

QATAR UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

AN IMPROVEMENT OF INTERFACIAL ADHESION BETWEEN AL FOIL AND LOW

DENSITY PE THROUGH BLENDING WITH FUNCTIONLIZED POLYMERS

BY

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the College of Arts and Sciences
in Partial Fulfillment of the Requirements for the Degree of
Masters of Science in Material Science and Technology

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ABSTRACT

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Title: _An improvement of Interfacial Adhesion between Al foil and low density PE through blending with functionalized polymers

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An enhancement of interfacial adhesion between low density PE (LDPE), particularly QAPCO LDPE packing grade and aluminum foil is an important challenge in designing of multilayered packaging (TetraPak type of packaging) due to insufficient inherent adhesion between both untreated components. Bad adhesion between them results in undesirable leaching of liquids from packaging and the penetration of oxygen into them what causes deterioration of packed liquids. The target of the thesis is a development of new modification protocols for modification of LDPE through blending with various grades of functionalized polymers. PE is the most common plastic that has been used in industry for many applications, which means that is the most available plastic. PE has limitation; one of this limitation is hydrophobic character that makes achieving necessary adhesion more difficult. The interfacial adhesion can be improved using many methods but adding additives to selected LDPE provided by QAPCO) is main focus in this thesis as a simple and effective modification process.

DEDICATION

This work dedicated to my family for the support. You have made me stronger, better and more fulfilled than I could have ever imagined.

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CHAPTER 1: INTRODUCTION

1 A Brief Overview on Polyethylene (PE)

1.1 General background

During the course of studying the decomposition of diazomethane in 1898, Hans von Pechmann discovered polyethylene (PE) by coincidence[1–3]. Pechmann observed that the product of the reaction he was studying was white in color and presumed a waxy nature[4,5]. Pechmann's colleagues Eugen Bamberger and Friedrich Tschirner characterized the material they found that, it contained a linear long chains of hydrocarbons ($-CH_2-$) and they named it PE instead of PE[6,7]. The discovery of PE almost went unnoticeable, as it was not regarded for industrial application. The rediscovery of it coincidentally as well on the hands of The Eric Fawcett and Reginald Gibson in 1933 at Imperial Chemical Industries (ICI). Similarly, they found the material white and waxy but this product comes from mixing ethylene and benzaldehyde and extreme high pressure is applied[8]. This experiment was difficult to replicate due to the introduction of oxygen during the reaction.[9]. It wasn't until two years later, in 1935, that a chemist named Michael Perrin from the same company ICI developed a method to reproduce this reaction. It was achieved here by introducing small quantities of an oxidizing agent (which, inadvertently, was present in an initial production of the material when it was initially produced) that were needed to initiate the reaction[7]. Therefore, PE was synthesized through high pressure, which made it possible to manufacture low density PE (LDPE) in the year 1939[10–12]. Due to the use of free-radical polymerization in this process, however, high branched LDPE is the only product that can be produced[13,14].

It was the invention of catalysts that led to the enhancement of polymerization at lower temperatures and pressures that made a huge impact on the commercial production of PE[15,16]. It has been established successfully that two different research

groups in two different countries have been able to synthesize linear PE. The first group is Philips Petroleum Company in the United States which is run by J.P. Hogan and R.L. Banks and the second group run by Karl Ziegler at the Max Planck Institute in Germany[17]. Robert Banks and J. Paul Hogan at Phillips Petroleum discovered the first catalyst based on chromium trioxide. When propane gas was passed through a nickel-oxide catalyst containing a chromium salt, they discovered a waxy solid. As a further step, further supplementary measurements were taken by replacing the propylene gas with ethylene gas, leading to the synthesis of linear PE [18–21]. On the other hand, Ziegler group published in 1950 the ‘Afubu’ reaction[22]. This reaction is characterized by the introduction of alkenes (ethene typically) into the Al-C bond of an aluminum alkyl, which results in the formation of a long-chained aluminum alkyl that can undergo further reactions or decompose into its respective alkene terminal[23,24]. Through a combination of accidental discoveries (the "nickel effect") and systematic research, Ziegler extended the ‘Afubu’ reaction to its logical conclusion (linear PE)[25,26]. The culmination of this catalyst system came with the addition of titanium as a co-catalyst, which permitted the production of linear PE in ambient conditions[27,28]. The Ziegler’s new catalytic system using titanium halides and organoaluminium that worked at even lower temperatures and pressures[29]. Ziegler catalysts are more expensive and more difficult to work with than Phillips catalysts as far as cost is concerned, but both are widely used in industrial applications [30]. After working with the system for many years, Karl Ziegler improved it by adding magnesium chloride to it [31]. So, both groups have used transition-metal catalysts to produce linear PE under (relatively) low pressure and temperature conditions. The resulting material was named high-density PE (HDPE), due to its significantly higher degree of crystallinity compared to PE produced through the high-pressure process[32]

PE is categorized into three categories based on its melting point: low, medium, and high density, each having specific industrial applications. Further categorization as per the following: 1) high density PE (HDPE), 2) ULDPE (ultra-low-density PE), 3) LLDPE (linear low-density PE), 4) MDPE (medium density PE), 5) HMWPE PE (high molecular weight) and 6) UHMWPE (ultra-high molecular weight)[33]. It is important to note that to produce LDPE, only an autoclave or high-pressure process combined with elements such as organic peroxide can be used. The manufacturing of LDPE, LLDPE, MDPE, and HDPE requires the use of transition metal catalysts, including Ziegler-Natta, Phillips, and single-site catalysts[34].

The LDPE class of PE remains an interesting one because it is thought to be the first thermoplastic polyolefin used on the market. During World War I, it was used to sheath electrical cables for radars[35,36]. A unique characteristic of LDPE is its low manufacturing cost and its ability to be fabricated into a wide range of different applications[37,38]. LDPE is the most common used plastic in the world because it has thermal stability and low toxicity[39–42].

1.2 Properties and synthetic processes of PE:

1.2.1 Structure:

PE has the simplest polymer structure, consisting of repeating units of methylene, as illustrated in figure 1[43,44]. To express the nomenclature of PE, the IUPAC uses the term poly (methylene). This repeating unit will consist of (-CH₂-CH₂-) with the IUPAC's name for the monomer ethene[45]. In addition, PE's molecular structure changes as its density changes, and this affects its properties in general, which is why this type of material is found in many countries around the world[46].

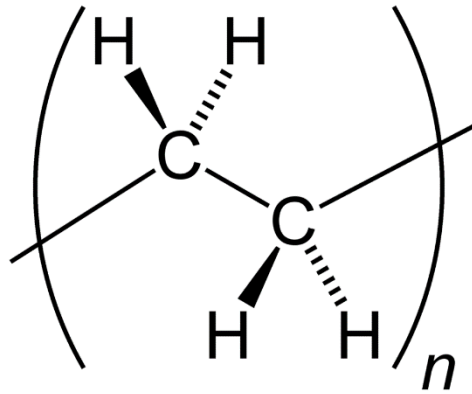


Figure 1: PE structure

1.3 Types of PE and its structure:

1.3.1 Low density PE (LDPE) :

LDPE is prepared by free radical polymerization at high-pressure condition. This type is composed of 3,500-40,000 carbon atoms, with a lot short branches in comparison to other forms of PE; LDPE is a solid with a slightly transparent color and a density range of 0.915–0.930 g/cm³, making it the least dense. It can resist temperatures of up to 80 °C for an extended period of time and up to 95 °C for a short period of time. The crystallinity of LDPE typically ranges from 50 to 70%. Furthermore, LDPE has high chemical resistance to a wide range of chemicals, including acids, alkalis, and inorganic solutions [47].

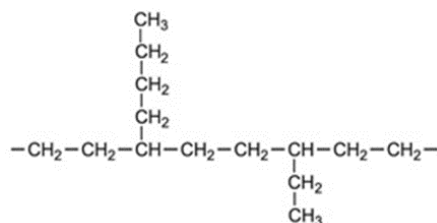


Figure 2: Structure of LDPE

1.3.2 Linear Low-Density PE (LLDPE) :

This type structurally like LDPE, synthesized by polymerization ethylene with small

amounts of 1-octene and 1-hexene with 1-butene using metallocene catalysts. It has short uniform branches and linear backbone LLDPE has a density of 0.915 to 0.940 g/cm³. It has a linear structure with several small branches made up of carbon atoms bound to hydrogen atoms. Polymerization of ethylene with long chain olefins is the most common way to make it. LLDPE outperforms LDPE in terms of tensile strength, impact resistance, and puncture resistance, although it has a narrower molecular weight dispersion. LLDPE is also exceedingly flexible and has the ability to elongate under stress, as well as having excellent electrical conductivity and characteristics. LLDPE mostly used in the packaging industry [48].

