CZECH TECHNICAL UNIVERSITY IN PRAGUE

FACULTY OF MECHANICAL ENGINEERING

INSTITUTE OF MATERIALS ENGINEERING

The application of plasma treated polyethylene and glass fibers in composites and sandwiches prepared via rotational molding.

DISSERTATION THESIS

BRANCH OF STUDY: Materials Engineering

AUTHOR: Zoya Ghanem

SUPERVISOR: Prof. Dr. Petr Spatenka

Declaration

I declare that I have developed this Ph.D. thesis on my own, using listed literature and documents and on the basis of consultations and under the guidance of the supervisor.

In Prague: …..…….

Zoya Ghanem

Signature

Abstract

This thesis studies the application of plasma-treated polyethylene and plasma treated glass fibers in composites and sandwich structures prepared via rotational molding. Polyethylene and polyurethane sandwiches were prepared using untreated polyethylene (UT.PE) and plasma-treated polyethylene (PT.PE). Additionally, different combinations of untreated polyethylene, and plasma-treated polyethylene, untreated and plasma-treated glass fibers were manually mixed and used to prepare composites by rotational molding.

The results showed that plasma treatment increased the adhesion between polyethylene plates and polyurethane foam. Composites prepared using plasma-treated powder and fibers showed better adhesion between the matrix and the fibers, hence better mechanical properties of the resulting composites compared to those of pure polyethylene samples and to composites prepared using untreated components. As an income of this study, treated polyethylene and polyurethane sandwiches are already applied at the industrial level by Olivo Cold Logistics.

Keywords: Rotational Molding; Polyethylene ; Glass fibers ; polyurethane; composites ; Plasma treatment ; adhesion.

Anotace

Tato práce se zabývá aplikací plazmové úpravy polyethylenu a skleněných vláken v kompozitech a sendvičových strukturách připravovaných technologií rotačního spékání. Sendviče z polyethylenu a polyuretanu byly připraveny s využitím neupraveného polyethylenu (UTPE) a plazmově upraveného polyethylenu (TPE). Dále byly provedeny různé kombinace neupraveného a plasmově upraveného polyethylenu s neupravenými a plasmově upravenými skleněnými vlákny, které byly manuálně smíchány a použity za účelem tvorby kompozitních vzorků.

Výsledky ukázaly, že plazmová úprava zvýšila adhezi mezi potahy z polyethylenu a polyuretanovou pěnou. Kompozity připravené s využitím plazmově upraveného polyethylenového prášku a skleněných vláken vykazovaly lepší adhezi mezi matricí a vlákny. Proto také došlo ke zlepšení mechanických vlastností výsledného kompozitu oproti vzorkům z nevyztuženého polyethylenu a kompozitům připravených z neupravených složek. Přínosem této práce je, že plazmově upravené polyethyleno-polyurethanové sendviče již našly uplatnění v průmyslové praxi, konkrétně ve firmě Olivo Cold Logistics.

Klíčová slova: Rotační spékání ; polyethylen ; skleněná vlákna ; polyuretan; kompozity ; plazmová úprava ; adheze.

Acknowledgements

I express my profound gratitude and deep appreciation to my academic supervisor **Professor Dr. Petr Spatenka** for his valuable guidance, support, patience, and enthusiastic encouragement throughout the entire period of this research, which enabled me to complete my thesis.

I especially extend my thanks to **Hana Sourkova** and all the surface treat .a.s. team for close cooperation, in the production of plasma-modified materials and other samples provided for research.

A special thanks to my mentor, **Dr. Vojtech Novacek,** for his support**.**

Many thanks to all of my colleagues in the Department of Material Engineering for their help and support throughout my entire journey.

Big thanks to my amazing family my boyfriend and friends for their encouragement that inspired me to complete the assignment.

To my **mom and dad,** I dedicate this achievement to you. Your endless love is the reason I always achieve my goals.

