 16 mark. In the case of PLAU and PLAC bottles filled with sugar/acidic solution, the upper-most sections (finish part) and bottom of the bottle lost clarity after 4 weeks and clarity kept decreasing with time. PLAU and PLAC bottles stored with the control solution also had clarity loss. The main reasons, which may be attributed to these changes, are same as explained for bottles exposed to alcohol. It was also observed that 10 PLAC bottles out of 32 containing control solution when inspected after 16 weeks developed cracks at the shoulder and the body of the bottles, which needs further investigation. The finish and the bottom also became opaque. There was no change in physical appearance of PETS and PETM bottles stored with all three solutions.

4.2 Physical Properties

4.2.1 Heat Deflection temperature (HDT)

The HDT of the samples was measured by using a DMA and they are reported in Figure 4-13 to 4-15. HDT for the PETM bottles are not reported below because during sample preparation the three layers of all the multilayer bottles delaminated.

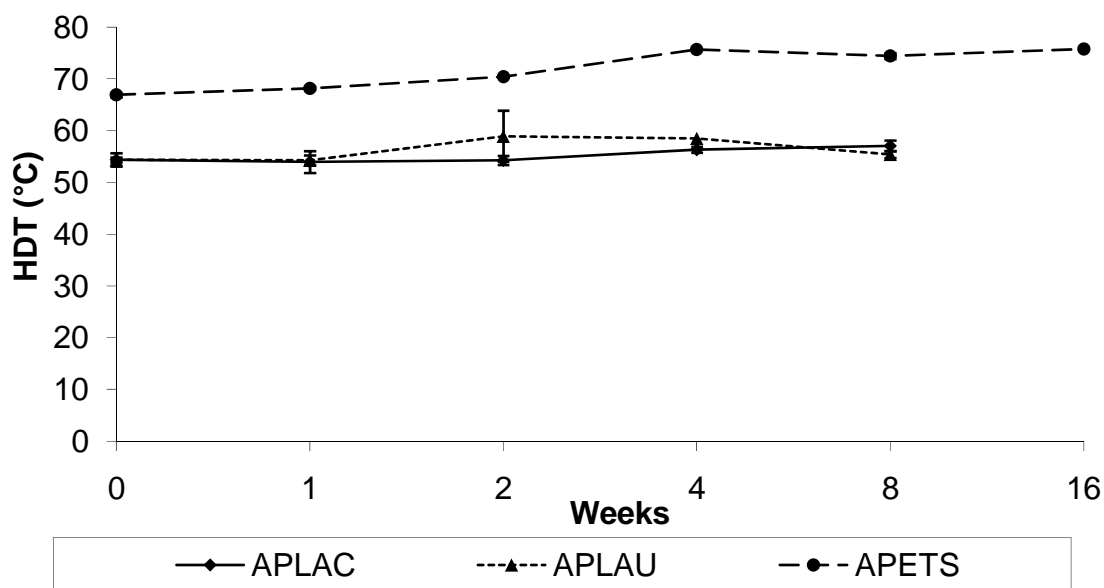


Figure 4-13. HDT values when exposed to alcohol solution

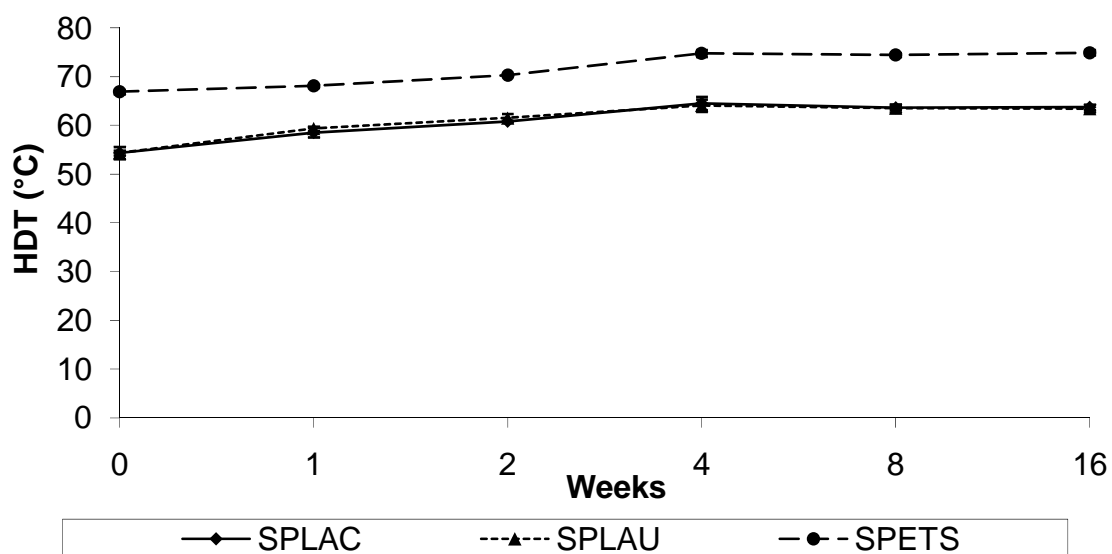


Figure 4-14. HDT values when exposed to sugar/acidic solution

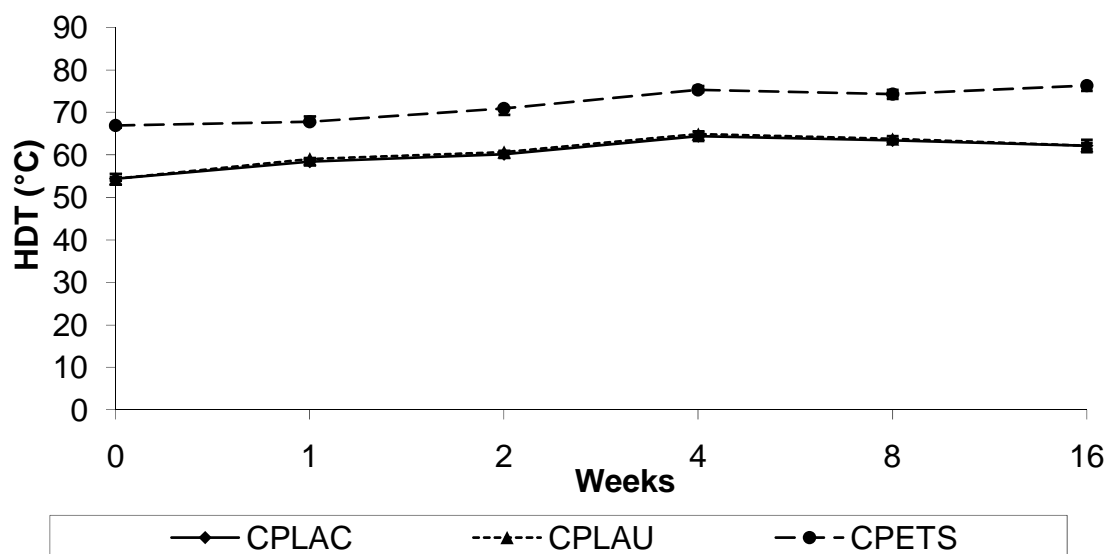


Figure 4-15. HDT values when exposed to control solution

Table 4-2. Heat deflection temperature, °C

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	54.4 ± 1.3aAα	54.3 ± 0.9aAα	58.9 ± 4.9bAα	58.5 ± 0.0abAα	55.4 ± 0.7aAα	ND
	Sugar		59.4 ± 0.4bBα	61.5 ± 0.9bcAα	64.1 ± 1.3cBα	63.6 ± 0.9cBα	63.5 ± 0.8cAα
	Control		59.1 ± 0.2bBα	60.7 ± 0.4bcAα	64.9 ± 0.7dBα	63.7 ± 0.7cdBα	62.2 ± 1.4bcdAα
PLAC	Alcohol	54.4 ± 0.5aAα	54.0 ± 2.1aAα	54.3 ± 0.9aAβ	56.3 ± 0.5aAα	57.1 ± 1.0aAα	ND
	Sugar		58.6 ± 1.0bBα	60.9 ± 0.2bcBα	64.5 ± 1.4dBα	63.6 ± 0.4cdBα	63.7 ± 0.5cdAα
	Control		58.4 ± 0.8bBα	60.2 ± 0.8bcBα	64.4 ± 1.0dBα	63.4 ± 0.4cdBα	62.2 ± 0.7cdAα
PETS	Alcohol	66.9 ± 0.4aAβ	68.2 ± 0.3abAβ	70.4 ± 0.2bAγ	75.7 ± 0.0cAβ	74.4 ± 0.6cAβ	75.8 ± 0.1cA
	Sugar		68.1 ± 0.3abAβ	70.3 ± 0.1bAβ	74.8 ± 0.7cAβ	74.5 ± 0.4cAβ	74.9 ± 0.6cAβ
	Control		67.8 ± 0.2abAβ	70.9 ± 1.3bAβ	75.3 ± 0.4cAβ	74.3 ± 1.0cAβ	76.3 ± 1.1cAβ

Note: Values are reported as average ± standard deviation.

ND: values could not be determined due to brittleness of the bottles at week 16.

Values followed by the same small letters between columns are not statistically significantly different at $\alpha=0.05$ (Bonferroni test $p\text{-value}<0.0001$). Values followed by the same capital letters for the same polymer and different solution do not have statistically significant difference at $\alpha=0.05$. Values followed by the same Greek letters for different materials and the same solution do not have statistically significant differences at $\alpha=0.05$.

PETS bottles' HDT values were different and higher than the PLAU and PLAC ($p < 0.0001$) with or without exposure to simulants. PLAU and PLAC bottles HDT were not significantly different ($\alpha = 0.05$) when exposed to similar conditions.

HDT for PLAU and PLAC increased approximately 17% in 4 weeks when exposed to sugar or control solution. HDT for PLAU bottles exposed to alcohol did not change in the first week, but it increased around 8% in the next 3 weeks. At the end of 8 weeks, HDT decreased by 6% compared to week 4. HDT could not be measured at the end of 16 weeks since the plastic had become too brittle. For PLAC bottles exposed to alcohol, HDT did not change significantly for the first 8 weeks, but after 16 weeks, plastic became so brittle that HDT could not be measured. HDT values of unexposed PET bottles were around 66.9 ± 0.4 °C. HDTs were higher after 4 weeks as compared to the first 2 weeks for all the three solutions. HDT at 2 weeks was greater than the initial HDT.

The increase in the HDT of PLA and PET in the solutions can be associated with the increase in molecular weight of the material as measured for PLA. The cross linking in the polymer might be the main reason for the increase in the molecular weight. We were not able to determine HDT for PLAU bottles exposed to alcohol (APLAU) and PLAC bottles exposed to alcohol (APLAC) after week 16 because the bottles became very brittle and also there was significant decrease in the molecular weight.

4.2.2 Glass transition temperature

The glass Transition temperature (T_g) of the samples was measured by using a DMA. T_g was determined using the tension mode. Measurements were made at weeks 0, 1, 2, 4, 8 and 16. Glass transition temperature of PETM could not be determined as these were multilayer bottles.

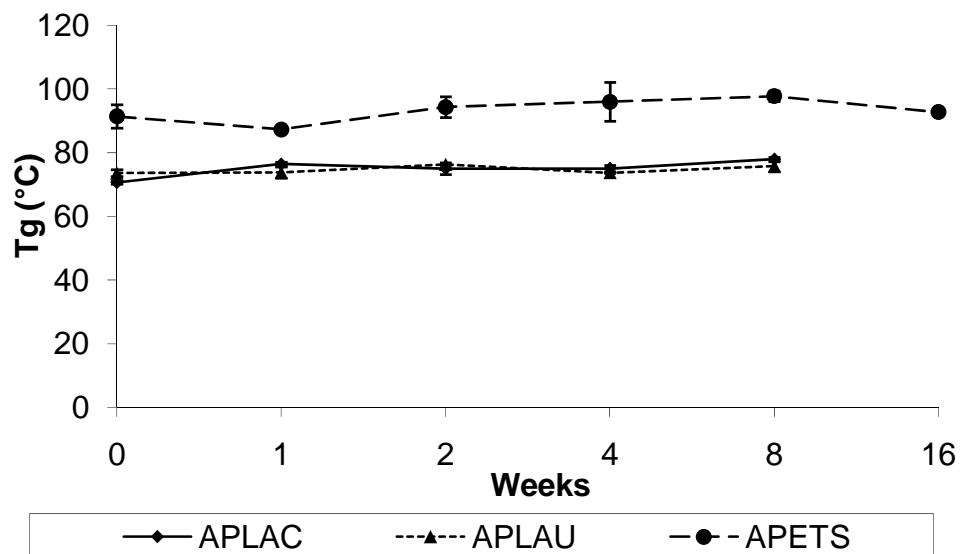


Figure 4-16. T_g when exposed to alcohol solution

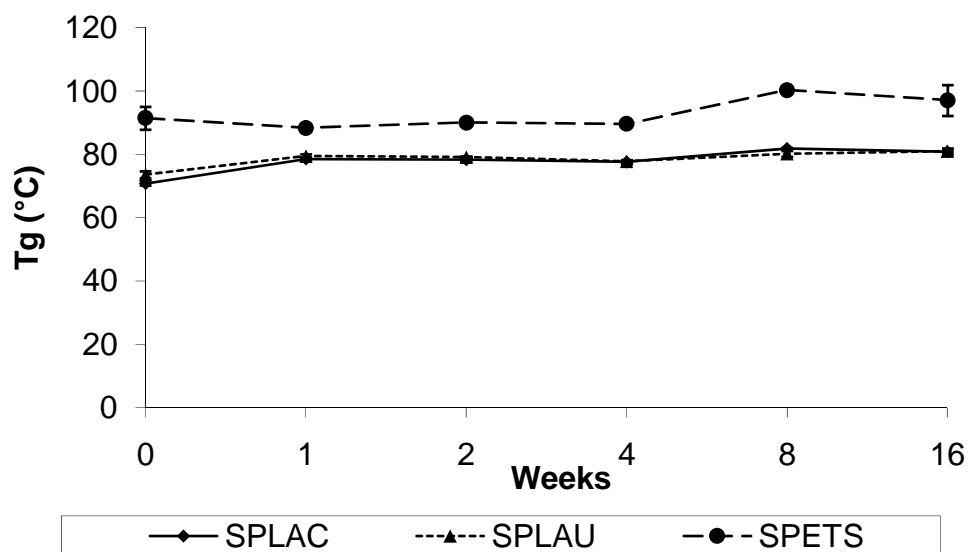


Figure 4-17. T_g when exposed to sugar/ acidic solution

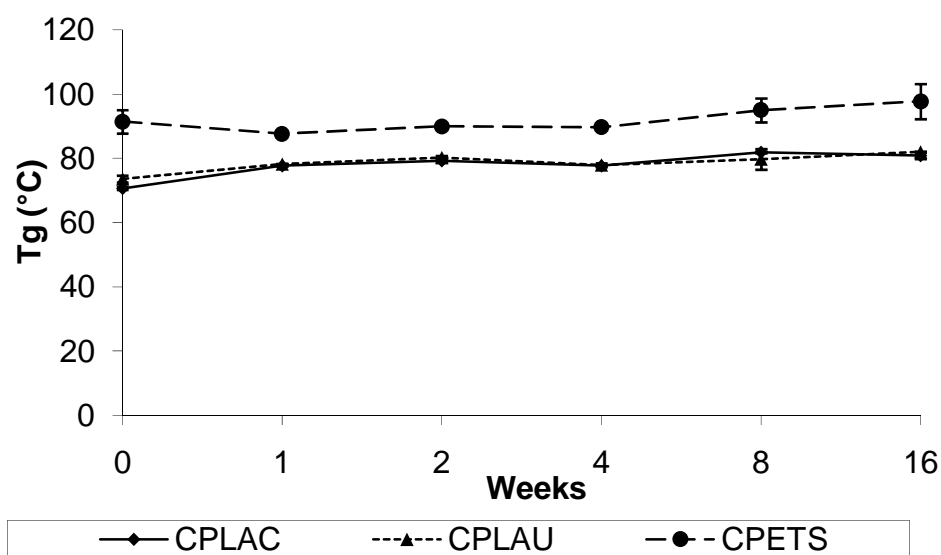


Figure 4-18. T_g when exposed to control.