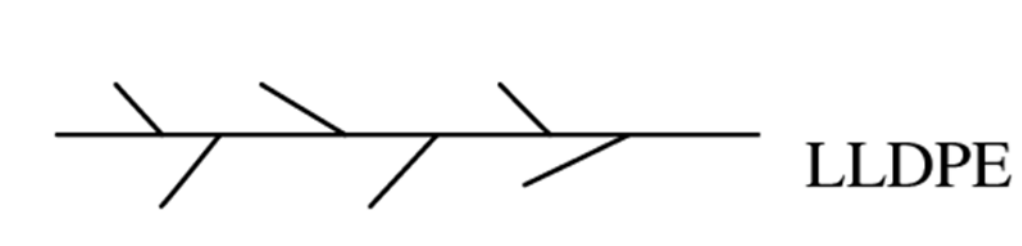


Figure 3: Structure of LLDPE.

1.3.3 High density PE (HDPE) :

HDPE has no degree of branching and manufactured at low temperature and low pressure using a suitable catalyst (e.g., Ziegler-Natta catalysts). It is derived from modifying natural gas or catalytic cracking of crude oil into gasoline. It has a high strength-to-density ratio, with a density ranging from 0.940 to 0.970 g/cm³. As a result, when compared to the rest of PE, it has the highest density. In comparison to LDPE, HDPE has a higher intermolecular strength and tensile strength. In reality, HDPE has a higher crystallinity than LDPE due to short chain branching at the polymer backbone (up to 90 percent). HDPE is utilized in a variety of industrial applications, including food preservation packages and bottles (for food, detergents, and cosmetics), as well as fuel tanks, pipes, and kitchenware. [49,50].

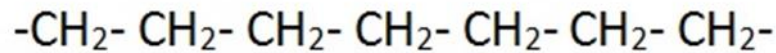


Figure 4: Structure of HDPE

1.4 Properties:

PE exhibits mechanical, chemical, electrical, and thermal properties[88,89]. Among PE's mechanical properties are high ductility, high impact strength, low hardness and rigidity, and low strength[90,91]. The low melting point of PE makes it unique in terms of thermal properties compared to other thermoplastics.[92–95]. Different types of PE have different melting points. The medium and high-density PE (MDPE and HDPE) are with range of 120 to 130 °C[96]. As a result of less branching, low-density PE has a lower range than high-density PE and has a range of 105 to 115 degrees Celsius[97]. The combustion will happen above 350 C[98–100]. Chemically, PE is a nonpolar macromolecule, its saturated hydrocarbon and behave chemically like paraffin[101]. In PE, crystallinity changes with density. A higher density will result in more crystallinity, which will affect mechanical and chemical properties[102]. Most of PE types have resistance to chemicals which means they will not be attacked by strong base or strong acids easily[103,104]. Electrically, it is a good insulator and is used in electrical equipment[105–107].

1.5 Application:

PE possesses several excellent properties that make it a perfect candidate for certain applications. For example, LDPE is a material with a low melting point, which makes it easy to mold[108]. LDPE is also more moisture resistant than other plastics, which makes it ideal for products intended for use in food packaging[109]. LDPE is considered a safe material because of its properties such as low toxicity[100,101], low

reactivity[112], and low flammability[113]. Furthermore, it has been used in food packing since it is relatively inert and nontoxic polymer[114,115]. Due to their ability to meet new application requirements, polymer blends have become increasingly popular in both research and application[84,85,106–128]. Blending chemically distinct polymers is an important method for designing products with better material properties in industrial manufacturing. Polymer blends offer a way to combine the beneficial properties of several polymers to improve properties that could not have been achieved with one polymer alone. Polymer blends are an important subject in the manufacturing of novel materials because they have greater properties than plain polymers[139]. Polymer blends are also important ecologically and economically[140]. Polymers can be divided into two main categories: semicrystalline and amorphous, depending on the arrangement of the monomer unit pattern, and this is what makes polymers popular [141]. A thermoplastic, for instance, has no free electrons within its bonds, so it is used as an electrical insulator[132–134]. However, PE is heterogeneous in nature, which means that LDPE for instance is composed of both crystalline and amorphous regions having different structures and differing reactivity[145].

There are numerous approaches to surface treatment of polymers, including the use of flame various chemical, mechanical, and physical modification by plasma techniques[146–149]. They all result in an increase in surface energy, which leads to an improvement in wettability and a stronger bond between the polymer and metal layers[150–154]. LDPE is most used in food packaging in combination with aluminum foil. The objective is to increase the interfacial adhesion between the LDPE and aluminum foil. This can happen by adding additives to LDPE to increase the hydrophilicity resulting in better wetting of Al surface[155,156]. The interfacial adhesion happens when two different materials are bonded together physically. The

aluminum foil is hydrophilic, and LDPE is hydrophobic so, the interfacial adhesion will be increased by increasing the hydrophilicity of LDPE by adding polar groups[147–153].

To achieve enhanced interfacial adhesion, both materials must possess the same properties. A hydrophobicity that is equal between the two polymers can create a strong bond between the two materials. With this property, greater dimensional stability can be achieved[164,165]. LDPE is often combined with additives to increase the interfacial adhesion between the polymer and the additives. It appears that LDPE grafted with maleic anhydride is a very suitable additive (e.g., commercial product OREVAC)[166–168]. The addition of that component will increase the hydrophilicity of LDPE that will lead to enhanced interfacial adhesion with the aluminum foil. LDPE is hydrophobic polymer with relatively low wettability (surface free energy) and this is one of the reasons to add OREVAC to LDPE to enhance its wettability and therefore its adhesion characteristics.

CHAPTER 2: LITERATURE REVIEW

2.1 General background:

Human civilisation has been profoundly influenced by the materials we use in our daily lives[169]. The polymer industry dominates our fast-evolving daily needs and provides endless opportunities for the development of new technologies in today's world. Most construction materials are composed of polymeric materials, such as polyolefin, polyester, or polyamide[170]. Consequently, the development of new functional polymers will undoubtedly have a significant impact on the future of polymer chemistry. Synthetic materials have historically been created by altering natural polymers, such as cellulose or polyisoprene, through esterification and cross linking[171].

PE is the most extensively used plastic on the planet[172]. They are made from ethylene that's been catalytically polymerized[31]. It's a long-chain thermoplastic polymer made from the combination of monomer molecules, such as ethylene[173]. LDPE is a semi-rigid, transparent polymer. Short and lengthy side-chain branching are more prevalent in LDPE. At high pressure and temperature, LDPE is made via free radical polymerization. Since plastics became widely used as a material for many goods, there have been numerous factors that influence resin behaviour[175]. The term "functionalized polymer" refers to macromolecules with chemically bound functional groups that may be used as catalysts, reagents, protective groups, among other applications[176]. Functional polymers are important in a variety of technical applications, such as optics[177], electronics[178–180], and catalysis[176,181–184]. They're also commonly employed in analytical instruments (such as chromatography columns)[185,186], membranes[187], and solid phase peptide[188] and oligonucleotide synthesis[189]. A functionalized polymer is an inexpensive, simple-to-produce material with desirable properties for functional organic compounds. The

creation of diverse functional polymers for specific purposes has gained increasing importance in recent years [190].

Plastic mixing helps to integrate the qualities of multiple components that create blends that perform better[191]. Blending allows for the use of lower-cost resins while retaining or improving the quality characteristics. It is possible to save money, increase throughput, and tailor material specs to meet specific needs by blending[192]. Combining different polymers can also result in a unique combination of properties not found in one polymer alone [193].

2.2 PE in food packaging industry

There are many plastics produced around the world, but PE is the most frequently used[194]. In the packaging sector, three varieties of PE are typically utilised viz., HDPE, LDPE, and LLDPE [195].

According to its physical characteristics, PE can be stiff and hard or malleable and mushy. The degree of branching of the polymer chain, as well as other features of films and other types of packaging, are determined by the processing conditions[196–198]. Soft and pliable films are commonly used to package and store a variety of products and waste[199–201]. PE has become a preferred plastic over many other plastics due to its low manufacturing cost and the ease of use[202]. They may be manufactured into robust, strong films that are moisture and water vapour resistant[203–205]. In comparison to other plastics, they have a low barrier to oils and fats, as well as gases like carbon dioxide and oxygen, while barrier qualities improve with density alone [206].

Depending on the material's thermal history and film thickness, PE packaging might appear milky-opaque, opaque, or clear[207]. PE coated with a protective tint function as a barrier between the items and UV radiation, thus preventing damage to the contents[208,209]. The cold resistance of PE is better, which can handle

temperatures as low as -80°C [210]. In addition to its durability and flexibility, PE is extremely resistant to fatigue, tearing, and chemical reactions[211,212]. PE is also a superb insulating material. PE is without a doubt less expensive than other polymers due to its size; LDPE would enable greater transportation savings[213]. PE has the property of being elastic, which makes it an ideal material for packaging food items.[214,215] Additionally, PE is widely used in automotive industry to produce better and safer vehicles[216]. PE is used to create valuable plastic bags, sealable plastic sachets, flasks, kitchen utensils, and meal boxes, flex films, tapes, pallet, and plastic sheeting. Because of their durability, PE storage bags are often used by industrial companies for large, heavy items [217].