Table of Contents

List of the abbreviations:

PE/ UT.PE	Polyethylene
PU	Polyurethane
PT.PE	Plasma Treated polyethylene
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
HDPE	High Density Polyethylene
LMDPE	Linear Medium Density Polyethylene
UHMWPE	Ultra High Molecular Weight polyethylene
PEEK	Polyaryletherketone
PLA	Polylactic Acid
CF4	Tetrafluoromethane
TFE	Tetrafluoroethylene
PA	Polyamide
PP	polypropylene
EPS	Expanded Polystyrene
O2	Oxygen
H2	Hydrogen
Ar	Argon
N2	Nitrogen
NH3	Ammonia
F2	Fluorine
H2	Helium
MAPE	Maleic Anhydride Grafted Polyethylene
3-APS	(3-Aminopropyl) triethoxysilane

CBA	Chemical Blowing Agent
FS	Fumed Silica
HNT	Halloysite Nanotubes
CNT	Carbone Nanotubes
GF	Glass fibers
UTGF	Untreated Glass Fibers
WF	Wood Fibers
CPW	Capirona Wood Particles
PWP	Pine Wood Particles
SGB	Spherical Glass Beads
RGP	Irregular Glass Particles
CaCO3	Calcium Carbonate
omMMT	Montmorillonite
PIAT	Peak Inner Air Temperature

Introduction

Rotational molding is a processing technique that is used to produce plastic hollow parts with very low residual stresses with the help of temperature and slow rotation. It was introduced for the first time as a molding technique in the late 1930s and used liquid polyvinyl chloride to produce balls and toy dolls. Later in the 1950s different grades of polyethylene powders were introduced to the process and still represent about 85% to 90% of all rotational molding productions worldwide; since then, this method has been used for the processing of various thermoplastic polymers like different types of polyethylene, polypropylene, polyvinyl chloride, etc., and thermosetting polymers such as epoxy resins ,polyurethane, phenolic resins, and unsaturated polyester. The market growth of this process in the field of the plastic industry is in the range of 10% to 20% per year. This process enables the production of various sized products that are small to very large in size. Typical products of rotational molding are storage tanks, shipping containers, kayaks, and barriers.

The low residual stresses, low cost, and the ability to produce complicated large seamless hollow parts in one piece are the most important advantages of the rotational molding technique. However, the process has major disadvantages, which are high temperature and a long production cycle, and this limited the materials that can be used in the process to a specific type of polymers that can withstand elevated temperature for a relatively long period [1],[2]. These materials are considered not suitable in applications where product strength and rigidity are important. Therefore, the preparation of multilayer skin-foam and skin-foam-skin sandwich, as well as composites products via rotational molding, dragged the attention of researchers to improve the mechanical and thermal isolation properties of the final products.

In multilayer constructions and in composites as well, the key for good mechanical properties is the adhesion between the components (between layers in multilayer structures ,between the matrix and the filler in composites). The main drawback of polymers is the low surface energy, which creates poor adhesion between different polymers, and between the polymers and other materials such as metals, glass, and ceramics. It is reported that almost 75% of available polymers need additional surface treatment to improve their wettability, gluing, or bonding to another material before they can be used; these pretreatments include chemical treatment (i.e. chemical etching), physical treatments (i.e., radiation treatment, plasma treatment), biological processes (i.e., physical adsorption and chemical conjugation of biomolecules) and mechanical methods (i.e., mechanical roughening of the surface) [3].

Plasma treatment has been established as a fast, clean, and effective method for the surface treatment of polymers and different types of fillers ; it takes milliseconds to interduce new functional groups such as carboxylic and hydroxyl into the surface layers of materials without altering the bulk properties of the materials. Plasma treatment is cost-effective and easy to control. For a long time, plasma treatment has been used mainly for the treatment of flat polymeric surfaces, such as films and foils [3],[4]. As a result of many complications related to the three-dimensional geometry of the powder, the large surface area of the powder that needs to be treated and the need for a special mixing to overcome the bad flowability and agglomerations of the powder [5], in the beginning Plasma treatment of powders did not attract much attention, but in the last decades more research was conducted to overcome these obstacles and treat different types of polymeric powders to improve their wettability and surface energy before using them in different applications. Plasma treatment of glass fibers and another type of fibers and fillers has also been used to improve their adhesion to different types of polymers.

The present work investigates the potential application of plasma-treated polyethylene and plasma-treated glass fibers to produce PE-PU sandwiches and glass fibers composites via rotational molding technique.