Table 4-3. Glass transition temperature, °C

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	73.6 ±1.1aAα	73.8 ±1.7aAα	76.3 ±0.3aAα	73.7 ±0.2aAα	75.8 ±1.7aAα	ND
	Sugar		79.4 ±0.7abAα	79.1 ±0.2abAα	77.7 ±0.3abBα	80.1 ±1.0bAα	81.0 ±0.6bAα
	Control		78.2 ±0.1abAα	80.2 ±0.6bAα	77.9 ±0.6abABα	79.7 ±3.2bAα	82.0 ±0.1bAα
PLAC	Alcohol	70.7 ±0.5aAα	76.4 ±0.6abAα	75.0 ±1.8abAα	75.1 ±1.0abAα	78.0 ±0.7bAα	ND
	Sugar		78.5 ±0.6bAα	78.3 ±0.8bAα	77.6 ±0.6bAα	81.8 ±0.3bAα	80.8 ±1.1bAα
	Control		77.7 ±0.2bAα	79.3 ±0.7bAα	77.7 ±0.3bAα	81.9 ±0.3bAα	80.8 ±1.0bα
PETS	Alcohol	91.4 ±3.7acAβ	87.3 ±0.3cAβ	94.4 ±3.2abAβ	96.0 ±6.1abAβ	97.8 ±1.1bAβ	92.7 ±0.5acbA
	Sugar		88.3 ±0.2bAβ	90.0 ±0.4bAβ	89.6 ±0.6bBβ	100.2 ±0.9cAβ	97.0 ±4.9aAβ
	Control		87.6 ±0.4aAβ	89.9 ±0.1aAβ	89.7 ±0.1aBβ	95.0 ±3.7aBβ	97.7 ±5.5bAβ

Note: Values are reported as average ±standard deviation.

ND: values could not be determined due to brittleness of the bottles at week 16.

Values followed by the same small letters between columns are not statistically significantly different at $\alpha=0.05$ (Bonferroni test p-value<0.0001). Values followed by the same capital letters for the same polymer and different solution are not statistically significantly different at $\alpha=0.05$. Values followed by the same Greek letters for the different material and same solution are not statistically significantly different at $\alpha=0.05$.

T_g for PLAU and PLAC increased around 11% and 14 % respectively between week 0 and week 16 for sugar and control solutions. In the case of PLAU bottles containing sugar and control solutions, T_g 's were higher at week 8 and 16 than week 0, but T_g values at week 1, 2 and 4 were not significantly different to week 0, 8 and 16. For PLAC bottles stored with sugar and control solutions, although T_g value increased between week 0 and week 16, the values between week 1 and week 16 were not significantly different. In case of PLAU bottles stored with alcohol, T_g values increased between week 0 and 8, but values were not significantly different. Value for week 16 was not able to be determined due to brittleness of bottles. Whereas the results of PLAC stored with alcohol showed that the T_g value at week 8 was different than week 0, but the values at week 1, 2, and 4 were not significantly different from week 0 and 8. The increase in T_g values for PLAU and PLAC bottles can be associated with the increase in the crystallinity of the bottles. During the visual inspection of bottles, it was observed from week 4 onwards the cap and the bottom of the bottles lost clarity, which indicated the increase in crystallinity of the bottles.

In both PLAU and PLAC there was an increase in the T_g from week 0 to week 16. This can be attributed to the increase in molecular weight of the polymers. We also observed that the increase in T_g of PLA bottles exposed to alcohol is less compared to sugar and control solution. This is due to the fact that the molecular weight of PLAU and PLAC exposed to sugar and control is significantly more compared to alcohol solution. We were not able to obtain T_g of PLAU and PLAC at the 16 week mark, the reason is the same as explained in the previous HDT section.

4.3 Mechanical Properties Analysis

4.3.1 Tensile strength

Figures 4-19 to 4-21 shows the tensile strength of the PLAU, PLAC, PETS and PETM bottles exposed to alcohol, acidic/sugar, and control solution.

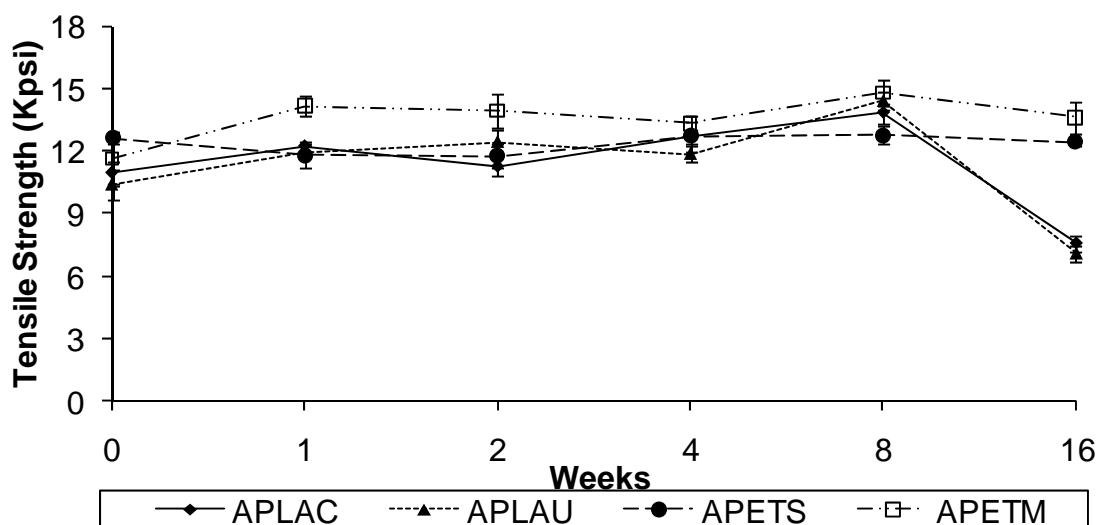


Figure 4-19. Tensile strength when exposed to alcohol

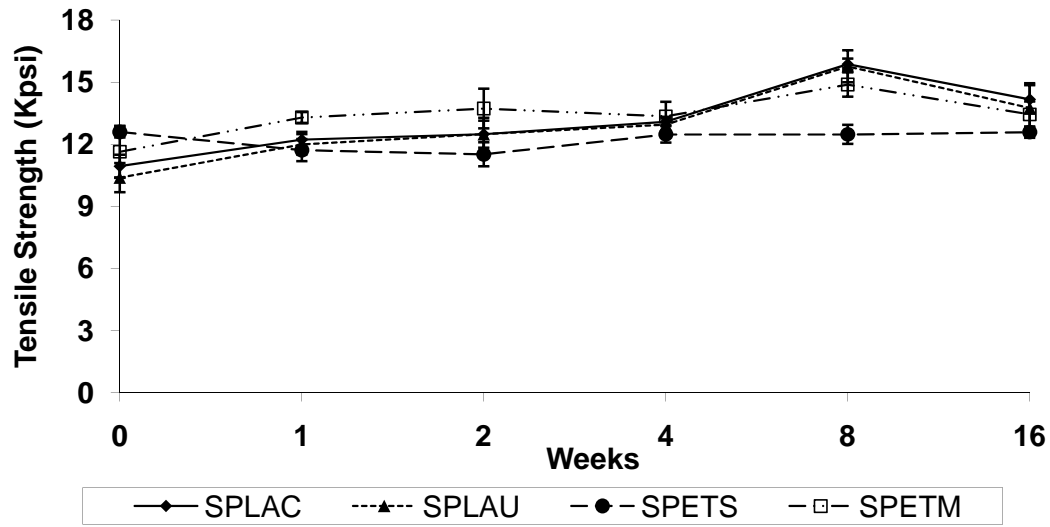


Figure 4-20. Tensile strength when exposed to sugar/ acidic solution.

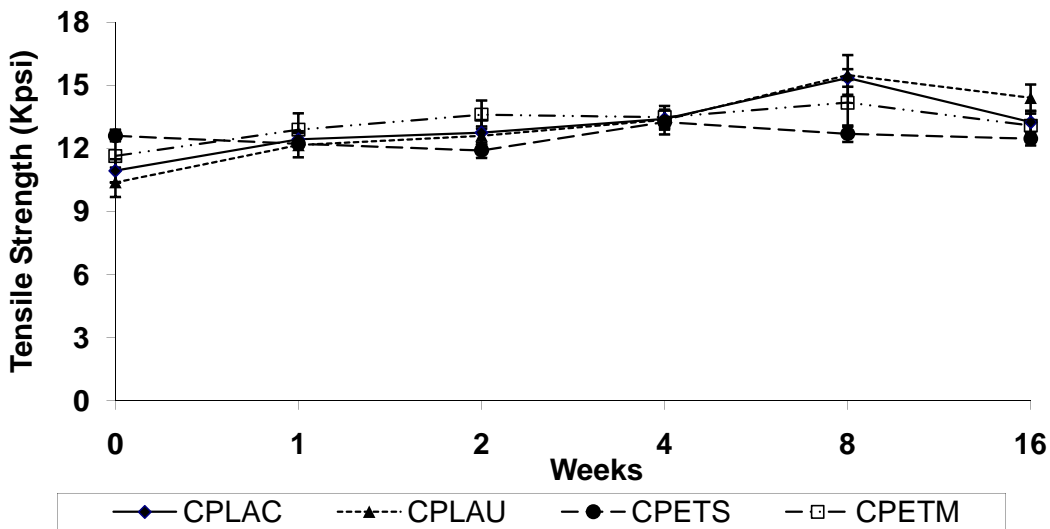


Figure 4-21. Tensile strength when exposed to control solution

Table 4-4. Tensile strength, Kpsi

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	10.4 ±0.7aAα	12.0 ±0.3abAα	12.4 ±0.6bAα	11.9 ±0.4abAα	14.4 ±0.5cAα	7.1 ±0.4dAα
	Sugar		12.0 ±0.5abAαγ	12.5 ±0.7bcAαβ	12.9 ±0.4bcABα	15.8 ±0.8dAα	13.8 ±1.2cBαβ
	Control		12.2 ±0.6bAα	12.6 ±0.4bAαβ	13.4 ±0.5bcBα	15.5 ±0.9dAα	14.4 ±0.6cdBα
PLAC	Alcohol	10.9 ±0.6aAαγ	12.2 ±0.3abAα	11.2 ±0.4aAα	12.7 ±0.4bcAαβ	13.8 ±0.5cAαβγ	7.6 ±0.4dAα
	Sugar		12.2 ±0.4abAαγ	12.5 ±0.8abABαβ	13.1 ±0.2bdAα	15.9 ±0.3cBα	14.2 ±0.7dBα
	Control		12.4 ±0.4abAα	12.8 ±0.6bBαβ	13.4 ±0.4bAα	15.4 ±0.4cBα	13.2 ±0.5bBαβ
PETS	Alcohol	12.6 ±0.3aAβγ	11.8 ±0.6aAα	11.8 ±0.6aAα	12.7 ±0.7aAαβ	12.8 ±0.5aAβ	12.4 ±0.1aAβ
	Sugar		11.7 ±0.5aAα	11.5 ±0.6aAα	12.5 ±0.4aAα	12.5 ±0.5aAβ	12.6 ±0.3aAβ
	Control		12.2 ±0.1aAα	11.9 ±0.4aAα	13.2 ±0.6aAα	12.7 ±0.4aAβ	12.5 ±0.4aAβ
PETM	Alcohol	11.6 ±1.3aAαγ	14.2 ±0.5bcAβ	13.9 ±0.9bcAβ	13.3 ±0.4cAβ	14.8 ±0.6bAγ	13.6 ±0.8bcAβ
	Sugar		13.3 ±0.3abAβγ	13.7 ±1.0bcAβ	13.3 ±0.7bAα	14.9 ±0.6cAα	13.5 ±0.7bcAαβ
	Control		12.9 ±0.8abAα	13.6 ±0.7bAβ	13.5 ±0.5bAα	14.2 ±1.2bAα	13.1 ±0.6abAαβ

Note: Values are reported as average ±standard deviation.

Values followed by the same small letters between columns are not statistical significantly different at $\alpha=0.05$ (Bonferroni test $p\text{-value}<0.0001$). Values followed by the same capital letters for the same polymer and different solution are not statistical significantly different at $\alpha=0.05$. Values followed by the same greek letters for the different material and same solution are not statistical significantly different at $\alpha=0.05$.

Tensile strength of PLAU bottles increased approx. 138, 152 and 140 % between weeks 0 and 8 for alcohol, sugar/ acid and control solutions, respectively. The increase in the tensile strength can be due to increase in molecular weight and crystallinity of bottles between week 0 and 8, which is translated into a fragilization of the samples [65]. At week 16 the tensile strength for bottles filled with alcohol decreased drastically to 49% of the week 8 values. The main reason for this decrease in tensile value can be associated with the molecular weight of PLAU. Due to hydrolysis of PLAU, the molecular weight decreased from 154,302 Da at week 8, to 25,864 Da at week 16 [65]. Similarly, the tensile strength for PLAU bottles exposed to sugar solution also decreased to 87% of the week 8 values, but for bottles filled with control did not show any significant difference.

A similar pattern was observed in the tensile strength of PLAC bottles. The tensile strength increased to 126, 145 and 140% between week 0 and 8 for alcohol, sugar and control solutions, respectively. At week 16, the tensile strength dropped to 54% of the week 8 values for bottles filled with alcohol. For materials exposed to sugar and control solutions, tensile strength decreased to 89% and 86%, respectively, of that of week 8. Due to hydrolysis of PLAC, the molecular weight decreased from 176,984 Da at week 8, to 27,427 Da at week 16 [65]. Tensile strength of the PETS bottles remained constant between week 0 and 16 regardless of the exposure solutions.

Tensile strength of PETM increased approx 125% when exposed to any of the three solutions between week 0 and 8. Between week 8 and 16, there was no statistically significant change in tensile strength.

Tensile strength of both PLAU and PLAC increased between week 0 and 8. The values of tensile strength of PLAU and PLAC exposed to alcohol obtained at the week 16 were half of the

values of week 8. On the other hand in the case of sugar and control solution, the drop in tensile strength at week 16 was significantly different from week 8, but not as much as the drop seen in the alcohol solution. The increase in tensile strength of PLAU and PLAC until week 8 in all the three solutions can be related to the increase of molecular weight of the polymer. When the molecular weight of the PLAU and PLAC decreased at week 16, the tensile strength also decreased correspondingly.

4.3.2 Compression Strength

The crush resistance for PLA, PLAC, PETS and PETM was measured by a compression test. The bottles tested by this technique were free of obvious defects such as rocker bottoms or bent necks. The compression strength of the bottles was measured according to ASTM D 2659-95 (2001). This test helps to determine the mechanical properties of blown thermoplastic containers when loaded under columnar crush conditions at a constant rate of compressive deflection. [ASTM D 2659-95 (2001)]. This also helps to determine how high we can stack the bottles during transit and during storage in warehouses.