2.3 Surface characteristic of PE

Particularly PE is distinguished from other plastics by its outstanding user-friendliness. By customizing its surface characteristics, it can gain access to the most profitable markets. Although PE is an inexpensive and easily processed material with excellent bulk properties, the inert nature of its surface has prevented its widespread use in specialty materials. Because of this, unique surface properties that PE lacks, such as printability, ruggedness, viscosity, selective permeability, and microorganism adhesion, are required in certain applications [218].

A material's surface properties have a direct influence on its ability to moisten, adhere, and stick to surfaces, as well as its biocompatibility. Since the 1970s, scientists have been attempting to understand what exactly constitutes a surface, as well as the interphase and how deep into a material, the surface extends. In this respect, surface properties differ greatly from bulk properties. Unlike hard solids, the surface of polymer materials is highly sensitive to temperature and time-dependency[219]. The reason for this is their viscoelastic behaviour, which is dependent on both thermodynamics and kinetics. It is possible that there is a non-equilibrium chaotic environment on the surface

of the polymer as it can constantly reorganize and restructure in response to external stimuli, such as environmental conditions, solvent, etc. These structural changes are a result of the surface's tendency to continually reduce its free energy. The surface chemistry, reactivity, and appearance of the relevant material can vary with ambient and processing conditions, affecting any intended alterations or applications, even when bulk properties are considered [220].

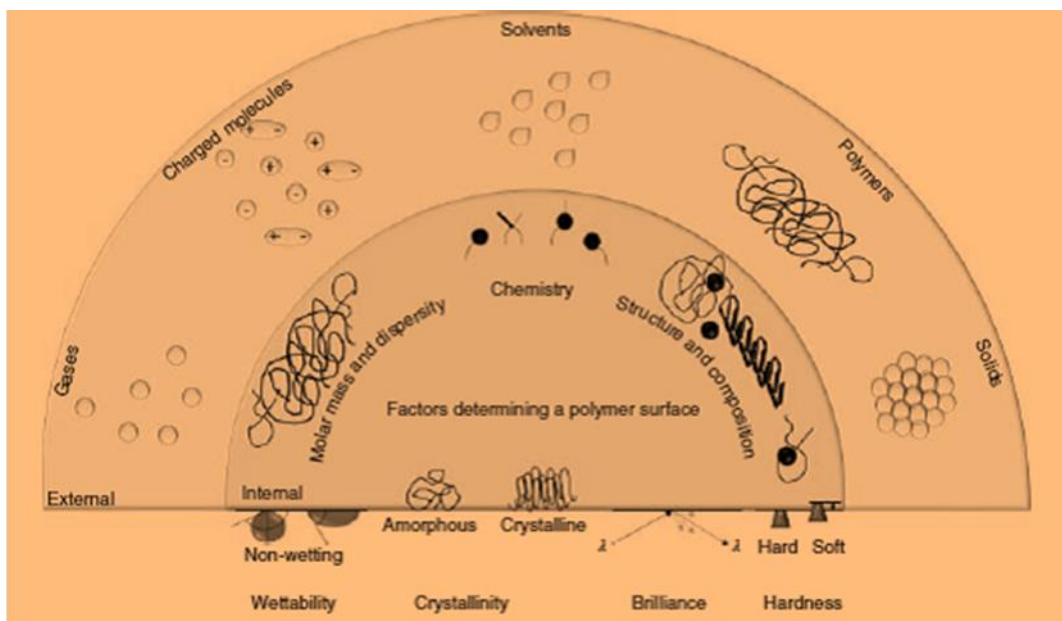


Figure 5: A diagram depicting the parameters that influence the qualities of a polymer surface.

2.4 Polymer Metal adhesive

Coatings, polymer mixes, paints, multilayered sandwiches, adhesive joints, and composited materials all use adhesion to represent a contact between two solids. There are two types of adhesion: "intrinsic" adhesion and "measured" adhesion. The first refers to the adhesive's and substrate's direct molecular forces of attraction. The second is derived from the measurement of the adhesive joint's strength. Adhesion formation requires intrinsic adhesion forces across the interface. [210]. Adhesion knowledge is crucial in a variety of industries, including packaging, automobiles, aeronautics, aerospace, electronics, and sports [211]. Surface chemistry, physics, polymer chemistry, rheology, mechanics, physics, fracture analysis, and many other disciplines are all involved in adhesion[212]. Adsorption, electrostatic attraction, diffusion, and mechanical interlocking are the four primary theories of adhesion that are well known. Adsorption theory states that forces cause macromolecules in the mobile phase (such as adhesive, printing, and ink) to be adsorbed on the substrate (in range from dispersion to chemical bonds)[213]. According to electrostatic theory, there is a charge transfer between two materials that meet at an interface and have different band structures, and so they are bound by electrostatic forces (Figure 11). This approach is only useful for incompatible materials, such as polymer adherence to a metallic surface[214]. When an interface is removed, the diffusion theory deals with the diffusion of macromolecules from the mobile phase into the substrate. The mobile phase flows into the imperfections of the substrate surface and the interlocking action is depicted in the last theory (mechanical interlocking) (Figure 12)[215]. The roughness and porosity of the substrate are adequate factors in this earliest adhesion theory, as the wettability is sufficient in so far as the adhesive is concerned (Figure 12A). Non-wetted parts, cause failures (Figure 12B)[213].

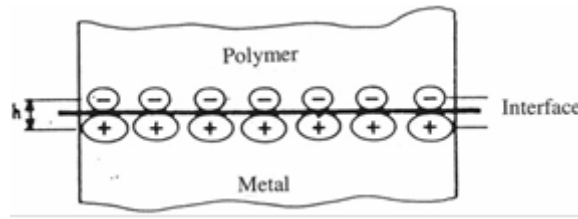


Figure 6 : Electrical double layer at polymer-metal interface.

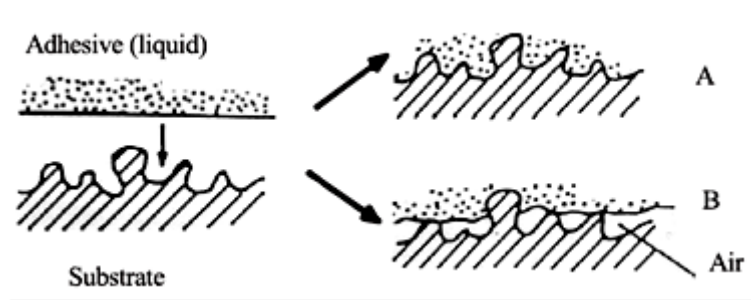


Figure 7 : Good wetting (A) and poor wetting (B) by mechanical interlocking, from Fourche.

A unique sort of adhesion is represented by a weak boundary model. The contact between the adhesive and the substrate would not fail in this model, but the failure would be driven by the creation of a weak boundary layer [216]. As a result, in order to achieve good adhesive qualities, the weak border layer should be removed. With the exception of Al, which has a coherent oxide layer, this problem can occur in metals with a scaly oxide layer that causes failure at the boundary [217]. The weak interface is also caused by a low-molecular-weight component in PE, which can be eliminated by surface preparation. Bikerman classified the model of weak boundary layers into seven categories, as indicated in the figure (Figure 13)[218].

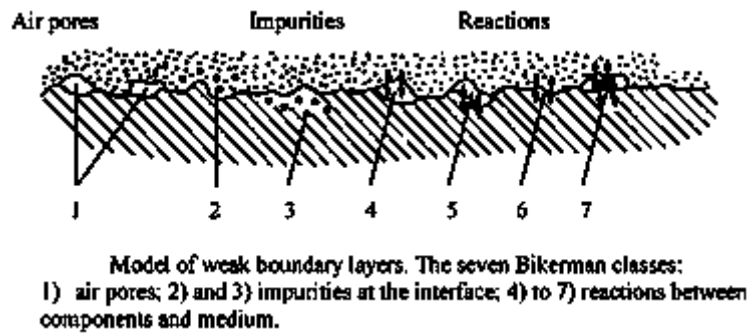


Figure 8 : Seven classifications of weak boundary layers according of Bikerman.

Polyolefins are among the most frequently used polymers in a variety of applications, including packaging, construction, and transportation. Polyolefins can be combined with other materials, such as metals, to improve a variety of properties. A laminate consisting of polyethylene and aluminum foil, for example, is commonly used in the drinks and food (flexible packaging) industries. Heat-sealing qualities are provided by polyethylene (PE), whereas barrier properties are provided by aluminum (Al) [219].