Chapter 1:Theoritcial Background

1.1 Rotational molding process:

The rotational molding process consists of four different stages, which is presented in Figure 1. In the first stage, the polymer is loaded into a hollow metal mold, the amount of material is determined depending on the surface area of the mold, the required thickness of the final product, and the density of the plastic, the mold is then closed, placed in the oven, and starts to rotate around two axes while the temperature inside the oven is increasing. The mold rotation is relatively slow – typically between 4-20 rev/min, so the process should not be confused with centrifugal casting in which the mold rotates at high speed and the plastic is thrown against the mold wall. The speed ratio around the two axes can be set to different values depending on the shape of the plastic part. The most widely used speed ratio is 4:1. After the polymer is melted and sintered, the mold is cooled by air or water spry, and finally the finished part is removed from the mold and another cycle starts [2].

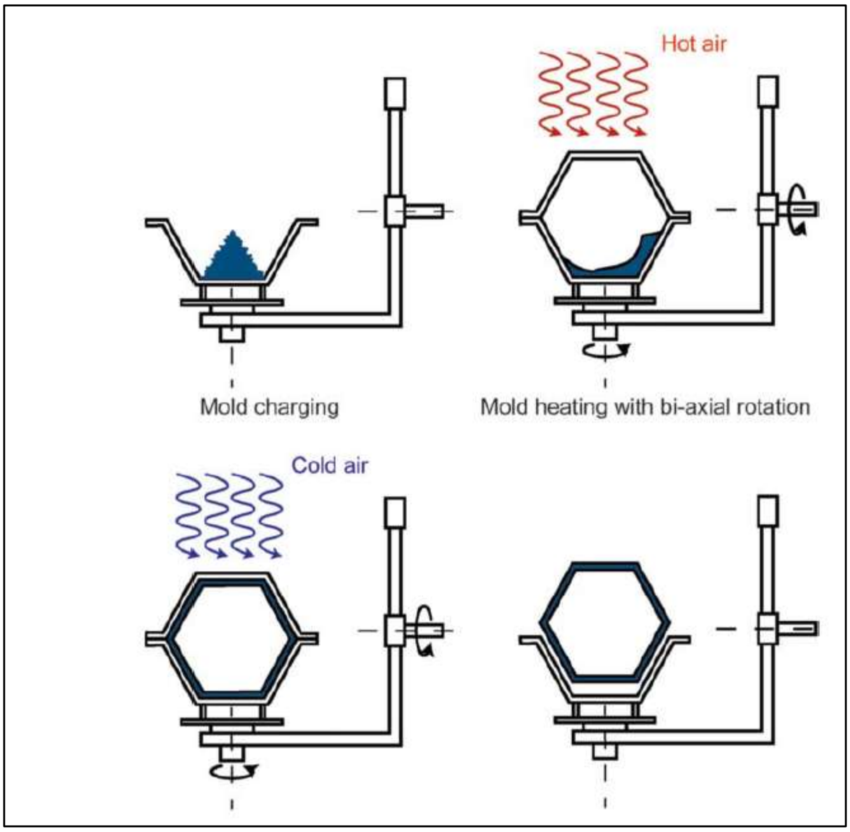

Figure 1: Rotational molding process [2].

The melting and densification processes during rotational molding are shown in Figure 2. The melting process starts when the powder particles adhere to the mold walls as they reach a temperature above the polymer melting temperature. The particles stick to the mold wall and to each other, building up a loose powdery mass against the mold wall; sintering and coalescence of the powder continue until it becomes a homogeneous melt. During the sintering process, pockets of gas are trapped in the melt. These pockets of gas, called bubbles or pinholes, do not move through the melt because the viscosity of the melt is too large for this to happen, so the bubbles remain where they are formed and slowly diminish in size over a period of time. However, a small number of very fine bubbles remain in the final product close to the inner surface.

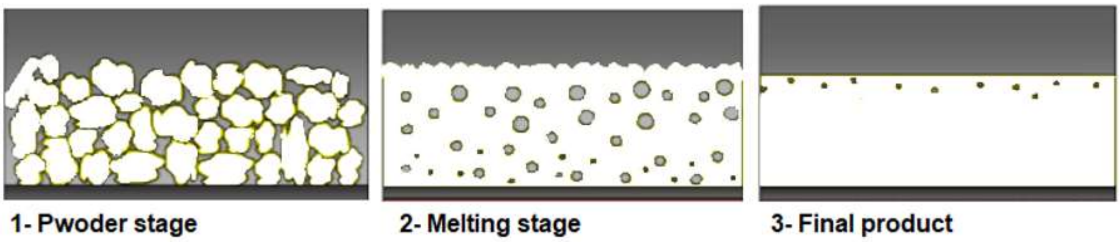

Figure 2: Different stages of rotational molding cycle.