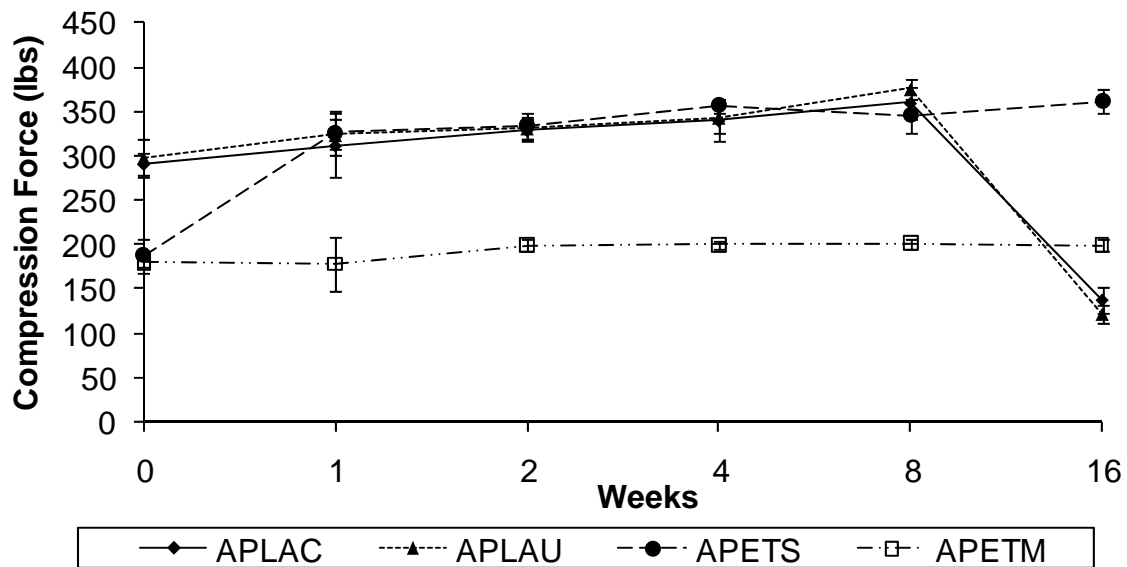


Figure 4-22. Compression strength when exposed to alcohol solution

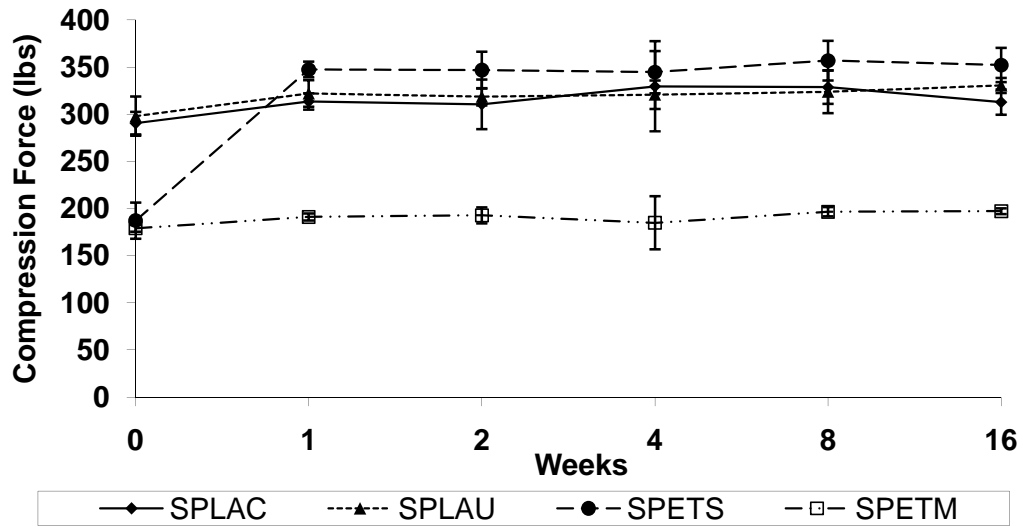


Figure 4-23. Compression strength when exposed to sugar/acidic solution

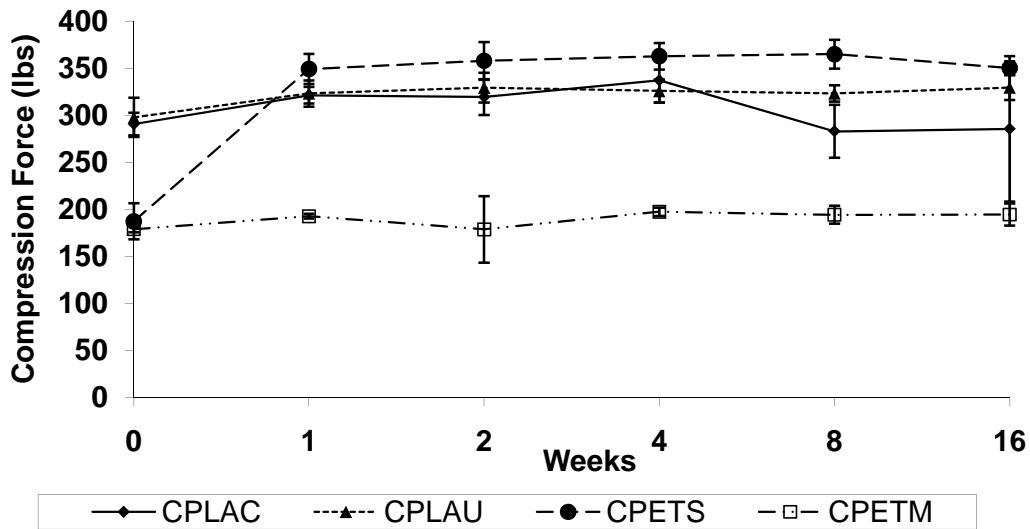


Figure 4-24. Compression strength when exposed to control solution

Table 4-5. Compression strength (lbs)

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	297.9 ±20.9aAα	323.8 ±16.7abAα	331.2 ±11.7abAα	343.4 ±17.3abAα	375.5 ±11.4bAα	122.0 ±10.6cAα
	Sugar		322.1 ±14.0aAα	318.6 ±9.1aAα	320.9 ±15.0aAα	323.9 ±22.5aAα	330.5 ±8.0aBα
	Control		323.2 ±8.9aAα	329.4 ±15.9aAα	325.9 ±12.2aAα	323.3 ±8.7aAα	329.5 ±13.3aBα
PLAC	Alcohol	290.6 ±12.1aAα	311.3 ±36.4abAα	328.8 ±12.9abAα	339.9 ±23.3abAα	359.5 ±17.4bAα	137.3 ±14.1cAα
	Sugar		313.6 ±8.9aAα	310.74 ±26.3aAα	329.7 ±47.9aAα	328.8 ±17.8aABα	312.9 ±13.9aBα
	Control		321.4 ±8.9aAα	319.5 ±19.0aAα	337.3 ±23.6aAα	283.0 ±28.2aBβ	285.6 ±77.2aBβ
PETS	Alcohol	187.2 ±19.2aAβ	325.7 ±25.0bAα	333.5 ±15.7bAα	356.3 ±7.9bAα	345.1 ±19.5bAα	361.6 ±13.8bAβ
	Sugar		347.4 ±8.3bAα	346.9 ±19.5bAα	344.7 ±22.4bAα	356.9 ±21.1bAα	352.2 ±18.1bAα
	Control		349.3 ±16.1bAα	358.0 ±20.1bAα	362.8 ±14.1bAα	365.0 ±15.4bAα	350.3 ±7.3bAα
PETM	Alcohol	178.9 ±3.5aAβ	177.5 ±31.0aAβ	198.8 ±7.2aAβ	199.8 ±4.3aAβ	201.0 ±5.6aAβ	198.8 ±7.1aAγ
	Sugar		190.9 ±3.7aAβ	192.7 ±8.4aAβ	184.8 ±28.1aAβ	196.5 ±5.0aAβ	197.1 ±2.9aAβ
	Control		192.7 ±2.5aAβ	178.8 ±35.4aAβ	197.5 ±4.4aAβ	194.3 ±9.6aAγ	194.5 ±11.8aAγ

Note: Values are reported as average ±standard deviation.

Values followed by the same small letters between columns are not statistically significantly different at $\alpha=0.05$ (Bonferroni test $p\text{-value}<0.0001$). Values followed by the same capital letters for the same polymer and different solution are not statistically significantly different at $\alpha=0.05$. Values followed by the same Greek letters for the different material and same solution are not statistically significantly different at $\alpha=0.05$.

Compression strength for PLAU and PLAC did not significantly change between weeks 0 and 16 for sugar and control solutions. When bottles were exposed to alcohol solution, the compression strength did also not change significantly between week 0 and week 4. The value at week 8 was different and higher than week 0, but was not different from weeks 1, 2 and 4. The value at week 16 decreased drastically, around 41 % for PLAU and 47% for PLAC. The decrease in compression strength for PLAU and PLAC bottles stored with alcohol can be associated with the decrease in molecular weight of PLA.

The compression strength of PETS bottles before storage was 187.2 lbs. There was an increase of 73% for alcohol solutions and 87% for sugar and control solutions. But after week 1, there was no significant difference observed through week 16 with exposure to any of the three solutions.

For compression strength of PETM bottles no difference was observed between week 0 and with exposure to any of the three solutions.

The same pattern as for tensile strength was observed in compression strength values for PLAU and PLAC. Compression strength behavior of the PLAU and PLAC can again be related to molecular weight, i.e. increase in molecular weight leads to increase in compression strength and drop in molecular weight means decrease in compression strength.

4.4 Barrier Properties

4.4.1 Water Vapor transmission rate

Figures 4-25 to 4-27 shows the WVTR of the PLAU, PLAC, PETS and PETM bottles exposed to alcohol, acidic/sugar, and control solution.

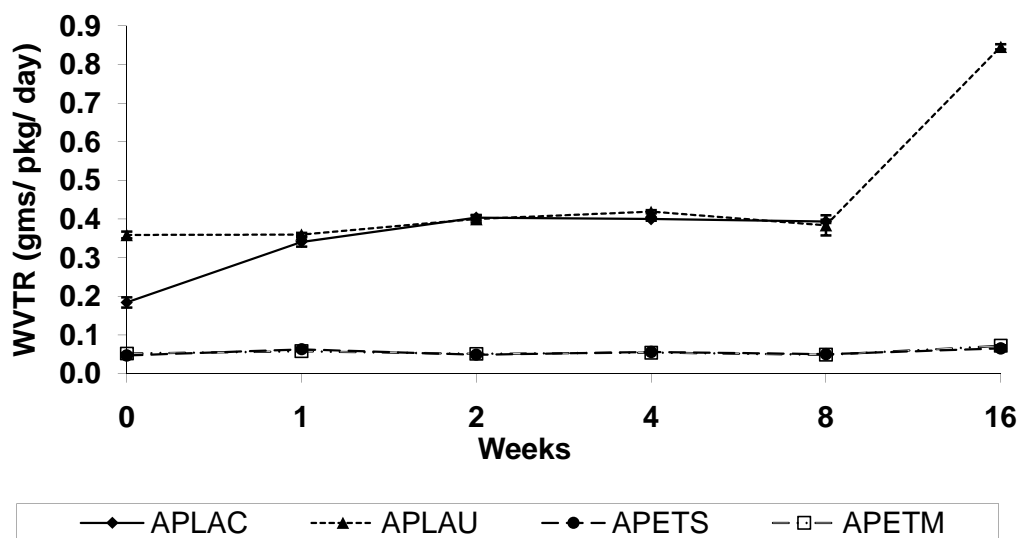


Figure 4-25. WVTR when exposed to alcohol solution

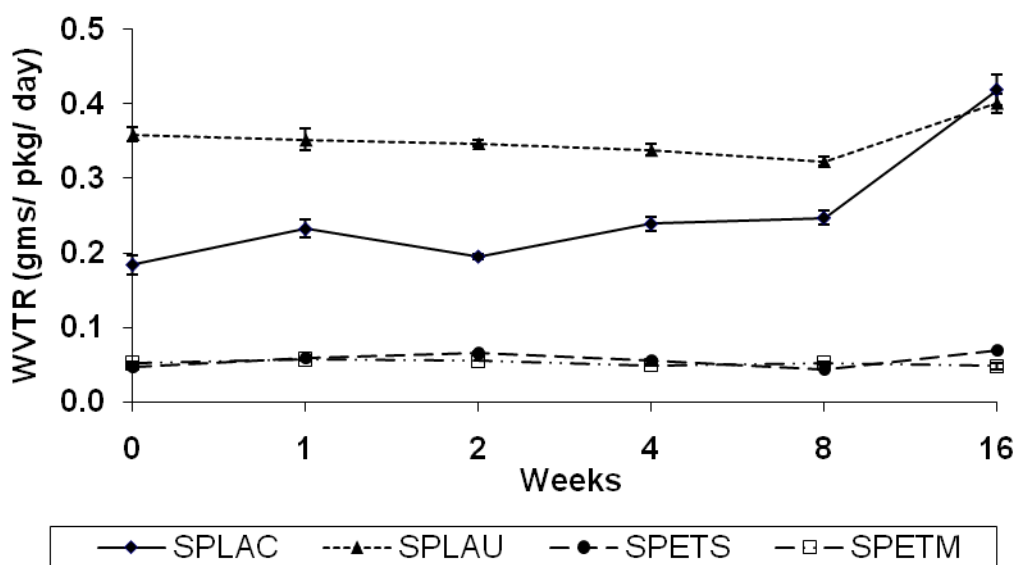


Figure 4-26. WVTR when exposed to sugar/acidic solution

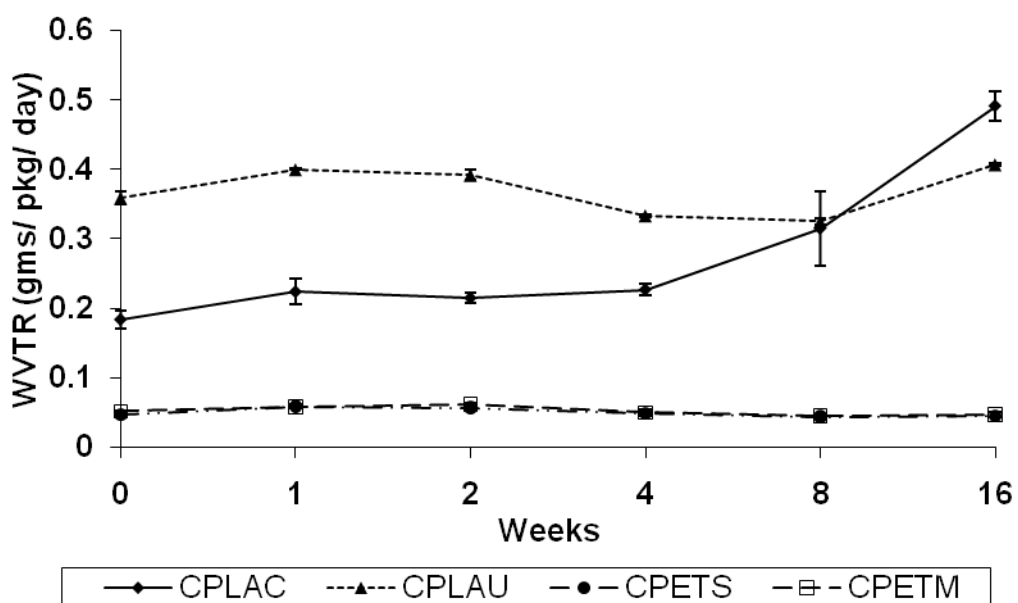


Figure 4-27. WVTR when exposed to control solution

Table 4-6. WVTR values (gm/pkg/day)