2.5 Adhesion improvement between PE and aluminum

Adhesion promoters in adhesive technology

Adhesion to the substrate is obviously the most important property of an adhesive, but adhesion is also important in the performance of surface coatings, which must adhere to protect and acquire optimal mechanical properties in particulate- and fiber-filled composites. To obtain high initial adhesion, a variety of surface preparation approaches have been applied, ranging from the removal of surface contaminants to chemical modification (phosphating of steel, anodic treatments of aluminum). None of these approaches address the most pressing issue in adhesion science: the detrimental effect of water on organic/inorganic connections. In many technologies, hydrolytic stability is required.

Al foils are commonly used in flexible packaging because they provide excellent light protection and prevent materials from being transported. Lacquering or 2-component-adhesive lamination can be used to transform these foils into flexible packaging laminates. Extrusion coating and lamination have become more popular in recent years, but the annealing process remains crucial. Surfaces with good adhesion and chemical resistance are produced using this method when compared to unwinding properties (high speed). As a result of the reaction between oxygen and humidity in the environment during the annealing process, a continuous oxide layer and new metal surface are generated instantaneously [220]. The oxygen layer changes during annealing at temperatures about 300 °C, accompanied by a loss of water, resulting in a very compact oxide with increased resistance (Figure 14). The corrosion resistance of Al foil is provided by this barrier layer, while the top layer gives strong adhesion to coatings. During annealing, there are variations in the environment from the outside to the inside of the Al coil. Because of this phenomenon, a thicker oxide layer grows along the borders than in the middle, as shown in (Figure 15).

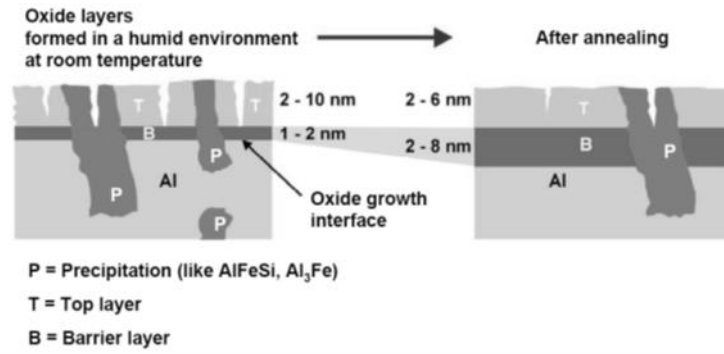


Figure 9: Precipitation embedded in the surface and oxide growth during annealing process.

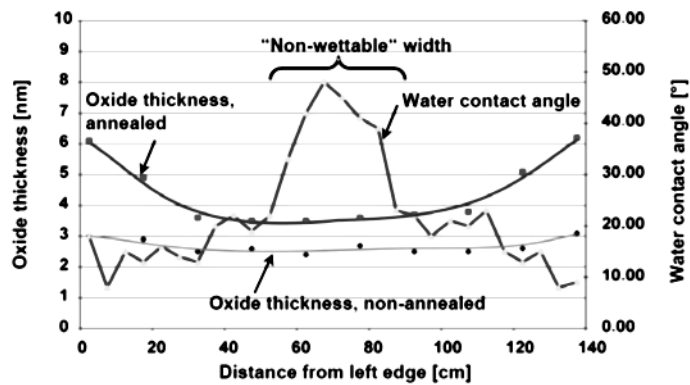


Figure 10:Oxide thickness by IR-absorption.

Adhesion promoters can be used to improve the initial bond strength between adhesives and substrates. These improve substrate wetting or secondary bonding via van der Waals forces, dipole–dipole interactions, hydrogen bonding, or acid–base reactions, among other mechanisms [221]. A coupling agent is a chemically reactive substance that can react with both the substrate and the polymer.

Type of promoters use in adhesive technology

Adhesion promoters can be employed as pretreatments or additives in general. The promoter is employed as a prepared primer or as a solution in a suitable solvent or solvent mixture[222].

Silanes with the general structure $R-Si(OR')_3$, where R is an organofunctional group and R' is a hydrolysable group, are the most technologically relevant category of adhesion promoters now in use and have a strong theoretical foundation. Silane molecules are bifunctional in that they contain polar silanol groups as well as organofunctional groups that can react with polymers. Bascom [223] In his investigation of the structure of silane films deposited on glass and metal substrates, Bascom used a variety of approaches (vinyl-, amino-, and chlorofunctional silane films were deposited as polysiloxanes). They were easily pierced by the wetting solutions, according to contact angle measurements. Many recorded values below the minimal c value (approximately 35 mJ/m² for polyesters and 43 mJ/m² for epoxides) show that the critical surface tension (c) of the silane layer is not an important element in adhesion promotion for optimum wetting to occur. Plueddemann concludes that wettability is less important than silane reactivity in copolymerization [224].

Organometallic compounds based on zirconium are active adhesion promoters. Because zirconium compounds are soluble in both water and organic solvents, they appear to have a wide range of applications in the polymer industry. Hydrolysis dominates aqueous chemistry, which is influenced by zirconium and hydrogen ion concentrations, as well as the nature and concentration of anions present. Zirconium acetylacetonate, zirconium methacrylate, and the family of neoalkoxyl zirconates are all solvent soluble chemicals. Neoalkoxytrisneodecanoyl zirconate, neoalkoxytris(dodecanoyl) benzene sulfonyl zirconate,

neoalkoxytris(ethylenediaminoethyl) zirconate, neoalkoxytris(m-aminophenyl) zirconate, and zirconium propionate are some commercial. Wang[223] has reported the production of a soluble linear Schiff base zirconium-based coordination polymer, as well as other hybrid copolymers, and shown that hot-melt poly(methyl methacrylate), polyethylene, and polypropylene have better adhesion on Al substrates.

Titanate coupling agents have six functions [225], although only three of these are important to their application as adhesion promoters. The alkoxy group of titanate reacts with free protons on the mineral surface to generate an organic monomolecular layer; transesterification results in cross-linking with carboxyl and hydroxyl groups in the polymer; and chain potential entanglement are all examples. Titanate coupling agents are unique in that their reaction with free protons on the substrate surface leads in the formation of a monomolecular layer on the mineral surface, whether the mineral is a filler particle or a metallic substrate.

A large number of inorganic, organometallic, and organic compounds have been investigated, usually in specific adhesives and coatings, in addition to other adhesion promoters. Tritolyl phosphate, for example, has been studied as a thermoplastic adhesive pretreatment for bonding poly(vinyl chloride) to aluminum [226]. When employed as either pretreatment primers or additives, hydroxybenzamines of the general formula have been reported to improve the adherence of a wide range of coatings on zinc, cadmium, and other metallic substrates [227]. In steel-epoxide systems, aminoethylpiperidine has been demonstrated to be helpful [228], and primers based on piperidine derivatives improve adhesive adherence to aluminum and stainless steel[226].

CHAPTER 3: METHODOLOGY

3.1 Materials:

The low-density PE (LDPE) from Qatar Petrochemical Company (QAPCO, Qatar) with the identification code on it LDPE EC-02 was used in project. Using a mounted hot press machine, the granular materials were hot-pressed into thin transparent sheets (Carver 3895, USA). Table 1 summarizes the basic physical features of LDPE grade as well as their possible applications. The main goal of this project was to investigate a various possibilities for a creation an interfacial adhesive joints (LDPE/Al laminates) by bonding LDPE sheets with aluminum (Al) foils (GLAD®, China), and characterize its physical properties.

Table 1: The physical properties and potential uses of the tested LDPE grades

Polymer properties	EC02
Density @ 23 °C (ASTM D-1505)	0.923 g/ cm ³
Melt flow index 190°C/2.16 kg (ASTM D-1238)	4.0 g/10 min
Melting Point (ASTM E-794)	108 °C
Recommended uses	Extrusion of very high clarity blown and cast films

Furthermore, the following materials are used:

- Acetone (C₃H₆O, molar mass M = 58.08 g/mol, density D= 0.787-0.791 g/cm³ at 20°C/4°C, min.99.8% assay by G.C. method) was used to remove any impurities or contaminants from the LDPE and Al surfaces.
- Additivities are used for the surfaces modification:

1. NUCREL™ 960 is a copolymer of ethylene and meth acrylic acid, made with nominally 15 wt% meth acrylic acid.
 2. NUCREL™ 1202 is a copolymer of ethylene and meth acrylic acid, made with nominally 11.5 wt% meth acrylic acid.
 3. NUCREL™ 599 is a copolymer of ethylene and meth acrylic acid, made with nominally 10 wt% meth acrylic acid.
 4. OREVAC® 18302N is a maleic anhydride modified low-density PE.
 5. LOTADER® 3410 is a random terpolymer of ethylene, acrylic ester and maleic anhydride, polymerized by high-pressure autoclave process.
 6. Poly(ethylene-co-methacrylic acid) from ALDRICH Chemistry.
- Ultra-pure water (purity > 99 percent, water purification system Direct-Q ®, France), formamide (purity > 98 percent, FLUKATM, Belgium), and ethylene glycol (purity 98 percent, FLUKATM, Belgium) were used as testing liquids with different surface tension to measure the contact angle when the liquid–vapor interface meets a solid substrate, as well as to determine the changes in total surface free energy.