Many parameters affect the rotational molding process, such as the rotation speed around the axes [6], rotation speed ratio of the main and auxiliary axes [7], oven temperature and residence time in the oven [8], cooling rate [9]–[11], size and shape of the powder particles [12], these parameters play a major role in the quality and mechanical properties of the final product.

The process temperature, heating time, and cooling rate have a major effect on the mechanical properties of the final product. If the temperature in the oven is too low or if the residence time in the oven is too short, then the fusion and consolidation of the plastic will not be complete, and this results in low strength, low stiffness, and a lack of toughness in the end product. On the other hand, if the temperature is too high or the plastic is heated for too long, then degradation of the plastic will occur, and this will result in brittleness. The cooling rate also has a significant effect on the final properties of the product. Cooling in rotational molding is normally only from the outside of the mold, and this can cause warpage and distortion of the molded part, this is why mostly cooling by air is used in rotational molding.

The internal air temperature of the mold (PIAT) plays a critical role in optimizing the rotational molding process. The thermogram of the internal temperature of the mold during rotational molding of a semicrystalline polymer is shown in Fig 3, the molding stages can be clearly recognized in the thermogram. The beginning of melting can be noticed at point (1), where the curve is slower as more energy is absorbed to melt the powder and form a thin film of melt on the inside surface of the mold. Point (2) indicates the beginning of the densification period, and the curve accelerated again until PIAT is reached at point 3,where the heating of the mold stopped and the cooling starts, the curve inverts, and the cooling proceeds gradually until point (4) when crystallization begins. A semi-plateau is observed here as well and continues until point (5),which corresponds to the end of crystallization and solidification. Subsequently, a slight slope change is observed at the point (6) caused by the separation of the plastic from the mold surface and the subsequent formation of an insulating layer of air between them, and finally the finished product can be removed from the mold at point (7) [2].

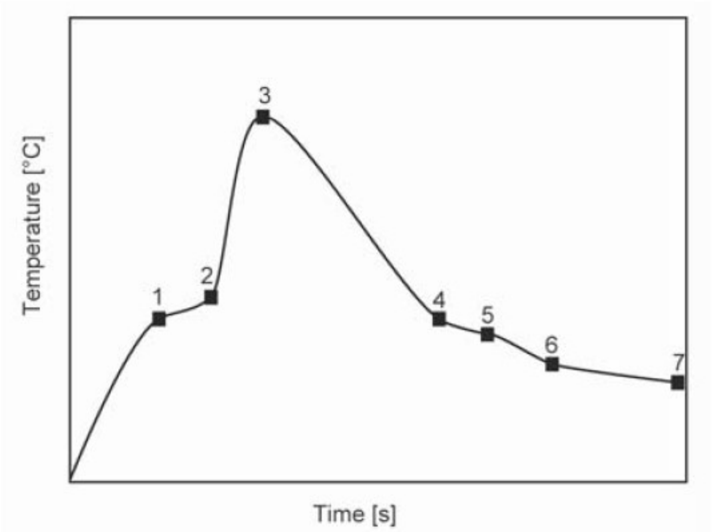

Figure 3: Thermogram for the rotational molding cycle of a semi-crystalline polymer [2].

The rotational molding process continues to improve and researchers in this field have introduced many techniques to improve the process conditions and the mechanical properties of the final products, such as reducing the cycle time [13], bubbles removal [2],[12],[14], and introducing sandwich structures and composites into the process.

1.2 Foam core sandwiches:

Sandwiched structures with foam core are a special type of composites which consists of two thin stiff faces connected to a lightweight thick foamed core. The use of foams as a core improves mechanical properties as well as buoyancy, thermal and sound insulation, and dimensional stability. Open-cell and closed-cell polyether sulfone polyvinylchloride, polyurethane, polyethylene or polystyrene foams, balsa wood, syntactic foams, and honeycombs are commonly used as core materials; if higher core strength is required, metal foam such as aluminum foam can be used as a core material. Skin materials are thermoplastics or thermoset polymers, glass and carbon fibers composites, and metal sheets. The main goal of foam sandwiches is to have maximum flexural stiffness with minimum weight [15]. As a result of their special properties, including light weight ,enhanced mechanical properties, good thermal and acoustic isolation properties, sandwich structures have been widely applied in aerospace, automobile and marine industries [15]–[19].