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	0.36 ±0.01aAα	0.36 ±0.00aAα	0.40 ±0.01aAα	0.42 ±0.00aAα	0.35 ±0.03aAα	0.85 ±0.01bAα
	Sugar		0.35 ±0.02abAα	0.35 ±0.00abAα	0.34 ±0.01abBα	0.32 ±0.01bAα	0.40 ±0.01aBα
	Control		0.40 ±0.00aAα	0.39 ±0.01aAα	0.33 ±0.00bBα	0.32 ±0.00bAα	0.41 ±0.00aBα
PLAC	Alcohol	0.18 ±0.01aAβ	0.34 ±0.01bAα	0.40 ±0.01cAα	0.40 ±0.00bcAα	0.39 ±0.00bcAα	ND
	Sugar		0.23 ±0.01abBβ	0.19 ±0.00abBβ	0.24 ±0.01abBβ	0.25 ±0.01bBβ	0.42 ±0.02cAα
	Control		0.22 ±0.02aBβ	0.22± 0.01aBβ	0.23 ±0.01aBβ	0.32 ±0.05bCα	0.49 ±0.02cBβ
PETS	Alcohol	0.05 ±0.00aAγ	0.06 ±0.00aAγ	0.05 ±0.00aAβ	0.06 ±0.00aAβ	0.05 ±0.00aAγ	0.06 ±0.00aAβ
	Sugar		0.06 ±0.00aAγ	0.06 ±0.00aBγ	0.05 ±0.00aAγ	0.04 ±0.00aAγ	0.07 ±0.00aAβ
	Control		0.06 ±0.00aAγ	0.06 ±0.00aABγ	0.05 ±0.00aAγ	0.04 ±0.00aAγ	0.04 ±0.00aBγ
PETM	Alcohol	0.05 ±0.00aAγ	0.06 ±0.00aAγ	0.05 ±0.00aAβ	0.05 ±0.00aAβ	0.05 ±0.00aAγ	0.07 ±0.00aAβ
	Sugar		0.06 ±0.00aAγ	0.05 ±0.00aBγ	0.05 ±0.00aAγ	0.05 ±0.00aAγ	0.05 ±0.00aBγ
	Control		0.06 ±0.00aAγ	0.06 ±0.00aBγ	0.05 ±0.00aAγ	0.04 ±0.00aAγ	0.05 ±0.00aBγ

Note: Values are reported as average ±standard deviation.

ND: value was not determined at week 16 as the value crossed the sensor limit.

Values followed by the same small letter between columns are not statistically different at α=0.05 (Bonferroni test p-value<0.0001).

Values followed by the same capital letter for the same polymer and different solutions are not statistically different at α=0.05. Values followed by the same greek letter for the different material and same solution are not statistically different at α=0.05.

Exposure to alcohol had more severe effects, compared to sugar and control solutions, on WVTR. WVTR values for PLAU bottles were not significantly different between week 0 and 8, but at week 16, it more than doubled compared to week 8 for the bottles exposed to alcohol solution. This also can be explained with the help of molecular weight. Until week 8 there was an increase in the molecular weight perhaps due to cross linking. So there were no significant differences between the values obtained, but at week 16 the molecular weight dropped from 154 kDa to 25 kDa and the WVTR also increased more than doubled. For bottles exposed to sugar solution, there were no significant differences between weeks 0 and 16 but at week 8, it dropped and was different compared to week 0, 1, 2, 4, and 16. At week 8 the molecular weight value was a maximum, so we can say this drop in WVTR was due to the polymer having comparatively good barrier properties during that duration. Similarly for the bottles exposed to the control solution, the values at week 4 and 8 were lower and significantly different compared to weeks 0, 1, 2 and 16.

WVTR for PLAC bottles increased 228 and 267 % for bottles exposed to sugar and control solution respectively between week 0 and 16. For the bottles exposed to alcohol, WVTR increased by 219 % between week 0 and 2, thereafter values at week 4 and 8 were not different from week 2. WVTR at week 16 was beyond the equipment's measurement range. The SiO_x coating provided barrier in the initial first week but after that due to cracks (shown in the next section) WVTR value increased until week 16. WVTR for PETS and PETM for all the three solutions did not change significantly between week 0 and week 16.

4.4.2 Oxygen Transmission Rate

Figures 4-28 to 4-30 shows the OTR values for PLA, PLGA, PEG and PET bottles exposed to alcohol, acidic/sugar, and control solutions.

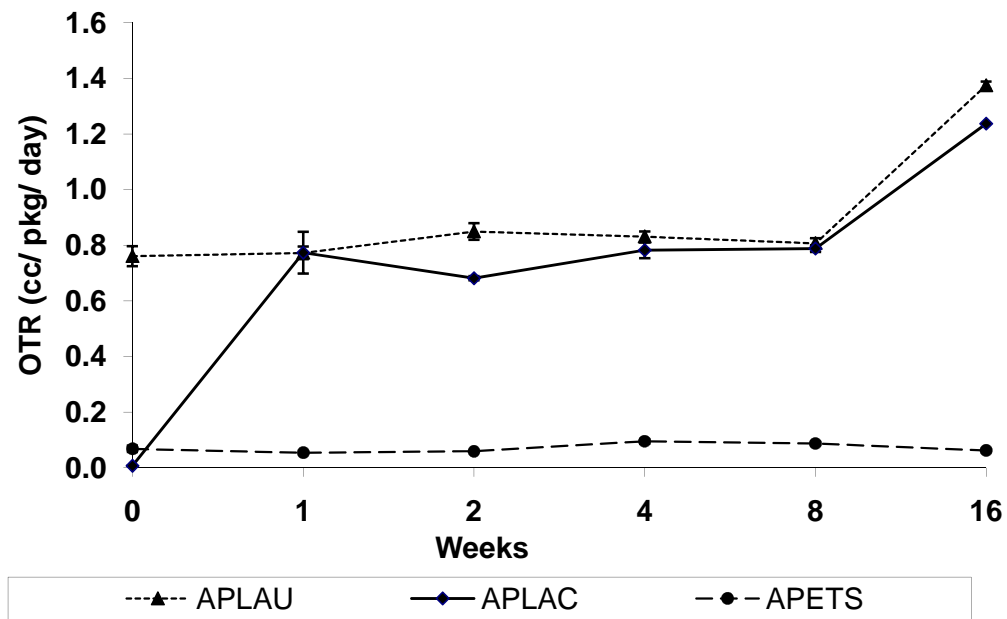


Figure 4-28. OTR of bottles when exposed to alcohol solution

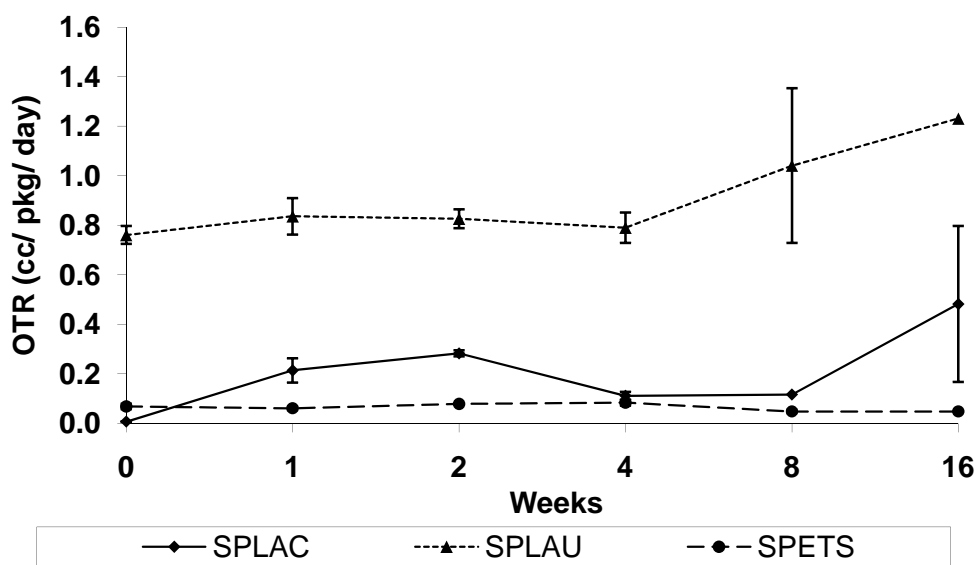


Figure 4-29. OTR of bottles when exposed to sugar/acid solution

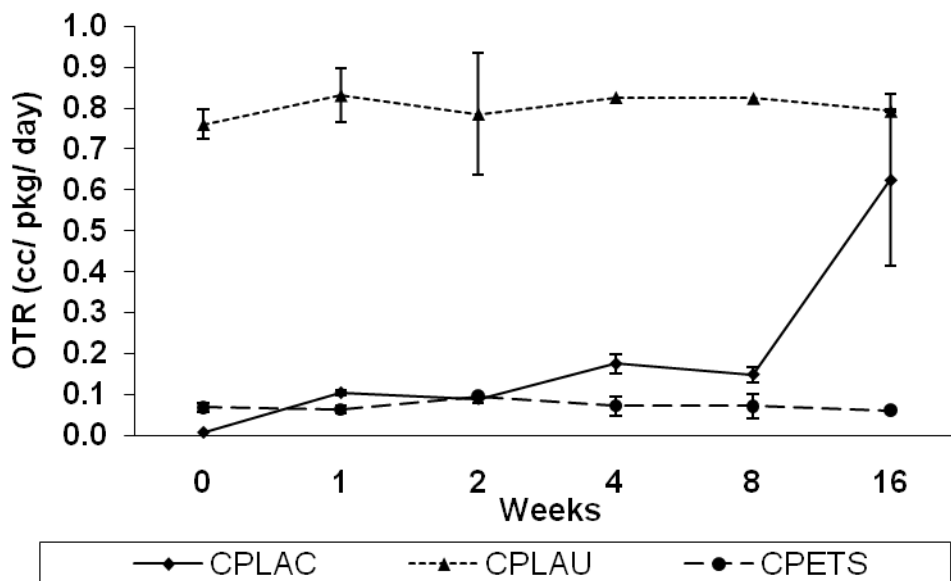


Figure 4-30. OTR of bottles when exposed to control solution

Table 4-7. OTR values (cc/pkg/day)

Material	Solution	Initial	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	0.76 ±0.04aAα	0.77 ±0.02aAα	0.85 ±0.03aAα	0.83 ±0.02aAα	0.81 ±0.02aAα	1.37 ±0.01bAα
	Sugar		0.84 ±0.07aAα	0.83 ±0.04aAα	0.79 ±0.06aAα	1.04 ±0.31aAα	1.23 ±0.00aABα
	Control		0.83 ±0.07aAα	0.79 ±0.15aAα	0.83 ±0aAα	0.83 ±0.00aAα	0.79 ±0.00aBα
PLAC	Alcohol	0.01 ±0.0aAβ	0.77 ±0.08bAα	0.68 ±0.01bAα	0.78 ±0.03bAα	0.79 ±0.01bAα	1.24 ±0.00bAα
	Sugar		0.21 ±0.05aBβ	0.28 ±0.01aABβ	0.11 ±0.02aBβ	0.12 ±0.00aBβ	0.48 ±0.31aBβ
	Control		0.10 ±0.01aBβ	0.09 ±0.01aBβ	0.17 ±0.02abBβ	0.15 ±0.02abBβ	0.63 ± 0.21bBαβ
PETS	Alcohol	0.07 ±0.01aAβ	0.05 ±0.00aAβ	0.06 ±0.00aAβ	0.09 ±0.01aAβ	0.09 ±0.01aAβ	0.06 ±0.01aAβ
	Sugar		0.06 ±0.01aAβ	0.08 ±0.00aAβ	0.08 ±0.01aAβ	0.05 ±0.01aAβ	0.05 ± 0.00aAβ
	Control		0.06 ±0.01aAβ	0.09 ±0.00aAβ	0.07 ±0.02aAβ	0.07 ±0.03aAβ	0.06 ±0.00aAβ

Note: Values are reported as average ±standard deviation.

Values followed by the same small letters between columns are not statistically significantly different at $\alpha=0.05$ (Bonferroni test p-value<0.0001). Values followed by the same capital letters for the same polymer and different solution are not statistically significantly different at $\alpha=0.05$. Values followed by the same Greek letters for the different material and same solution are not statistically significantly different at $\alpha=0.05$.

OTR for PLAU bottles exposed to alcohol solution did not change significantly between week 0 and 8, but at week 16 the value increased 170 % as compared to week 8 values. The main reason for such an increase can be also associated with the molecular weight. The molecular weight of the PLAU dropped from 154 kDa to 25 kDa during this period. At week 16, PLAU has lost most of its mechanical and barrier properties. Whereas OTR for PLAU bottles exposed to sugar and control solution did not had any significant difference between week 0 and 16. OTR for PLAC bottles exposed to alcohol had a significant difference between week 0 and week 1. The cause for such a difference in first week was due to crack formation (shown in the next section) in the SiO_x coating, which was clearly visible with an optical microscope at 1000x magnification, section 4.6. Basically the SiO_x coating failed after week 1. Afterwards there was no significant change between week 1 and week 16. No significant difference was found in OTR between week 0 and 16 for the PLAC bottles exposed to sugar solution. OTR for PLAC bottles exposed to the control solution did not change significantly between week 0 and 8. OTR after exposure to control solution for 16 weeks was significantly different from weeks 0, 1 and 2, but not different from week 4 and 8. Two samples were only tested and the variation was high, so the results obtained for PLAC exposure to the control are inconclusive. Either the sample size was not enough or likely one of the samples had imperfections. No significant difference was found in OTR values for PETS exposed to any of the three solutions.

4.4.3 Weight Change Analysis

Figures 4-31 to 4-33 show the average weight loss of the alcoholic, sugar/acidic, and control solution for the PLAU, PLAC, PETS and PETM bottles.