3.2 Experimental apparatus/equipment

This section describes the equipment/devices, which were used to prepare the LDPE specimens, surface characterizations and evaluate the interfacial adhesion in LDPE/Al bonded joints.

- **Samples preparation**

The LDPE with different additives (ionomers, grafted polymers) having different mass concentrations was blended using a plastograph internal mixer Plastograph EC & Mixer 50EHT (Brabender, Germany) at 30 rpm and temperature 160 °C (Figure 16 A). The LDPE and LDP/Al laminates were prepared by a hot mounting press (Carver 3895, USA) (Figure 16 B) at 160 °C temperature for 120 seconds under a pressure of 2 MPa. Aluminum foil (GLAD®,China) was used to prepare adhesive joints.



Figure 11:Plastograph internal mixer (A) and mounting press machine (B).

- **Wettability study**

The pristine LDPE surface and the modified polymer using additives should exhibit different values of the surface energy giving information about the wettability. The contact angle measuring system OCA 35 (Dataphysics, Germany) with an optical video-base employed to measure wettability changes before and after the modification

process (Figure 17). Water, formamide and ethylene glycol (testing liquids with different surface tension) will be used as testing liquids to evaluate the total surface free energy, polar and dispersive components using the conventional Owens-Wendt-Rabel-Kaelble (OWRK) method. A droplet of approximately 3 μl of each testing liquid will be placed on the samples and the contact angle will be evaluated.



Figure 12: Contact angle measuring system

- **Adhesion investigation**

For the study of adhesion qualities between LDPE and Al components that form a coherent laminate, the 90° peel test was used as an effective method. In the adhesion strength measurements, the peel tester LF-Plus (Lloyd Instruments, UK) was used, which was based on the ASTM D6862 standard test procedure. The NEXYGENPlus testing program is part of this system, which shows the results as numerical numbers or illustrative graphs. Prior to the start of the test, laminated LDPE/Al strips with dimensions of approximately 8 cm height and 2 cm width were tightly fastened on an acrylic two-sided tape (3M 4910k, VHB™). Then, under dynamic conditions, the peel strength (the force per unit width of the laminate) was measured: To ensure that the applied peeling force is evenly distributed over the surface, a 1kN load cell was applied at a 90° angle peeling on the specimen and operated at a slow speed rate ($v=10$

mm/min). The test time was set at a maximum of 360 s to ensure that the peel resistance was obtained from sufficiently large area of LDPE/Al laminates. The peel resistance of the LDPE/Al laminate was tested from a distance of 10 mm to 50 mm. Following the Standard Test Method for 90 Degree Peel Resistance of Adhesives (ASTM D6862), 4-5 different readings of LDPE-Al adhesives were obtained to provide one average value of the peel resistance,

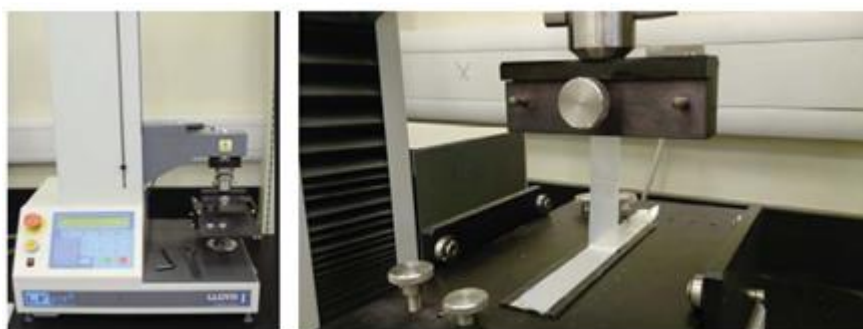


Figure 13. Peel tester.

- **Surface morphology analysis**

The surface topography/morphology and roughness of modified polymer surfaces relates to wettability. Scanning electron microscopy (SEM) was used to focus on the surface morphology (2D) of modified samples and the surface topography (3D) analyses carried out using atomic force AFM technique. The captured images should indicate surface morphology/topography after modification step and after peel tests to understand adhesion mechanism. It is worth noting that the surface modification often leads to morphology changes. Therefore, the obtained AFM and SEM images will serve as an indicator of this purpose. The information about surface morphology in two-dimensional scale of the prepared samples will be obtained by SEM microscope Nova NanoSEM 450 (FEI, USA) using a detector of secondary electrons Figure 19A. For

achieving better resolution, the samples coated by Au layer (few angstroms). AFM used for obtaining detailed information about characteristic changes in a small surface area after modification in three-dimensional scale. The measurements carried out by AFM MFP-3D system (Asylum research, USA) shown in Figure 19B. This equipment contains silicone probe with parameters of 2 N.m^{-1} and 70 kHz, spring constant and resonant frequency, respectively. All measurements will be carried out using tapping mode (non-contact) under ambient conditions in air. This technique provides us also information about the surface roughness (Ra parameter).

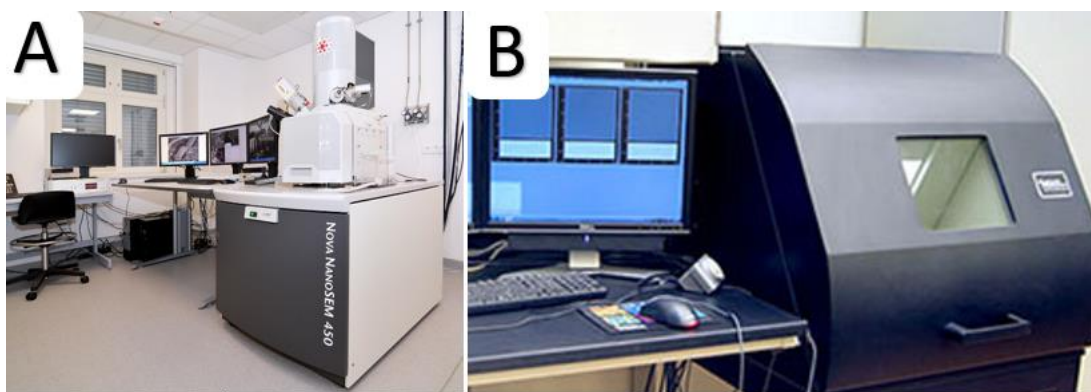


Figure 14 : Equipment for measurement of surface morphology/topography: A - SEM, B - AFM.

- **Chemical composition investigation**

The chemical composition changes in modified polymer surface analyzed by Fourier transform infrared spectroscopy (FTIR). FTIR spectrometer Spectrum 400 (PerkinElmer, USA) allowing analyzing the samples in the mid-infrared ($4000\text{-}500 \text{ cm}^{-1}$) region used for a detection of changes in samples modification (Figure 20). This technique will provide us qualitative data about chemical composition of prepared samples.



Figure 15 : FTIR spectrometer.

3.3 Experimental procedure

This research looked into prospective approaches for improving the surface properties of LDPE in order to improve its adhesion to Al and form LDPE/Al adhesive joints, which can then be employed in industrial applications such as food packaging. Because of the inert nature of LDPE surfaces and their non-polar hydrophobic tendency, the adhesion between LDPE and Al is quite low. Adding commercial additives LDPE was carried out in this study. A 90-degree peel test was also used to evaluate the adhesive quality of LDPE/Al laminates. It should be noted that untreated LDPE samples were used as control samples to compare the differences in surface attributes before and after modification process.

3.4 Preparation of LDPE thin sheets and LDPE-Al laminate

A hydraulic mounting press machine was used to transform the LDPE granulates into thin sheets (Carver 3895, USA). Ten grams of LDPE granules were placed between two transparent polyester sheets between two highly polished stainless-steel plates, with the goal of keeping the grains on the same level. Then, all of the previously prepared samples were placed between the upper and lower platens of the hydraulic press machine between using two stainless steel plates and polyester sheets and separation layers . The required conditions for conducting the experiment were

provided after turning on the equipment. The temperature of the LDPE granules was raised to 160°C, which was slightly higher than the melting temperature. Once the desired temperature was obtained, a one ton load was applied for two minutes to the LDPE granules to transform them into a thin sheet under the impact of the imposed temperature and pressure. Finally, the created LDPE sheet was gently cooled down to room temperature. The sheets' thickness measured with a Vernier caliper and determined to be about 320 µm for EC02 LDPE. The mounting press machine was used to make the LDPE/Al laminate, which followed nearly the same stages as the LDPE sheet preparation. The LDPE untreated/treated sheet was placed directly on the glossy side of Al foil, then progressively heated to 160 °C, then two tons compression molding was applied for two minutes to the LDPE/Al combination, and lastly the LDPE/Al laminate was cooled to room temperature.