Polyurethan foams is one of the most used foams in sandwiches structures as a result of their exceptional properties such as light weight, environment-friendliness, low density, impact, and shock absorption, processability, and outstanding elasticity. Estimated production of PU raw materials is around 12 million metric tons per year and still increasing [20]. PU foams and its sandwiches are currently used in many industrial sections such as automotive [21]–[24], furniture, refrigeration, sports, transportation, insulating materials [25]–[27], and marine application [28],[29].

1.2.1 Foam core sandwiches via rotational molding

Foam filling in rotational molding is used in a wide range of products such as ice coolers, buoys, refrigerator components, and reinforced structural components. Many types of foam have been used in rotational molding in single-layer or multi-layers, such as polyurethane foams (PU), expanded polystyrene foam (EPS), polyurethane foam (PE).

The foam filling can be done during the rotational molding process by adding a mixture of the polymer with chemical blowing agent (CBA) in powder form which will decompose within the polymer melt during melting creating the foam, or after the end of the molding process by injecting the foam into a cavity in the final rotomolded part, this method is the most used so far because it is less complicated.

S.J. Liu and Yang [30], prepared two layered polyethylene foam sandwiches (first layer of net LLDPE, second layer is LLDPE foam) using rotational molding and compared it with the un-foamed part prepared under the same conditions, the results showed that the two-layer foam part has better impact properties comparing with un-foamed part. D .Dou and D .Rodrigue [31], prepared polypropylene foamed parts, the results showed a decrease in all mechanical properties of the foamed samples comparing with un-foamed samples . In another study, foam sandwich panels consisting of two polyethylene face sheets and polyethylene foam as a core were prepared by rotational molding (Figure 4), the impact tests were carried out, and the results showed that the maximum impact energy level this sandwich material can absorb is 46 J [32].

Figure 4: PE/PE foam/PE Sandwich [32].

P. Ortega-Gudino et al. [33], prepared three-layer composite (polyethylene agave fibers composites/ polyethylene foam / polyethylene), the fibers content varied from 0 to 15 wt% and chemical blowing agent varied from 0 to 7.5 wt.%,. Three layers could be detected in SEM images, but it can be noticed that gas diffusion occurred from the foamed second (middle) layer to the composite first (outer) layer (Figure 5). The results showed that adding the fiber increased tensile modulus with increasing fiber content compared to net polyethylene.

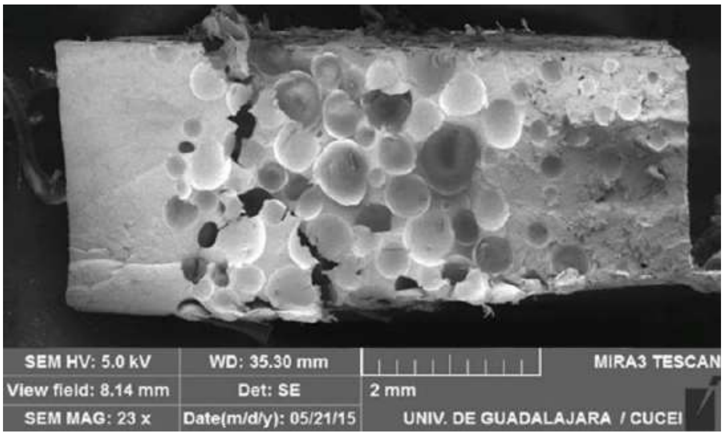

Figure 5: polyethylene-agave fiber composite/polyethylene foam/net polyethylene sandwich [33].

In all previous studies, foam was added during the process, and there were no details about the adhesion between layers and its effect on the final product properties. On the other hand, when different types of foam filling are injected after molding, there is no bond between the foam and the skin layer, the separation of the foam from the plastic skin layers is instantaneous, and the foam does not impart any additional stiffness to the product.