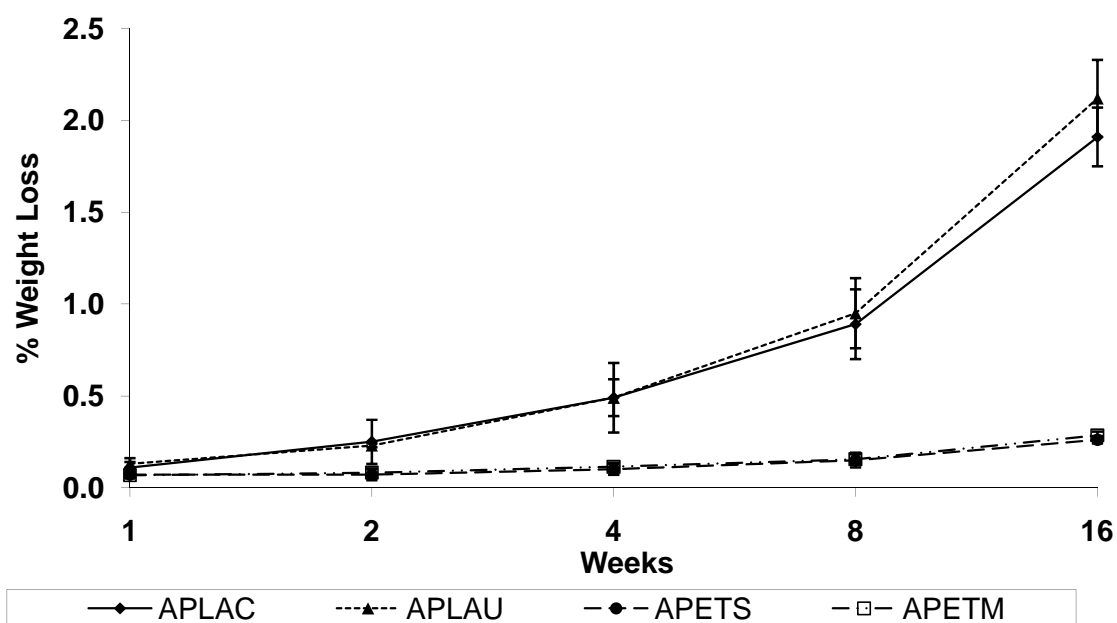


Figure 4-31. Weight loss of alcohol solution in bottles

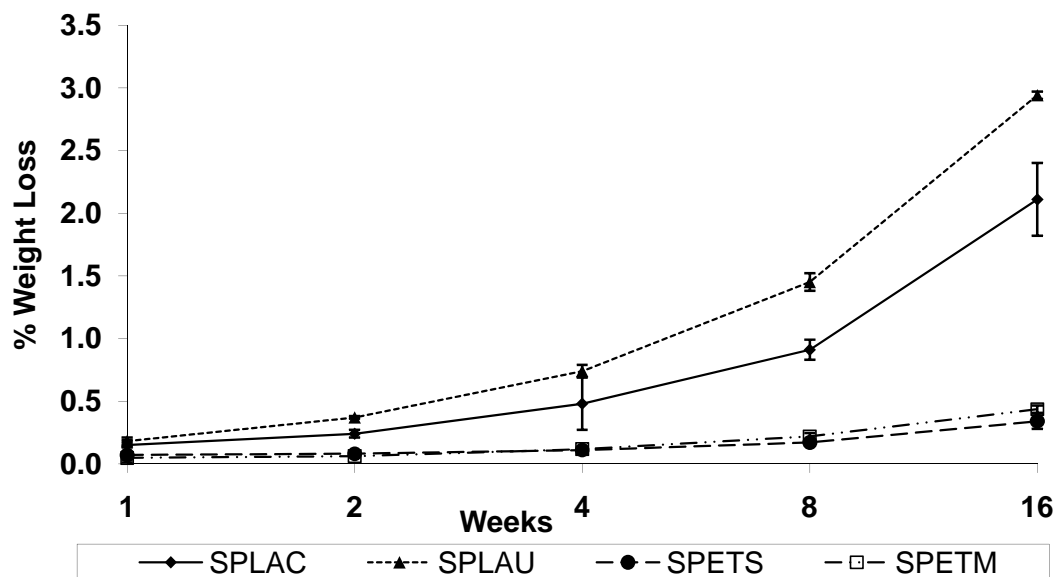


Figure 4-32. Weight loss of sugar/acidic solution in bottles

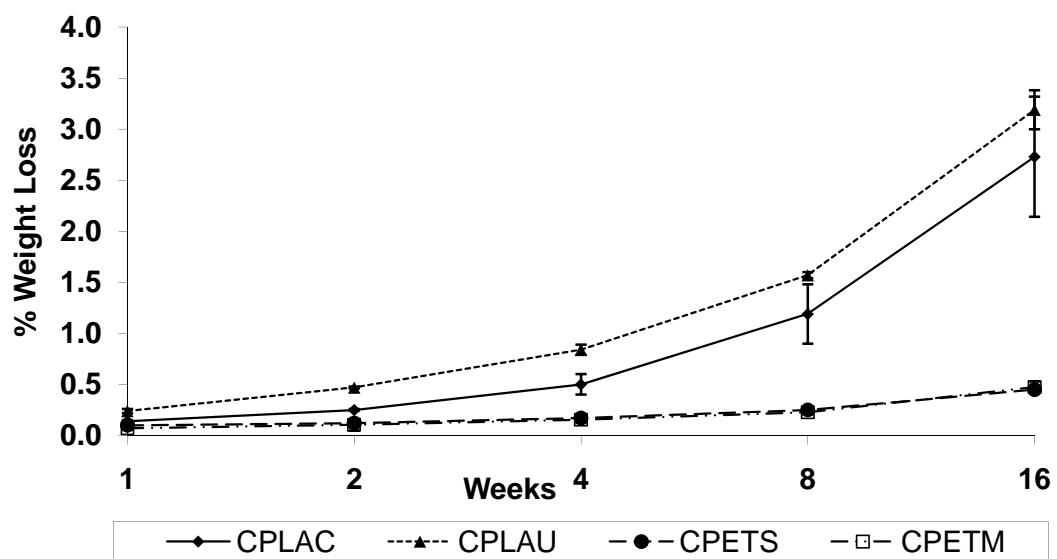


Figure 4-33. Weight loss of control solution in bottles

Table 4-8. Weight change (%)

Material	Solution	1 week	2 weeks	4 weeks	8 weeks	16 weeks
PLAU	Alcohol	0.13 ± 0.03aAα	0.23 ± 0.01abAα	0.49 ± 0.10bAα	1.02 ± 0.29cAα	2.12 ± 0.21dAα
	Sugar	0.18 ± 0.01aAα	0.37 ± 0.01aABα	0.74 ± 0.05bBα	1.44 ± 0.07cBα	2.94 ± 0.03dBα
	Control	0.24 ± 0.02aAα	0.47 ± 0.01bBα	0.84 ± 0.05cBα	1.57 ± 0.04dBα	3.19 ± 0.19eCα
PLAC	Alcohol	0.11 ± 0.03aAα	0.25 ± 0.12abAα	0.54 ± 0.38bAα	0.98 ± 0.39cAα	1.91 ± 0.16dAα
	Sugar	0.15 ± 0.06aAα	0.24 ± 0.03abAαβ	0.48 ± 0.21bAβ	0.90 ± 0.09cAβ	2.11 ± 0.29dBβ
	Control	0.14 ± 0.01aAα	0.25 ± 0.01aAβ	0.50 ± 0.10bAβ	1.18 ± 0.28cBβ	2.73 ± 0.59dCβ
PETS	Alcohol	0.07 ± 0.02aAα	0.07 ± 0.03aAα	0.10 ± 0.03aAβ	0.15 ± 0.03aAβ	0.26 ± 0.02aAβ
	Sugar	0.06 ± 0.02aAα	0.08 ± 0.02aAβ	0.11 ± 0.02abAγ	0.17 ± 0.02abAγ	0.34 ± 0.06bAγ
	Control	0.10 ± 0.03aAα	0.12 ± 0.02aAβ	0.17 ± 0.02aAγ	0.25 ± 0.02abAγ	0.45 ± 0.02bAγ
PETM	Alcohol	0.07 ± 0.02aAα	0.08 ± 0.02abAα	0.11 ± 0.02abAβ	0.16 ± 0.03abAβ	0.29 ± 0.02bAβ
	Sugar	0.05 ± 0.01aAα	0.06 ± 0.01aAβ	0.12 ± 0.01aAγ	0.22 ± 0.03aAγ	0.44 ± 0.03bAγ
	Control	0.07 ± 0.01aAα	0.10 ± 0.06aAβ	0.16 ± 0.03aAγ	0.23 ± 0.02aAγ	0.47 ± 0.05bAγ

Note: Values are reported as average ±standard deviation.

Values followed by the same small letters between columns are not statistical significantly different at $\alpha=0.05$ (Bonferroni test p-value<0.0001). Values followed by the same capital letters for the same polymer and different solution are not statistical significantly different at $\alpha=0.05$. Values followed by the same Greek letters for the different material and same solution are not statistical significantly different at $\alpha=0.05$.

Weight loss was highest for the PLAU bottles in all the three solutions. In all types of bottles the highest weight loss took place in the control solution, then in the sugar & acidic solution and the lowest loss in the alcohol solution. The weight loss was highest in the case of control (water) as the polarity of water molecule is high compared to ethanol. So PLA being a polar molecule will sorb water faster and to a greater extent. Also the size of the water molecule is smaller than ethanol, so the diffusion of the water molecule may be faster and permeation may also occur faster. This means higher weight loss in the control solution. Weight loss in PETS and PETM bottles was very low compared to PLAU and PLAC bottles. The WVTR of the PETS and PETM is very small compared to PLA, so the weight loss was very low for PET bottles. Throughout the 16 weeks study, we found PETS and PETM showed similar weight loss patterns. But in the case of PLAU and PLAC bottles, weight loss was comparatively lower in PLAC bottles in all the three solutions.

4.5 Surface Roughness of PLA Bottles

The surface roughness (inside) of the PLA bottles was tested at four different times.

Stage 1

The roughness of uncoated PLA bottles, which were first produced during the initial stages of the project, was measured. When these bottles were sent for coating, it was indicated that the roughness of the bottles should be below 5 nm, in order to have uniform silicon oxide coating and have effective improvement in the barrier properties. When the roughness measurements of the bottles were carried out, it was discovered that the roughness value was 19.976 ± 3.765 nm between the bottles and the roughness value was 12.864 ± 6.259 nm within a bottle. So, the roughness was much higher than acceptable for efficient coating.

Table 4-9. Roughness of the 1st PLA bottle

Sample	Roughness (RMS), nm
Body (RB1)	19.928
Shoulder (RS)	8.010
Neck (RN)	10.653
Average	12.864 ± 6.259

Table 4-10. Roughness in the body of PLA bottles

Sample	Roughness (RMS), nm
1 st bottle (RB1)	19.928
2 nd bottle (RB2)	23.764
3 rd bottle (RB3)	16.235
Average	19.976 ± 3.765

Stage 2

In order to bring the roughness of the bottles below 5 nm, some changes were made in the technique of manufacturing the bottles, including the parameters. Four different techniques with variable manufacturing parameters were applied to study changes in the roughness values of the bottles. The change in the technique and parameters are confidential; therefore they cannot be discussed in this thesis. Bottles so produced were marked as types A, B, C and D. Three bottles of each type were used to carry out roughness measurements of the body of the bottles. The average roughness value of type A bottles were determined to be 4.387 ± 0.925 nm, for type B it was 6.546 ± 4.126 nm, for type C bottles it was 4.058 ± 1.575 nm and for type D bottles it was 5.877 ± 2.023 nm.

Table 4-11. Roughness of bottles made with different processes

Variable	Roughness (Ra), nm in body of the container
Sample made with Process A	4.387 ± 0.925
Sample made with Process B	6.546 ± 4.126
Sample made with Process C	4.058 ± 1.575
Sample made with Process D	5.877 ± 2.023

Note: Ra refers to the average roughness.

At this stage process A was selected for production as the roughness was closer to 5 nm and less variable as per the coating requirement.

Stage 3

To ensure the consistency in the manufacturing process of the bottles, the roughness of

uncoated PLA bottles made at different times was measured. Six PLA uncoated bottles were analyzed. An average roughness of 2.071 ± 0.808 nm was determined.

Table 4-12. Roughness of the bottle

Sample	Roughness (Ra), nm	RMS, nm
B1 (6:30)	2.474	3.376
B2 (7:00)	2.144	2.886
B3 (10:00)	2.75	3.579
B4 (2:45)	1.606	2.155
B5 (3:30)	3.728	9.762
B6 (8:30)	3.506	4.573
Average	2.701 ± 0.808	4.389 ± 2.751

Note: Ra refers to the average roughness; RMS refers to the standard deviation of the Z-values.

Stage 4

Coated PLA bottles provided by SIG Plasma GMBH were analyzed for surface roughness. The average roughness value of the coated bottle determined at the shoulder, neck and body was 8.080 ± 5.586 nm, and the roughness value determined between the bottles bodies was 13.581 ± 1.833 nm.

Table 4-13. Roughness of the 1st coated PLA bottle

Sample	Roughness (Ra),nm	RMS, nm
Shoulder (BS)	6.354	10.356
Neck (BN)	3.561	4.626
Body (BB1)	14.326	29.854
Average	8.080 ± 5.586	14.945 ± 13.225

Note: Ra refers to the average roughness; RMS refers to the standard deviation of the Z-values.

Table 4-14. Roughness of the body of coated PLA bottles

Sample	Roughness (Ra),nm	RMS, nm
1 st bottle body	14.326	29.854
2 nd bottle body	14.925	31.357
3 rd bottle body	11.493	15.285
Average	13.581 ± 1.833	25.944 ± 8.877

Note: Ra refers to the average roughness; RMS refers to the standard deviation of the Z-values.

Figures 4-34 to 4-38 show the AFM images for the data in Tables 4-12 and 4-13.

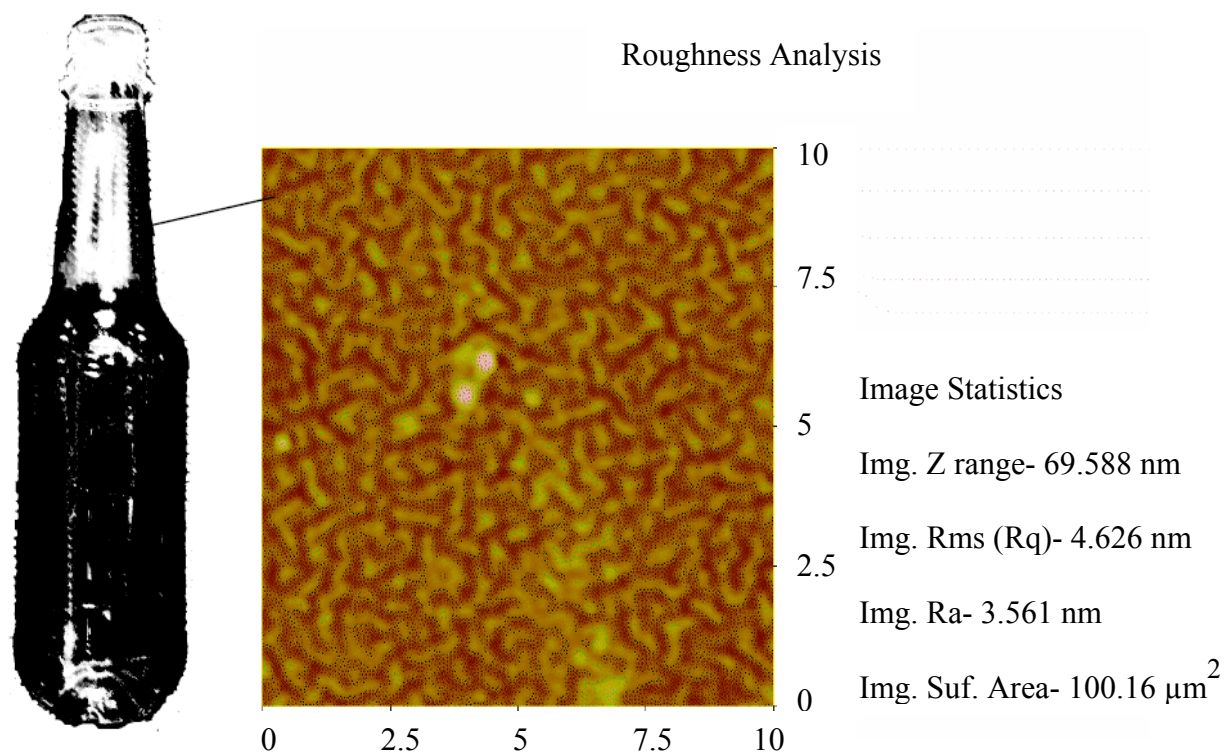


Figure 4-34. Roughness of neck of the coated bottle (BN)