3.5 Pre-treatment of LDPE sheets

Both sides of the LDPE sheet were immersed in a Petri dish containing an organic solvent such as acetone at room temperature for a brief period (a few seconds) to remove all undesired particles such as soot, dust, oil, and other contaminants. The LDPE sheets were then allowed to dry completely at room temperature before being surface treated. For the same purposes, this procedure might be applied to Al foils.

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Surface morphology and topography analysis:

Scanning electron microscopy (SEM)

Figures 20 show 2D SEM images taken to investigate the change in the textural and morphological properties of the LDPE and Al samples before and after peel tests. As shown in the figure 21 A unmodified surface was relatively smooth with low surface roughness, which can contribute to low wettability (surface energy) of LDPE., Figure 21 B represents the modified surface of LDPE and it is clearly seen that addition of 0.1 wt.% of Orevac did not change the surface properties significantly, as additive was homogeneously mixed with LDPE in the bulk. According to figure 21C the surface roughness of the LDPE after peeling has increased after adding OREVAC with a percentage 0.1wt%, due to adding hydrophilic groups such as: carbonyl group (C=O) and ether group (R-O-R) according to maleic anhydride structure, which were protruded on the LDPE surface after peel test. Moreover, the Al surface roughness also increased after the peeling test, which means the polar additives were attached to the polar Al surface after peel test indicating mechanical interlocking mechanism of adhesion.

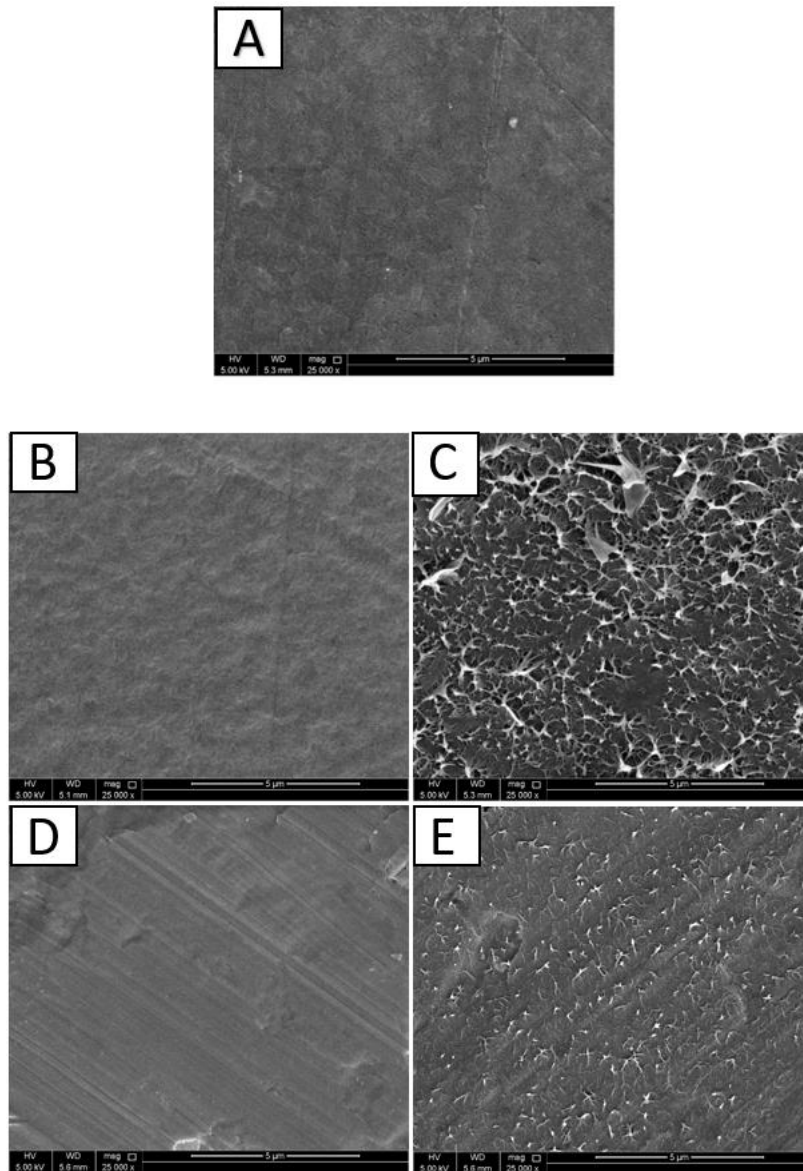


Figure 16: SEM images of: A) LDPE, B) LDPE/Orevac, C) LDPE/Orevac after peel, D) Al, E) Al after peel.

Atomic force microscopy (AFM)

The information about surface morphology/topography of LDPE and Al samples before and after peel test was obtained by the AFM technique. This technique was used to investigate a mechanism of adhesion between LDPE and Al in LDPE/Al laminates. The

AFM images of the LDPE and Al surfaces before and after peel tests are shown in Figure 22. The surface of unmodified LDPE excelled a relatively smooth surface morphology/topography with a characteristic texture originating from production process, while Ra value was 3.6 nm. Modification of LDPE with 0.1 wt.% of Orevac additive (LDPE-Orevac) did not lead to significant changes in surface roughness (Ra=4.0 nm) indicating incorporation of additive mainly into the bulk of LDPE matrix. The significant changes in the surface morphology/topography were observed after peel tests of the LDPE-Orevac/Al laminate. The surface roughness of LDPE modified with Orevac (Ra=19.5 nm) significantly increased after peel tests as results of mechanical coupling/interlocking mechanism of adhesion. This occurs when melted LDPE penetrates into the pores or cavities of the other material (Al) to be bonded together resulting in a creation of an adhesive bond strength (mechanical interlocking)[215]. Mechanical interlocking also represents a surface characteristics dealing with adhesion forces at the microscopic/macrosopic levels and not at molecular levels [229]. Moreover, a significant increase in surface roughness of Al after peel tests was observed, while Ra values increased from 7.3 nm to 49.2 nm as result of attached Orevac containing domains to the Al surface. These findings proved a remarkable mechanical interlocking mechanism of adhesion in the LDPE-Orevac/Al laminate.

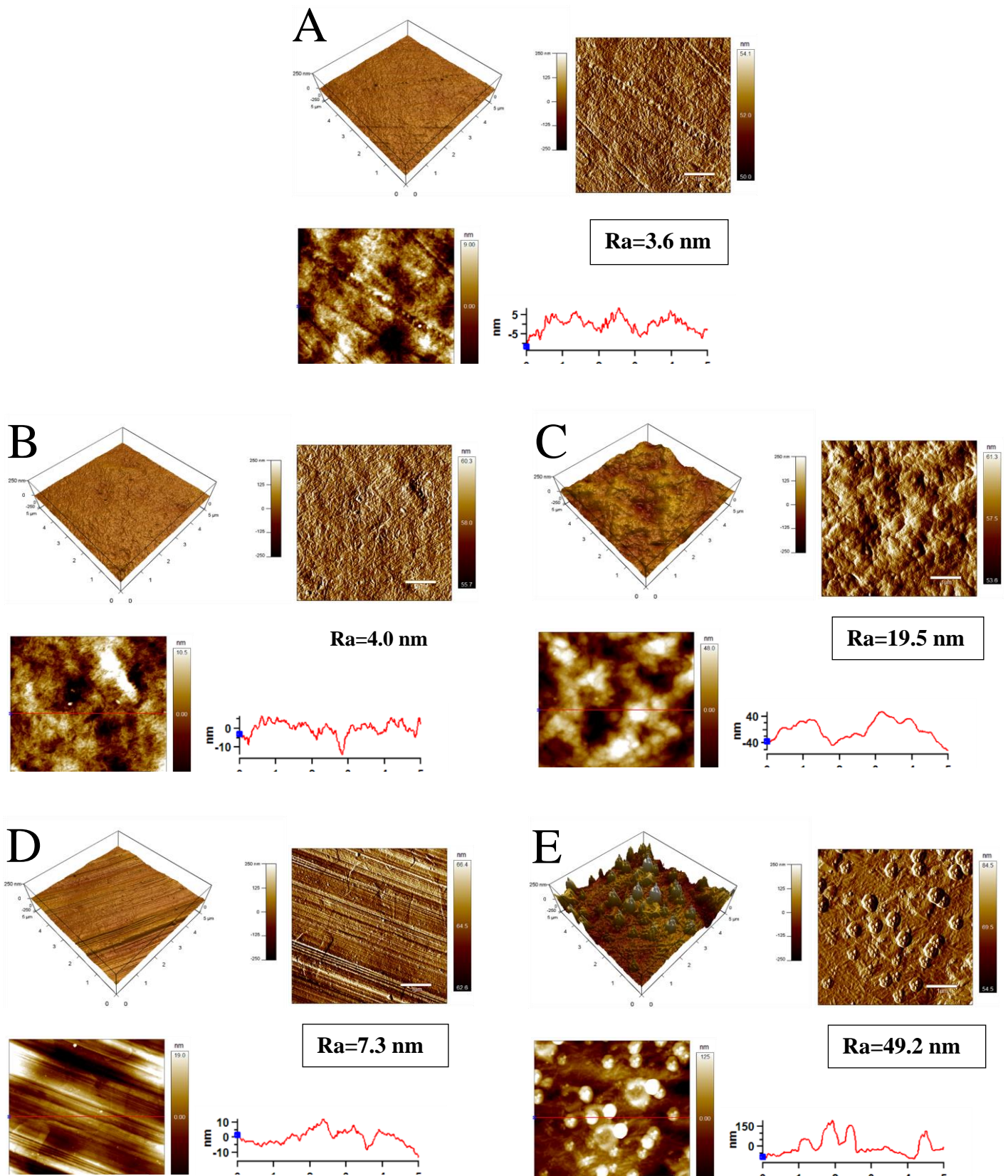


Figure 17: AFM images (3D Height, Amplitude, ZSensor with line profile) of: A) LDPE, B) LDPE/Orevac, C) LDPE/Orevac after peel, D) Al, E) Al after peel.