1.3 Composite materials:

Composite materials are materials consisting of two or more materials that have different chemical and physical properties. They have been introduced to almost every industry as a result of their special properties, which are a combination of its different components' properties. The most important properties include light weight, high strength / module-to-weight ratio, fatigue and corrosion resistance, low thermal expansion compared to traditional material such as metals (Figure 6) [34].

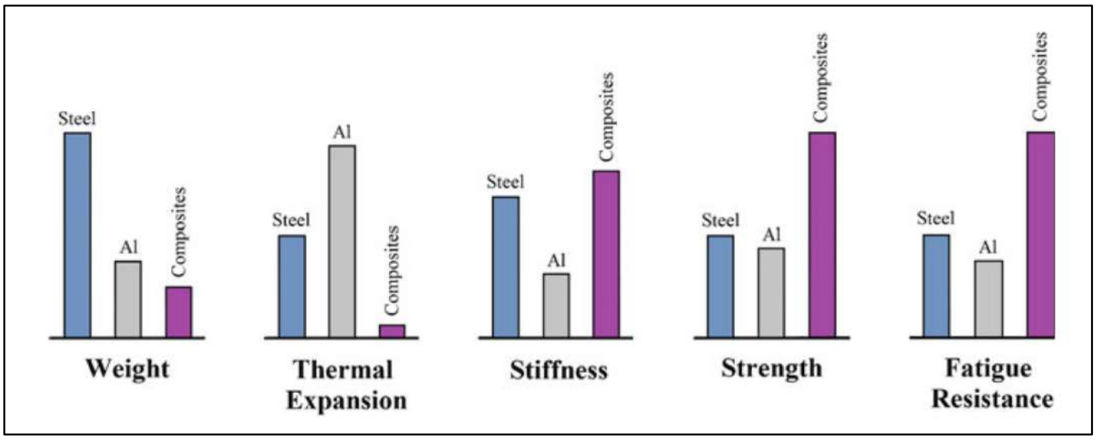

Figure 6: Comparison between conventional monolithic materials and composite materials [34].

Each composite material consists of three major components, the matrix , the reinforcements, and the interface between these two components. Depending on the type of matrix, composites can be divided into [35]:

- Metal matrix composite materials.
- Ceramic matrix composite materials.
- Polymeric matrix composite materials.

Reinforcements can be in the form of particles, flakes, whiskers, short fibers, continuous fibers, or sheets. The most commonly used reinforcements are fibrous form because of their high strength and stiffness and high aspect ratio, which allow the transformation of the load from the matrix to the fiber [34].

Polymer matrix composites have received the attention of researchers and manufacturers in the last few decades because of their low cost, high strength, and stiffness to weight ratio compared to metallic alloys, as well as their high electrical isolation and very good resistance to corrosion and chemical attacks. They have been used in many fields such as automotive, aerospace, medical product, Etc. [36]. Polymeric matrixes can be divided according to their matrix into thermosets (epoxy , polyester , polyurethan resins) and thermoplastics (polyethylene, polypropylene, polyamides , polyvinyl chloride). Reinforcements can be natural and synthetic fibers or particles, mats, and nanoparticles.

The processing of polymeric matrix composites is strongly dependent on the processability of the used matrix, the type, shape, and size of the reinforcements. Figure 7 summarizes all the processing techniques currently used to produce composites [37].