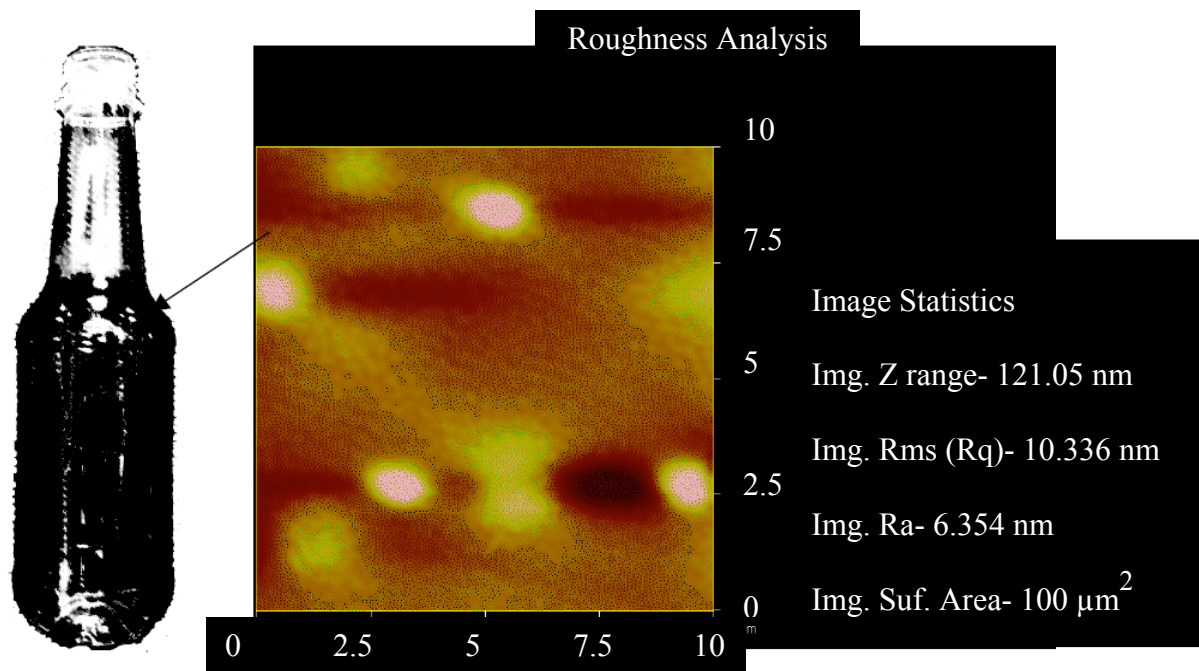


Figure 4-35. Roughness of the shoulder of the coated bottle (BS)

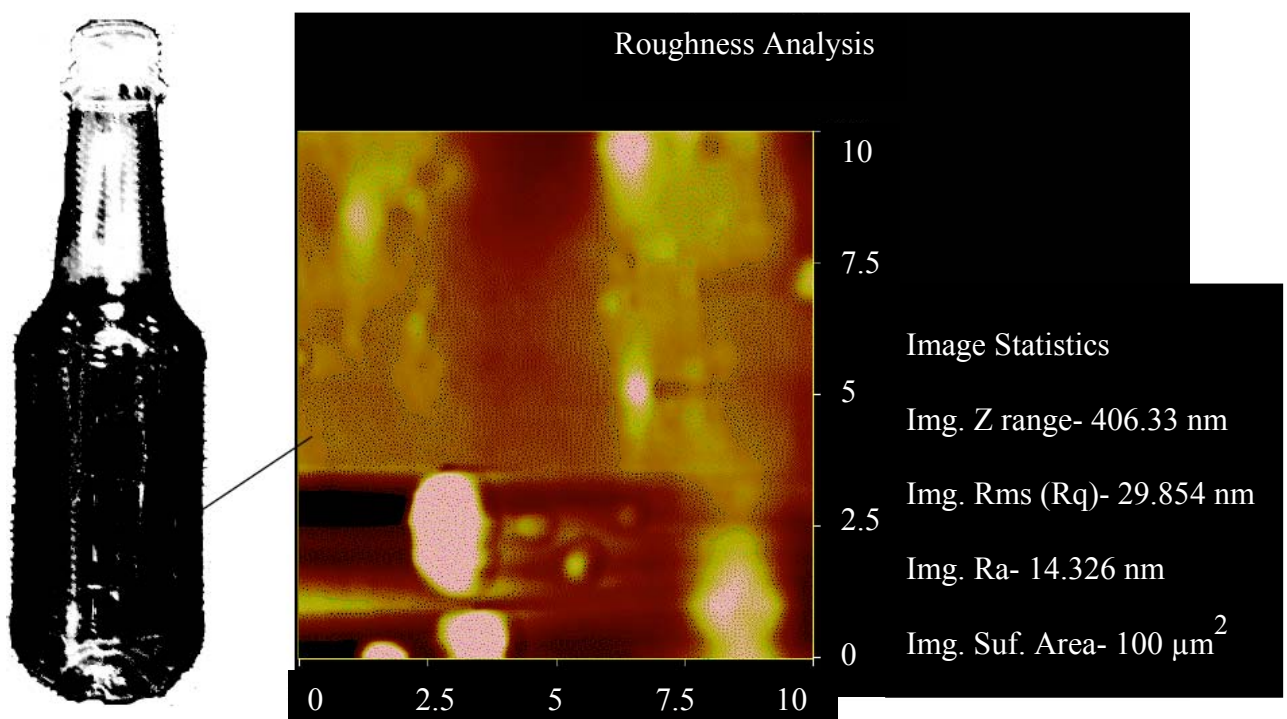


Figure 4-36. Roughness of body of the coated bottle (BB1)

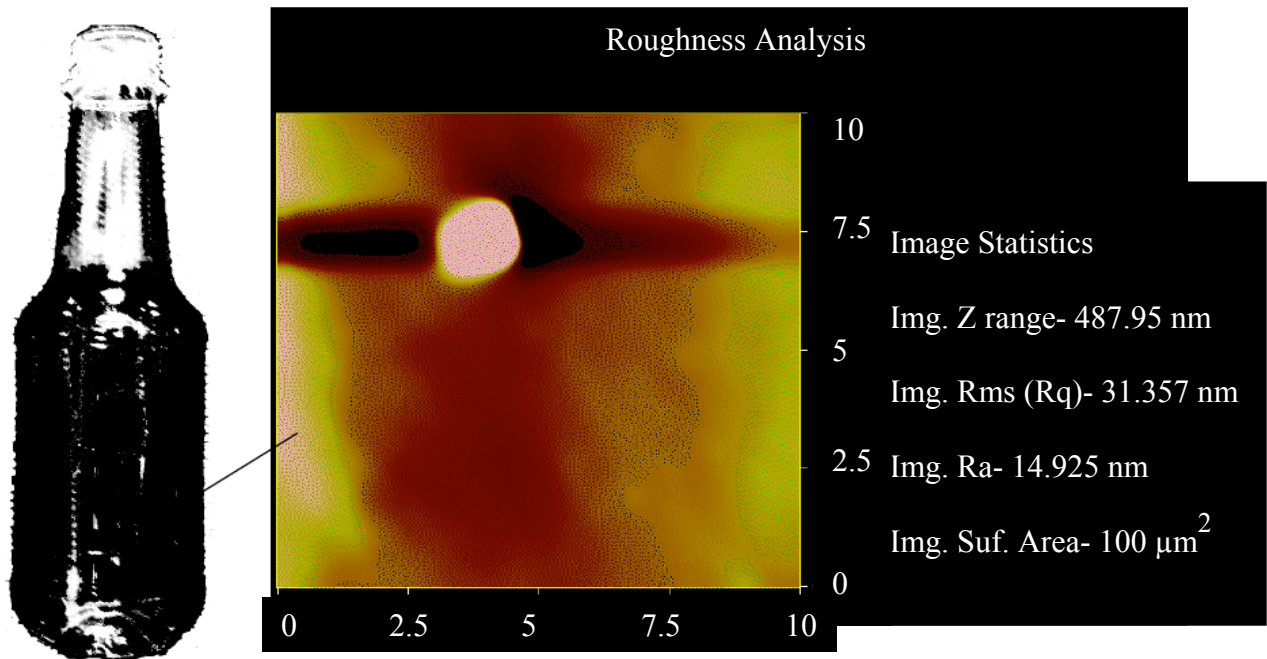


Figure 4-37. Roughness of the body of the coated bottle (BB2)

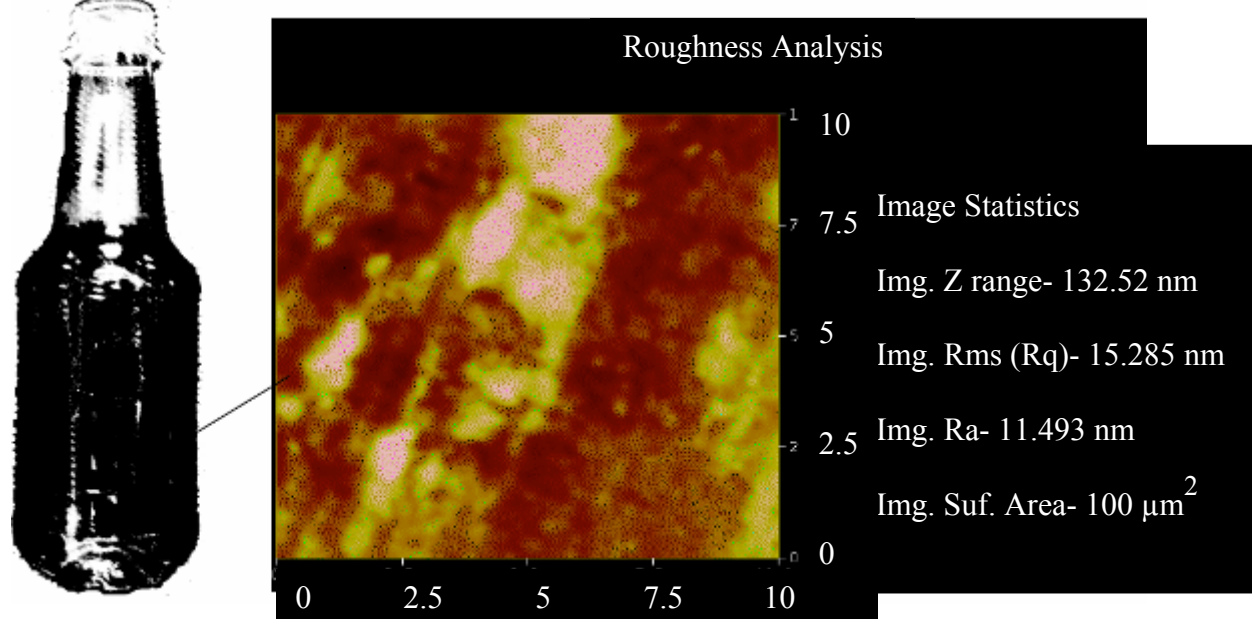


Figure 4-38. Roughness of the body of the coated bottle (BB3)

In order to determine the reason behind the sudden increase in the OTR values from week 0 to week 1 in PLAC bottles exposed to alcohol and to analyze the effect of alcohol on the coating, we used AFM. Also PLAC bottles containing alcohol from week 1 through week 16 were analyzed to see the changes happening during the shelf life study. Figure 4-39 to 4-46 show the images obtained by AFM showing valleys or fissures in the profiles of PLAC bottles stored with alcohol at weeks 1, 2, and 4.

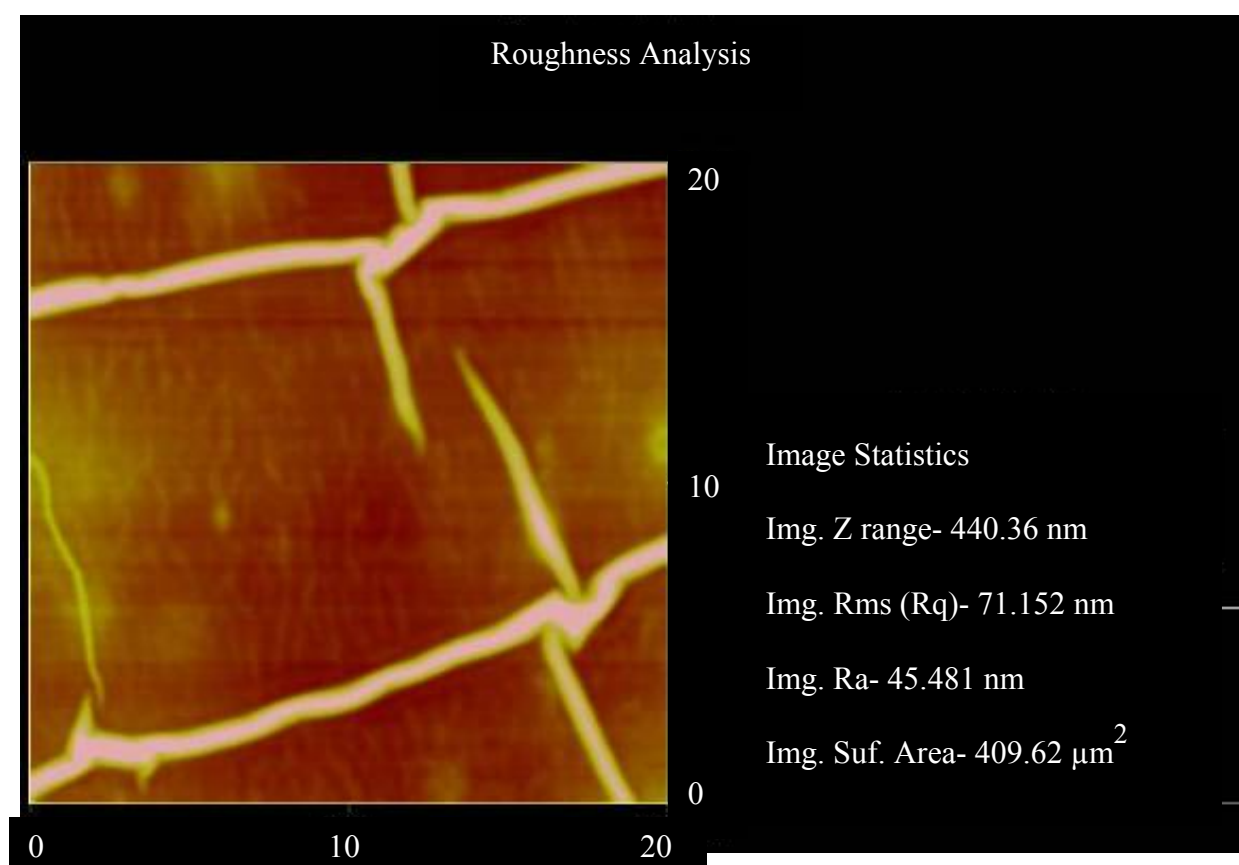


Figure 4-39. Body roughness of the PLAC bottle exposed to alcohol for one week.