4.2 Chemical composition investigation:

Fourier transform infrared spectroscopy (FTIR)

For the unmodified LDPE there is characteristic FTIR spectrum associated with peaks representing non-polar LDPE groups shown in figure 23; these peaks are: CH₂ asymmetric C-H stretch at 2917 cm⁻¹, CH₂ symmetric C-H stretch at 2852 cm⁻¹, CH₃ umbrella mode at 1377 cm⁻¹, and CH₂ rock at 718 cm⁻¹. However, for the modified materials new peaks appeared at the range of 1700 to 1800 cm⁻¹ and these represent mainly the polar carbonyl functional groups C=O originating from additives. FTIR spectra analysis confirmed the presence of additives in the top and underneath layers of LDPE (~ 1.66 μm penetration depth for ZnSe crystal), which are crucial for formation of adhesive joints with high adhesion characteristics.

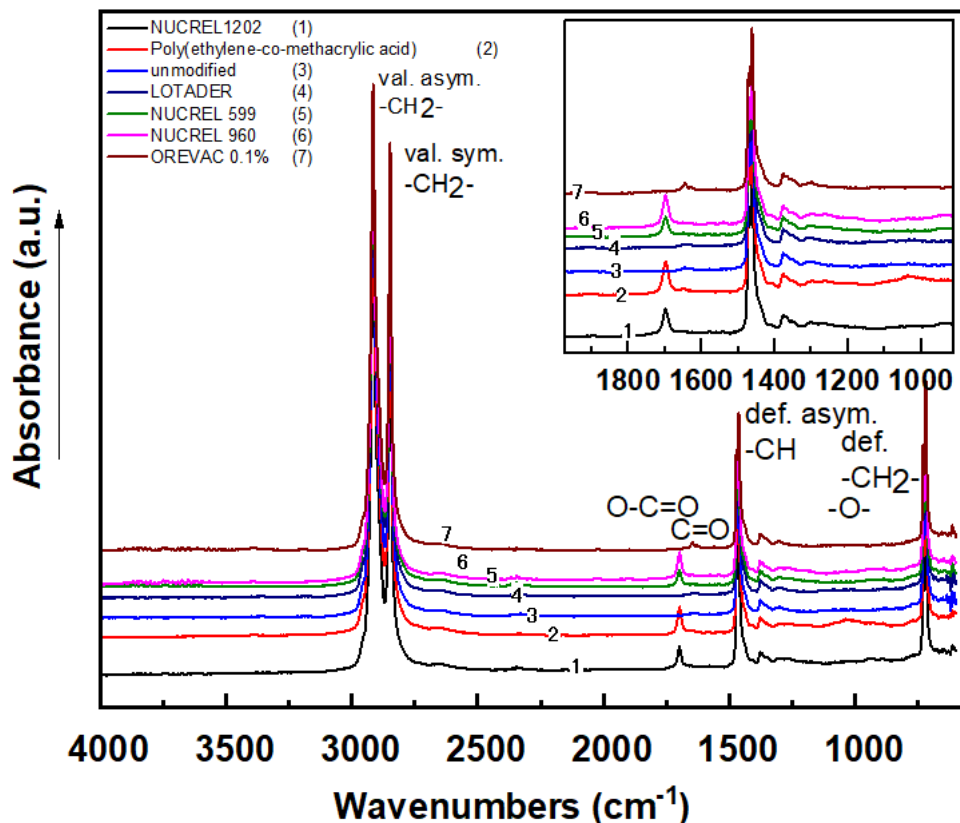


Figure 18: FTIR spectra of unmodified and modified LDPE grades

4.3 Surface wettability analysis:

The ability of a liquid to maintain contact with a solid substrate is referred to wettability. The contact angle of a liquid drop deposited on a flat, horizontal solid surface defines this interface feature. As a result, the relationship between surface wettability and contact angle can be stated as follows: a surface's wettability increases as the contact angle decreases, and vice versa. In this work, the contact angle measurements of unmodified and modified LDPE measured using three different testing liquids with different tension and polarity to evaluate surface free energy of the LDPE surface. As shown in figure 24, the contact angles of untreated LDPE achieved relatively high values (93.53° , 79.84° , and 67.28° for water, formamide and ethylene glycol, respectively) associated with hydrophobic surface of LDPE. Mixing of LDPE with additives did not lead to significant changes in the contact angles values indicating that the additive was mostly incorporated into the LDPE matrix's bulk. Moreover, polar additives could be diffused into deeper underneath layers in order to reach of thermodynamic equilibrium by attractive forces of additives present in the bulk.

Surface free energy and its derivatives polar and dispersive components were measured for unmodified and modified LDPE samples, with the aim to investigate the influence of adding additives on the characteristics of solid–liquid interactions, as can be seen from Figure 25. The surface free energy and its components values were carried out based on the contact angle measurements, so it was concluded that there no significant change on the surface free energy values. Based on surface morphology and topography analysis it is clearly seen that addition of additives did not change the surface properties significantly, as additives was homogeneously mixed with LDPE in the bulk. Polar component values increased after modification and this indicates that polar functional groups exists in the material.