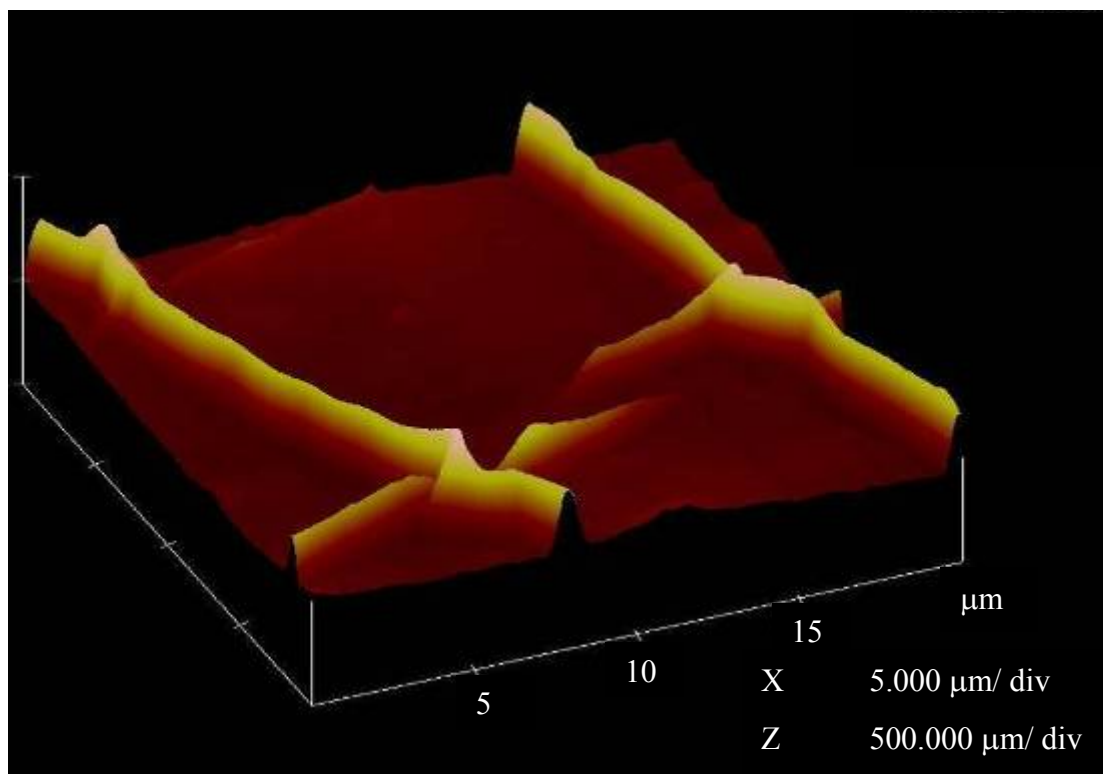


Figure 4-40. 3-D image of PLAC bottle body roughness exposed to alcohol for one week.

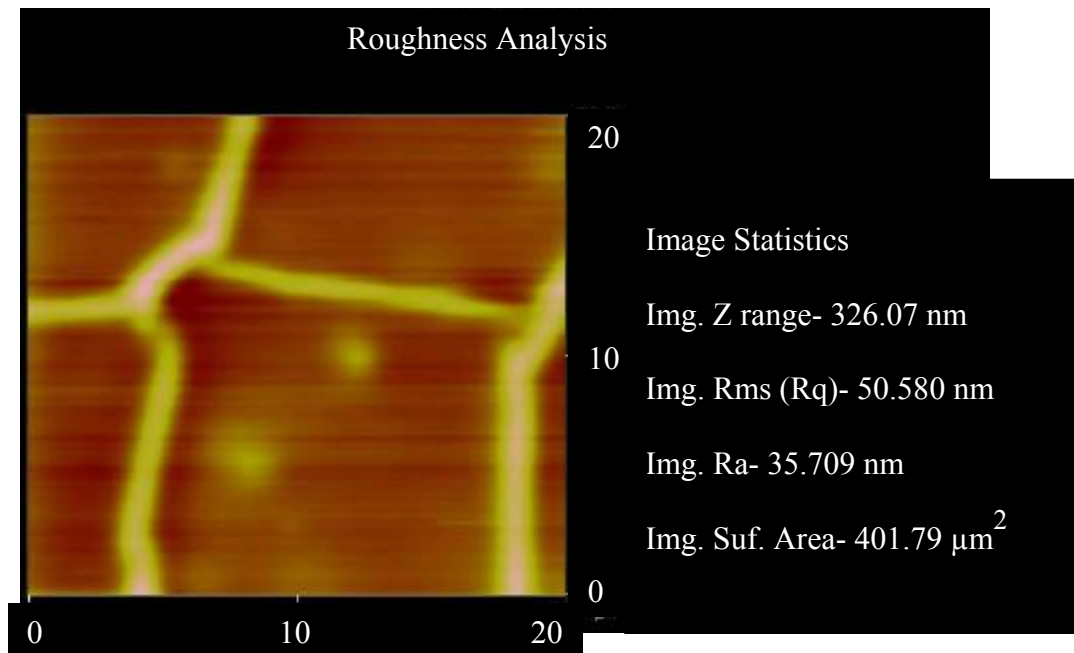


Figure 4-41. PLAC bottle body roughness exposed to alcohol for two week.

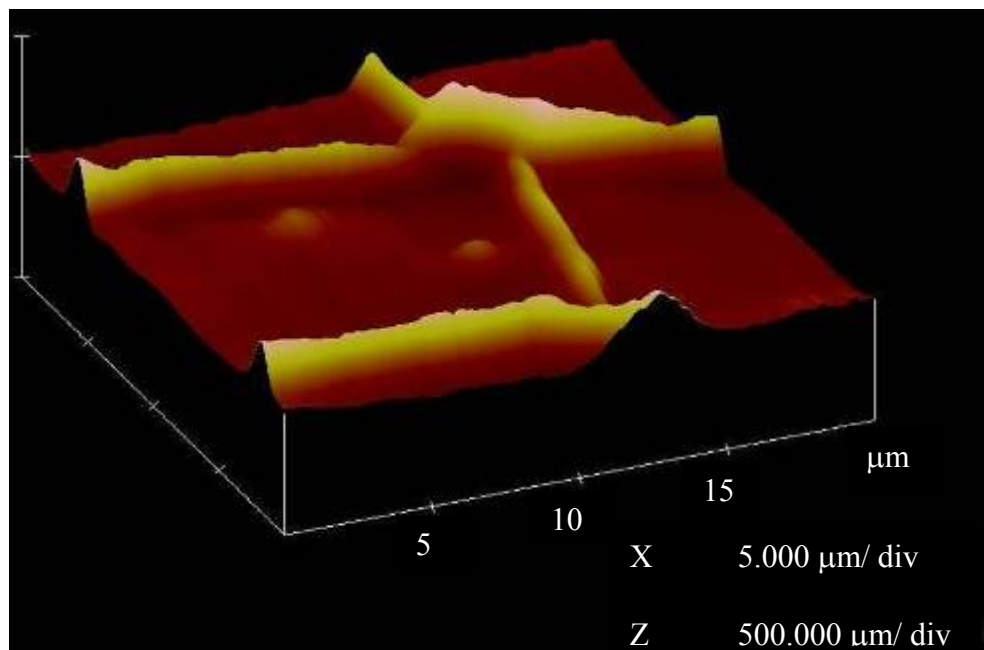


Figure 4-42. 3-D image of PLAC bottle body roughness exposed to alcohol for 2 weeks.

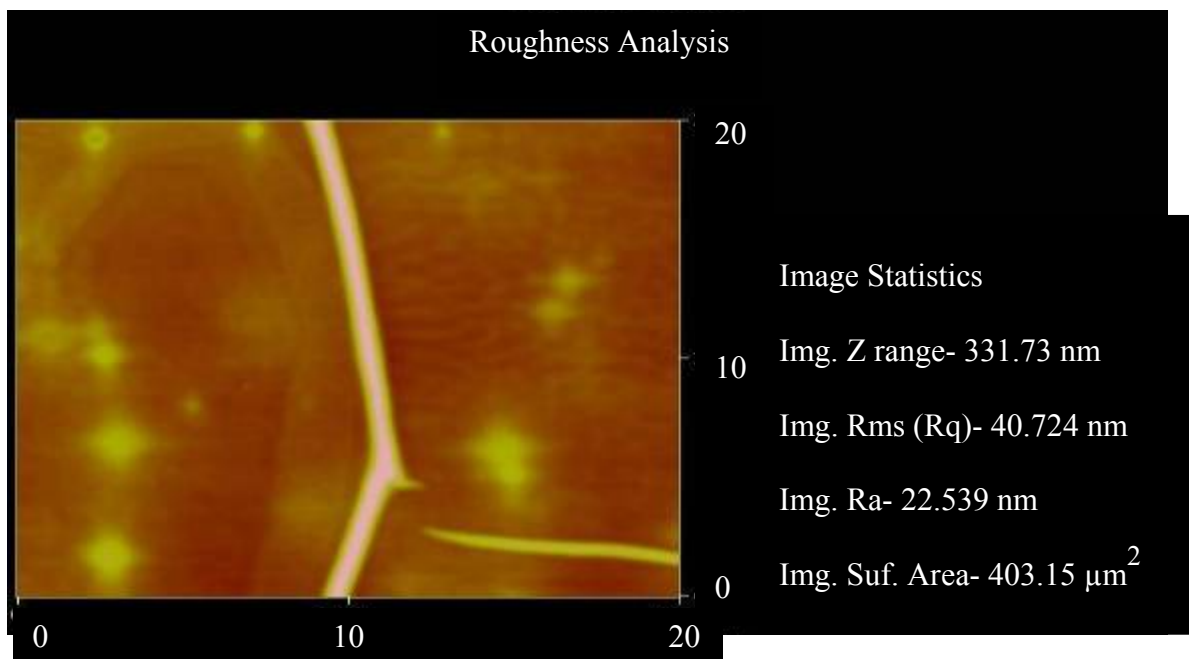


Figure 4-43. PLAC bottle body roughness exposed to alcohol at week 4

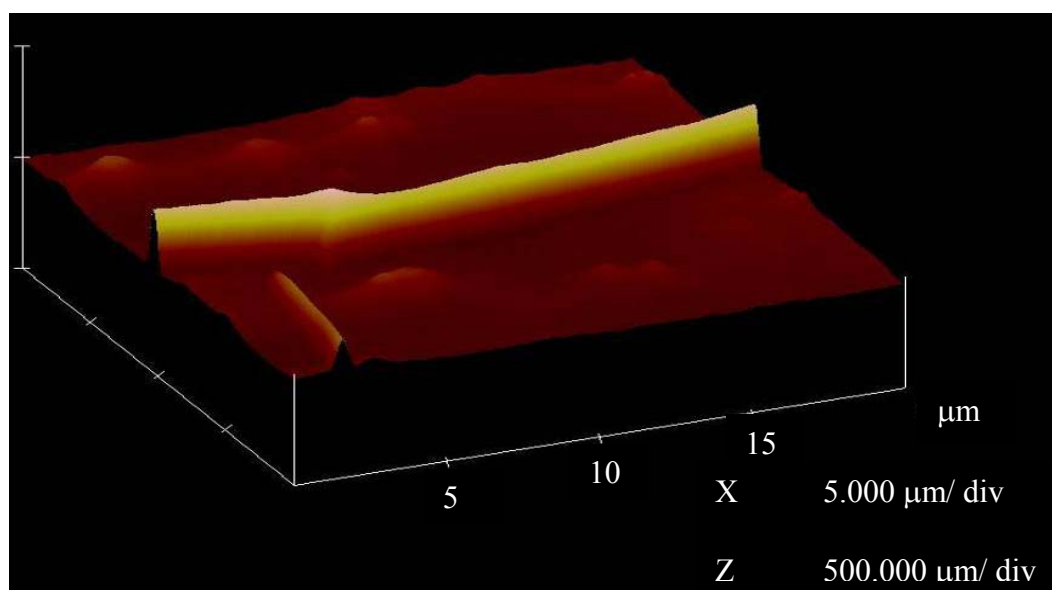


Figure 4-44. 3-D image PLAC bottle body roughness exposed to alcohol at week 4

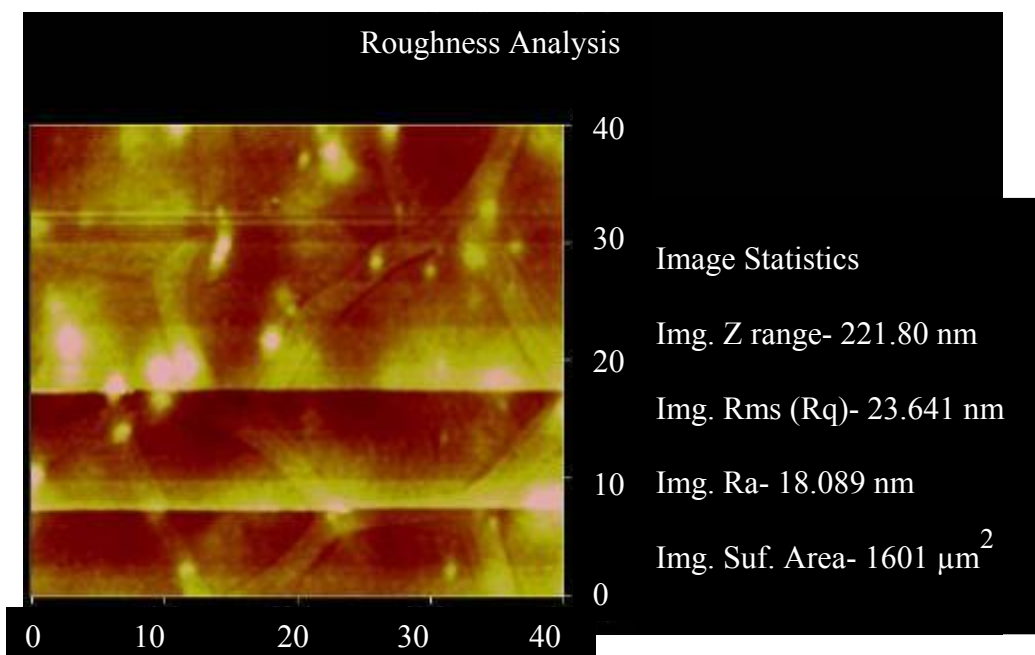


Figure 4-45. PLAC bottle body roughness exposed to alcohol at week 8

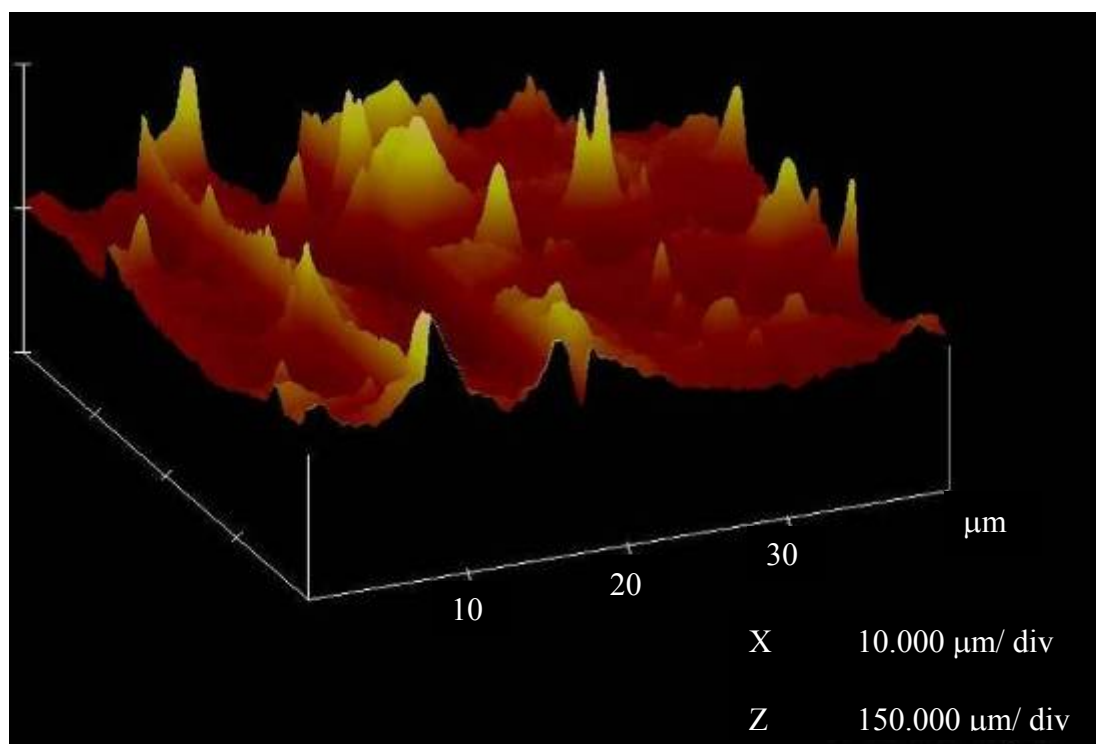
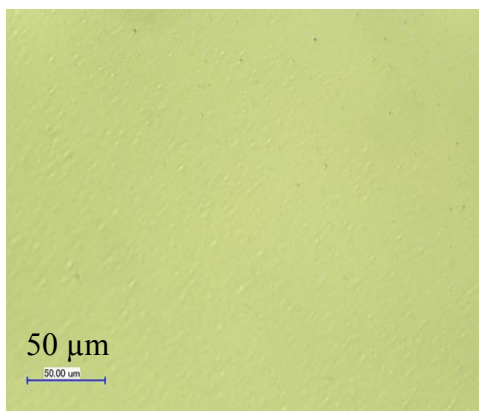