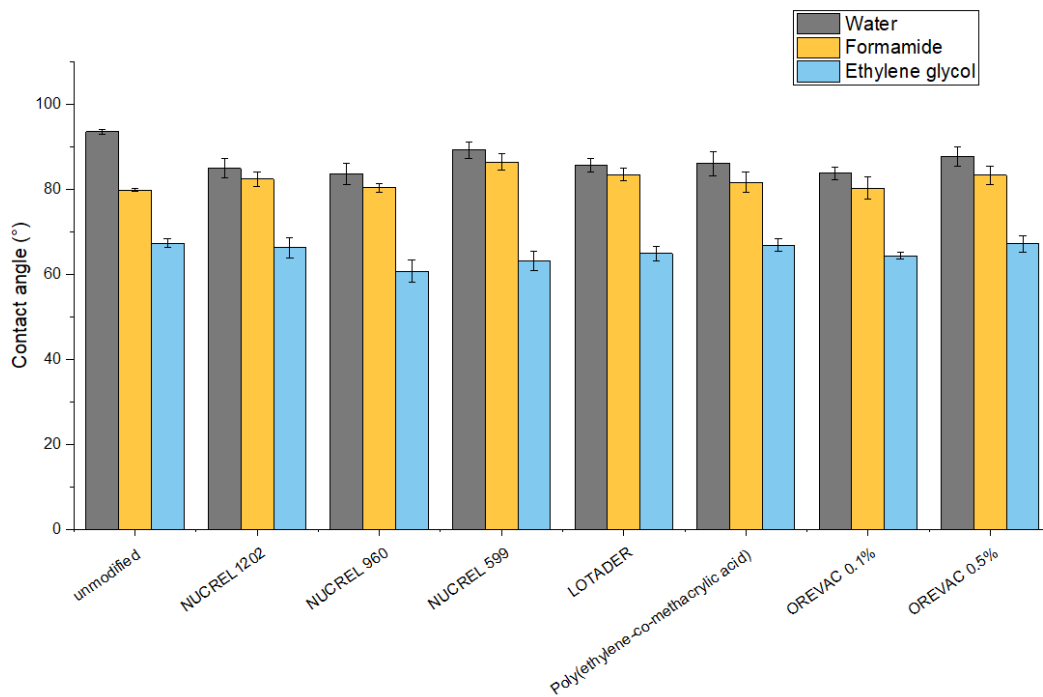


Figure 19: Contact angles (°) of LDPE samples

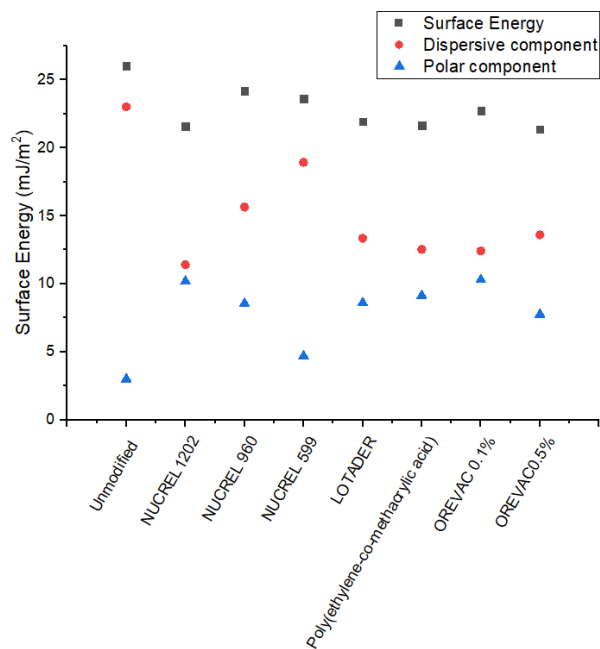


Figure 20: Surface free energy and its components (mN/m) of LDPE samples

4.4 Adhesive strength measurements:

Due to the hydrophobic nature and low wettability of untreated LDPE surfaces, the peel resistance of the pristine (unmodified) LDPE/Al adhesion joints was almost zero (not measurable) and LDPE was peel out of Al even during manipulation. The peel resistance of LDPE/Al laminates was then seen to increase as the additive concentration was increased, owing to the increase in hydrophilic functional groups. As seen in figure 26, all additives had improved peel resistance with increasing the concentration and the best adhesion was observed for 10 wt.% for all used additives except Orevac. In case of Orevac, even very low content led to remarkably improvement in peel resistance, while 0.1 wt.% led to 105.0 N/m peel resistance. An additional increase of Orevac content (0.5 wt.%) in LDPE led to adhesion, which was not measurable. Based on these results, it can be concluded that the addition of 0.5 wt.% of Orevac into LDPE had improved adhesion of LDPE/Al laminates satisfactory, which was the main goal of this research and can be applied in applications where strong adhesion is required.

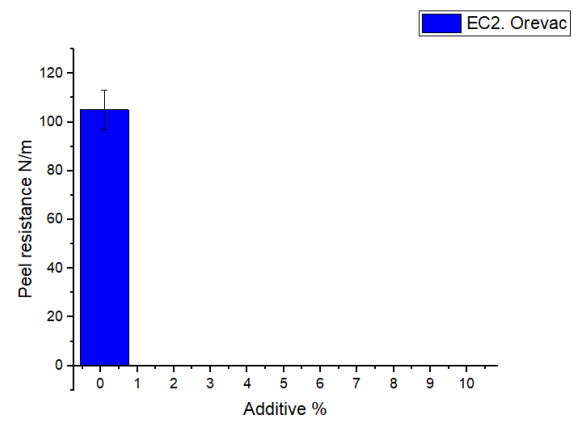
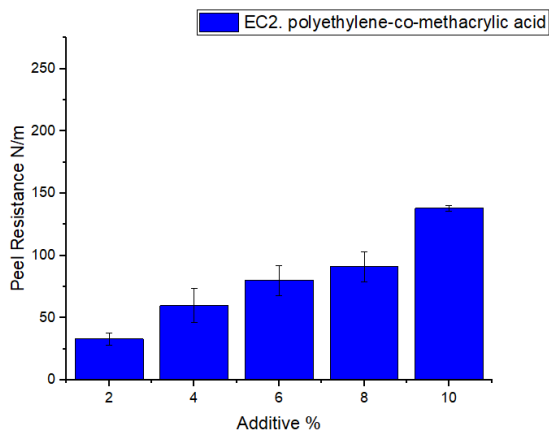
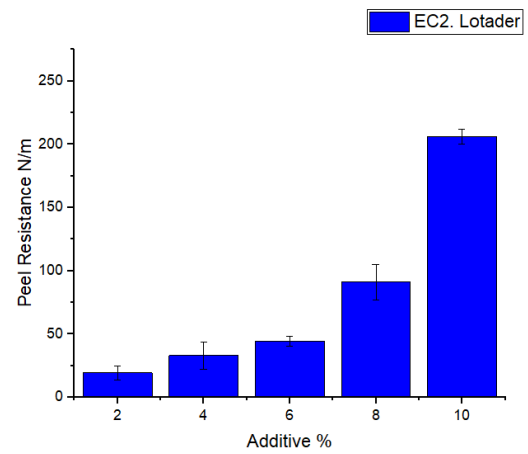
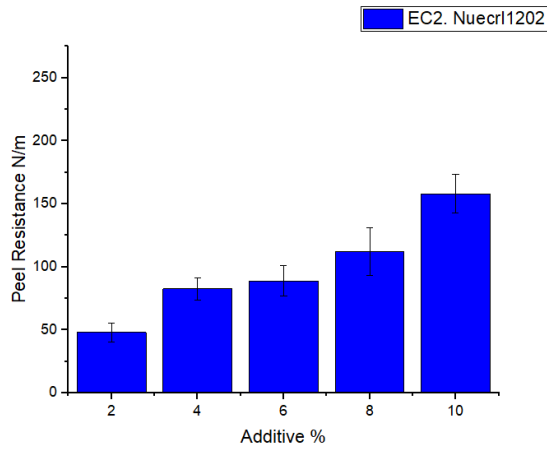
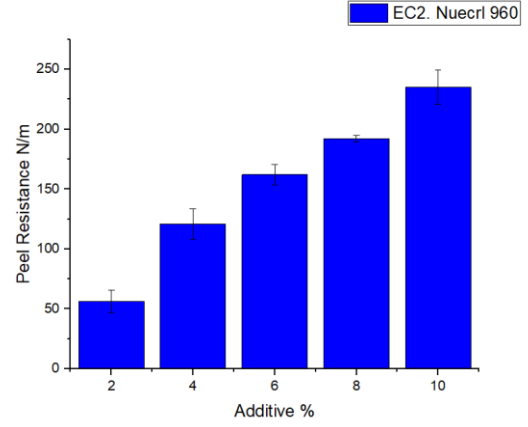
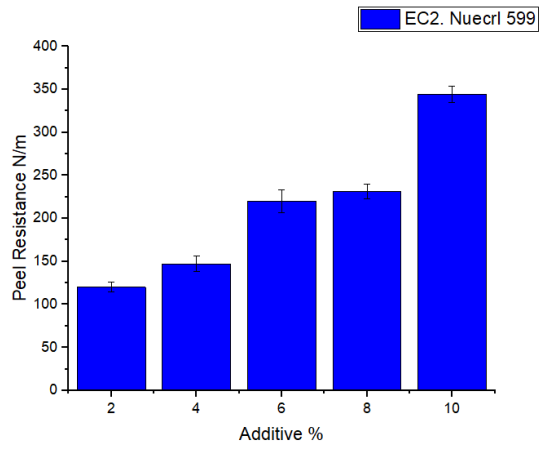


Figure 21: Peel resistance LDPE/Al

CHAPTER 5: CONCLUSION

The adhesion of QAPCO low-density polyethylene (LDPE) packaging grade to aluminum (Al) was improved successfully in this study by bulk modification of LDPE with polar additives. Commercially available additives based on ethylene copolymers with methacrylic acids or maleic anhydride grafted LDPE containing polar functional groups were used for this modification. This led to an improvement in adhesion characteristics of LDPE as results of enhanced wettability (polarity) of LDPE, which was proved by contact angles measurements. The best adhesion of LDPE/Al adhesive laminate was obtained for LDPE modified by Orevac additive, while 0.1 wt.% additive content lead to a significant increase in peel resistance (from zero to 105 N/m). This modification did not change the surface morphology/topography significantly as additive was homogeneously mixed with LDPE in the bulk. An additional increase of Orevac content (0.5 wt.%) in LDPE led to strong adhesion in the LDPE/Al laminate, which was more than strength of Al foil. Based on these results, it can be concluded that the addition of 0.5 wt.% of Orevac into LDPE had improved adhesion of LDPE/Al laminates satisfactory, which was the main goal of this research and can be applied in applications where strong adhesion is required.

This research was realized under QAPCO sponsorship as a part of searching of new applications of QAPCO products in designing of new food packaging materials. From this reason, the design of that research is mostly focused on practical aspects of the development of new materials. A comparison of materials developed and studied here with common commercial grades indicates their potential for designing of PE/Al sandwich structures (TetraPak – like structures) applicable in food packaging. Further research will be focused on the optimization of semi- large scale production of these laminates through co-extrusion process, as well as a health-related issue (e.g. a

potential release of contaminants from materials).

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