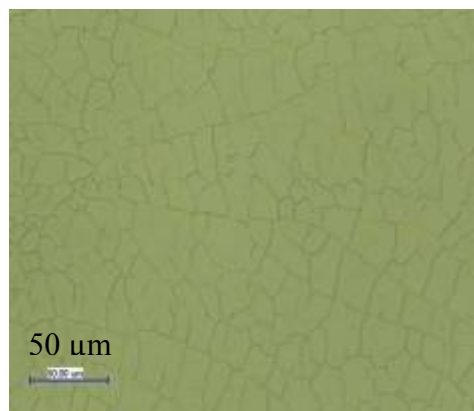
Figure 4-46. 3-D image of PLAC bottle body roughness exposed to alcohol at week 8

4.6 Optical Microscope Analysis of Coated PLA bottles

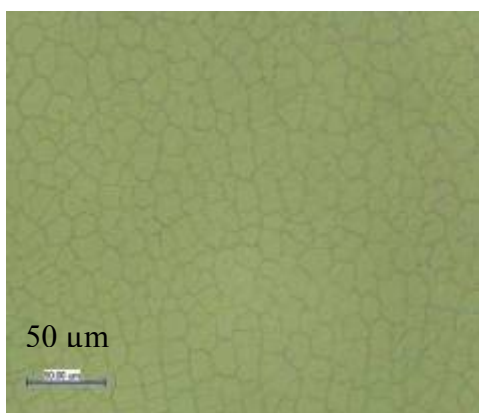
In order to investigate the changes occurring in silicon oxide coated PLA due to storage of alcohol and water during the shelf life study of 16 weeks at 37.8 °C and 70 % RH, samples were analyzed with optical microscopy. In the case of bottles stored with alcohol, the cracks were visible after just one week of storage, whereas in the case of control bottles no cracks were visible even after 16 week storage.



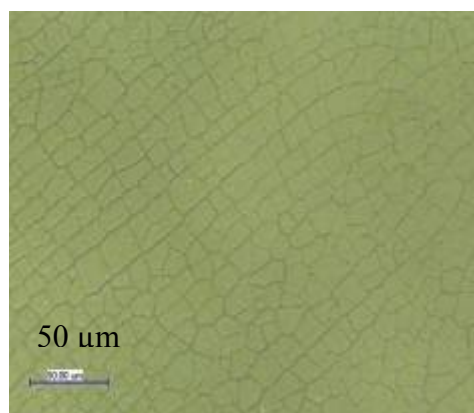
Week 0



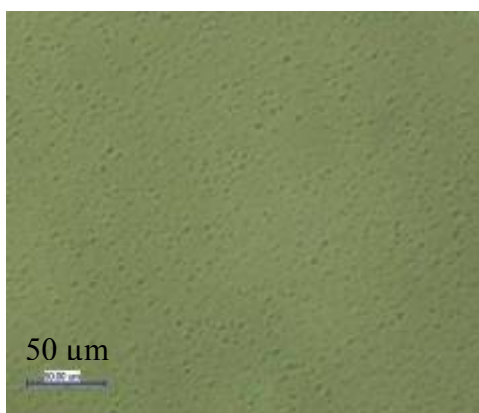
Week 1



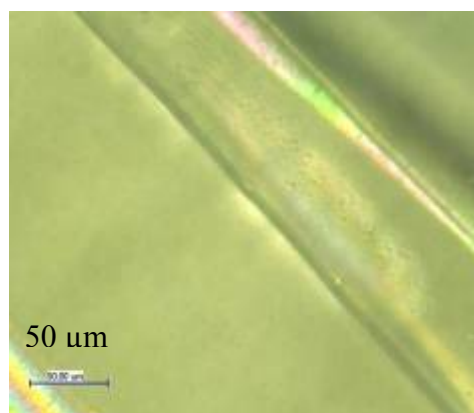
Week 2



Week 4

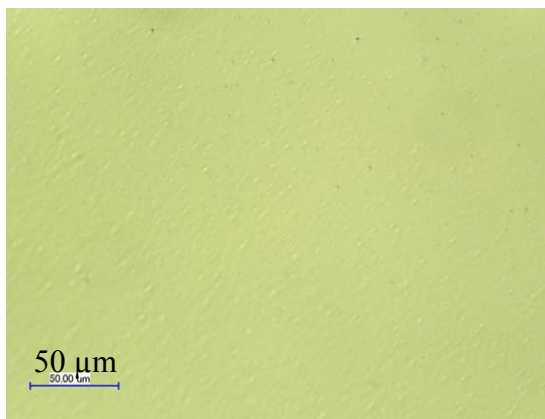


Week 8

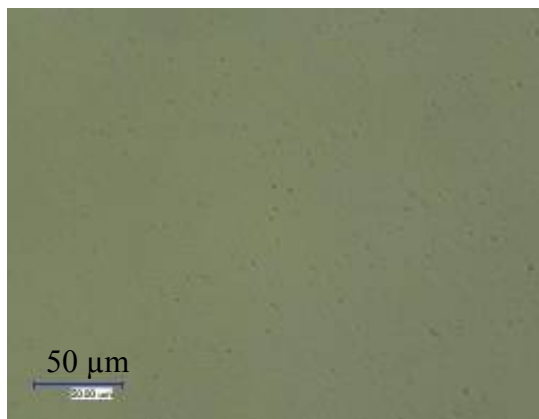


Week 16

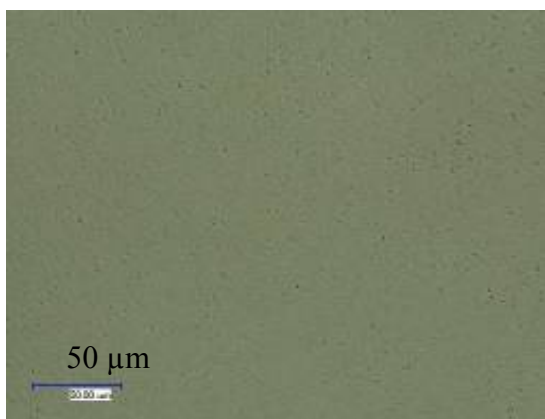
Figure 4-47. Optical micrographs of coated PLA bottles stored with alcohol



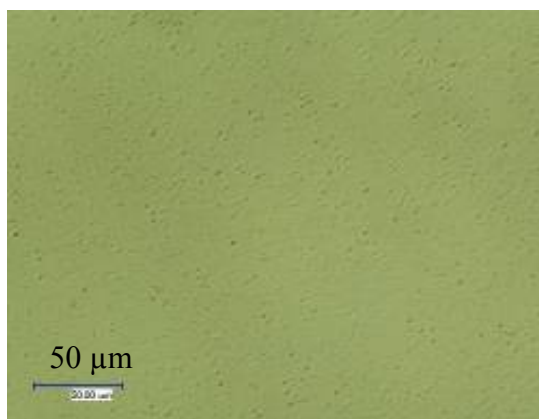
Week 0



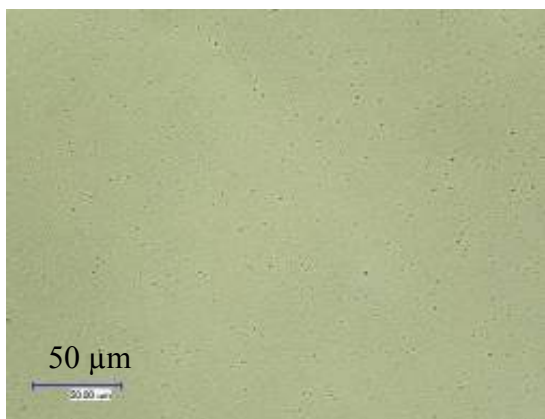
Week 1



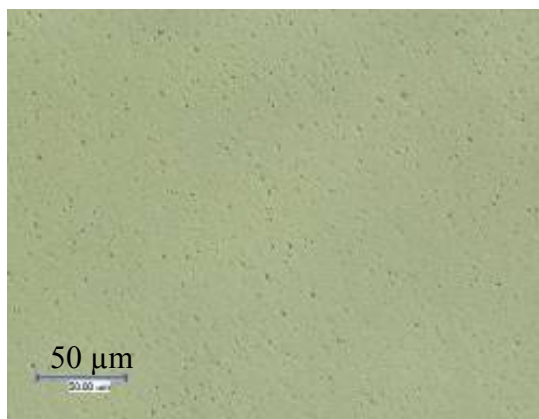
Week 2



Week 4



Week 8



Week 16

Figure 4-48. Optical micrographs of coated PLA bottles stored with control

CHAPTER 5 - CONCLUSION

The purpose of this study was to measure the changes in thermal, mechanical and barrier performance achieved by coating PLA bottles with SiO_x . The resulting characteristics were then compared with uncoated PLA and PET bottles. Four different types of bottles were used: PLA, SiO_x coated PLA (PLAC), single layer PET (PETS) and 3-layer co-extruded PET (PETM). Bottles were stored with two simulants (alcohol and sugar/acidic solution) and a control (distilled water) for 4 months at 37.8 °C and 70% RH. The bottles were tested at weeks 0, 1, 2, 4, 8 and 16.

It was observed that both PLAU and PLAC bottles exposed to alcohol visually showed similar aging symptoms. At week 4 onwards, the loss of clarity was apparent and after 16 weeks cracks were visible throughout the bottles. The bottles filled with sugar/acidic and control solution showed reduced clarity in the finish and bottom after 4 weeks. No change was observed in the physical appearance of PETS and PETM bottles.

Initially HDT and T_g of both PLAU and PLAC was similar and lower than that of PET. Throughout the duration of the study, both HDT and T_g of PET remained higher as compared to PLA. HDT and T_g of both materials increased with time. Increase in HDT and T_g of PLA was explained as a result of increase in the molecular weight, as reported elsewhere [65]. Due to the brittleness of PLA bottles exposed to alcohol, HDT and T_g could not be measured after 16 weeks of exposure. PETS did not show any significant change from week 8 to week 16. HDT and T_g of PETM could not be determined due to delamination.

The mechanical performance of the bottles was evaluated on the basis of tensile and compression strength. The tensile strength increased for PLAU and PLAC from week 0 to week 16, peaking at week 8 and then slightly decreasing. This was observed for both sugar/acidic and control solution and closely follows the trend for molecular weight change [65]. For the bottles

exposed to alcohol, tensile strength increased from week 0 to week 8 and then almost halved at week 16, dropping below even the initial value of unexposed containers. This also follows the trend for molecular weight change, which dropped more severely for PLA exposed to alcohol than other simulants [65]. PETS did not show any significant change throughout the study when exposed to any of the solutions.

Compression strength of PLAU or PLAC containers did not change for sugar/acidic and control solution from week 0 to week 16. Compression force is a direct response of the overall structure of the container. Additionally, with standard deviation being as large as 10% of the average value of unexposed container, this test is unlikely to yield statistically significant responses as a result of bottles exposed to simulants. Compression strength at week 8 for the bottle exposed to alcohol was statistically higher than week 0 but not different than week 1, 2, and 4. Compression strength of PET increased after one week of exposure but did not change thereafter for any of the three solutions.

WVTR of PLAU significantly increased in week 16 when exposed to alcohol as compared to sugar/acidic and control solution. Again, the drop in molecular weight of PLA exposed to alcohol was more severe than PLA exposed to either sugar/acidic or control solution [65]. After one week of exposure to alcohol we observed cracks in the SiO_x coating. This explains the similarity in behavior of PLAC with PLAU exposed to alcohol after one week of exposure and beyond.

OTR of PLAU significantly increased in week 16 when exposed to alcohol but this change was not observed when it was exposed to sugar/acidic and control solution. OTR of PLAC significantly increased after week 1 of exposure to alcohol and followed the trend for PLAU. This can be explained by the development of cracks in the SiO_x coating in the first week

of exposure after which it behaved like uncoated PLA. In case of exposure to control, increase was significant only after 16 weeks. There was no change in OTR for PET with any of the simulants.

Weight loss of container product over 16 weeks in PLAU and PLAC was higher in case of the control than of alcohol. The water molecule is smaller than the ethanol molecule, inducing a faster diffusion of water through the PLA matrix. Additionally, water has more affinity towards PLA given the similar polarity because of hydroxyl groups. This will mean a higher solubility coefficient for water as compared to alcohol. Both of these factors ultimately allow for a faster rate of permeation and thus higher loss of water over a period of time than alcohol.

Based on the above remarks, it can be concluded that SiO_x coating improves some of the properties of PLA to a certain extent. But the retention of those improved properties over the period of time is highly dependent on the nature of the product that coated PLA will be exposed to. For example, exposure to alcohol seemed to create cracks in the coating while the control solution was largely inert to the coating. Further studies are needed to establish this severe response to alcohol and the chemistry behind it. Interestingly, “limited” exposure to all of these solvents that had some polarity and capability to make hydrogen bonds increased mechanical and some barrier performance, although excessive exposure had exactly the opposite effect. This closely followed the trend for molecular weight change. The exact nature of the bonds formed and the dynamics of increasing and decreasing molecular weights would need to be done separately in a more substantial and detailed body of work focused solely on the chemical bond analysis between PLA and SiO_x .

Lastly, the barrier performance of coated PLA against oxygen was at par or slightly better than single layer PET as long as both the coating and polymer matrix were intact. Crack

development and loss of molecular weight significantly undermined this performance. This cannot be stated for barrier against moisture. PLA has a larger affinity towards moisture than PET and even after SiO_x coating; it had a higher transmission rate than PET. Both OTR and WVTR will likely improve and sustain for a longer period if a higher thickness of coating is applied. This could be covered in a future study.

In conclusion, coated PLA generally outperformed uncoated PLA as long as the coating was intact. It also came very close to emulating PET's barrier properties but is dependent on the type of product and length of exposure. SiO_x coating does not behave similarly to an elastic material and has a tendency to crack. Techniques to improve integrity of the coating over time need to be refined. Thermal and mechanical properties of PET are still superior to those of coated PLA.

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