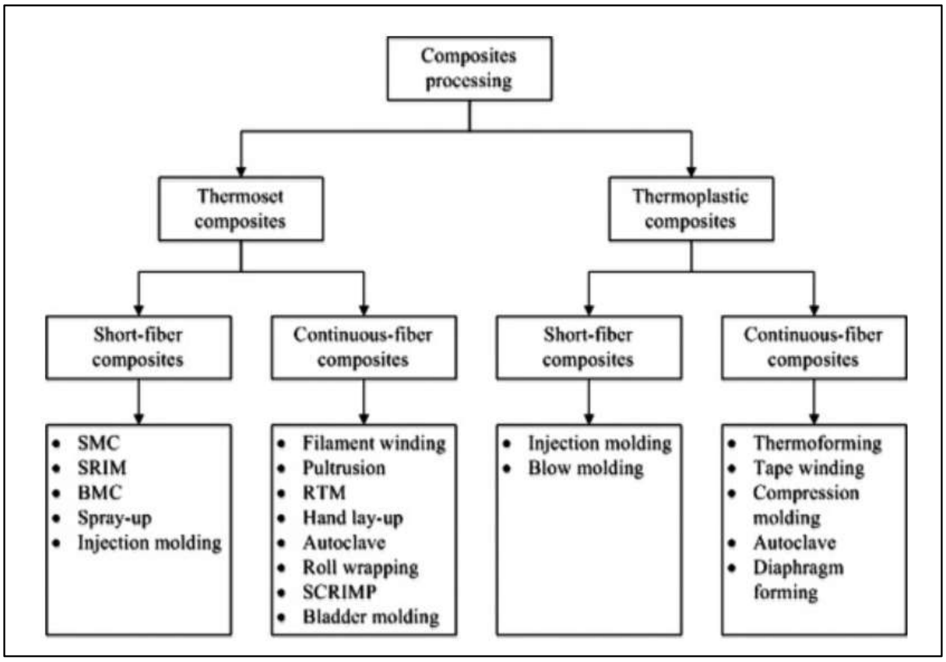

Figure 7: Processing techniques of polymer matrix composites [37].

1.3.1 Interface and Adhesion:

The interface is the bonding area between the matrix and the reinforcements in the composites (Figure 8), the final properties of the composites depend not only on the properties of the matrix and the reinforcements, but also on the quality of the interface area; bonding or adhesion between the matrix and the reinforcement should be very strong to transfer the stress between the matrix and the reinforcement.

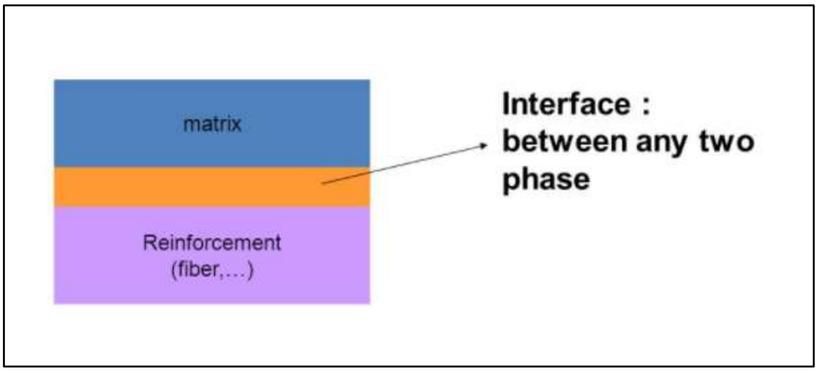

Figure 8: Interface between matrix and reinforcement in composites.

Good adhesion between the matrix and the reinforcements depends on two main factors. The first is the wettability , the second is the type of bonds between the two components [34].

Wettability is the ability of a liquid to spread on a solid surface. We can measure it by measuring the contact angle θ of a sessile drop of the liquid on the flat surface of a solid substrate, (Figure 9) [34].

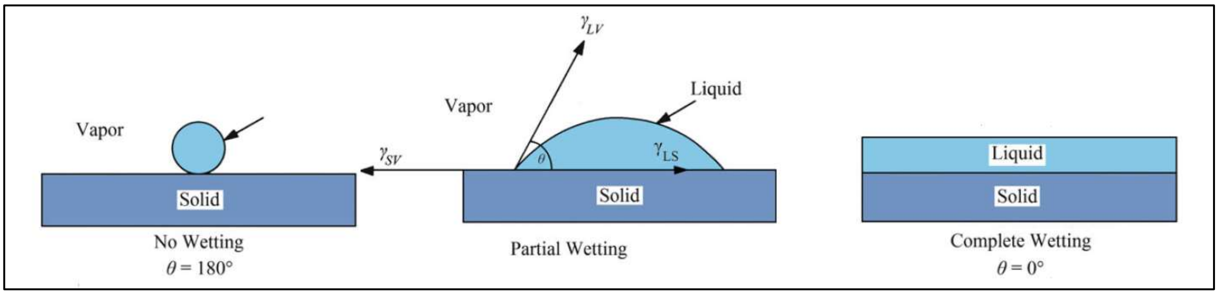

Figure 9: Wettability measurement [34].

The other factor which affects the adhesion is bonding (adhesion) between components. Classification of types of interfacial bonding in the composites is presented in Figure 10 [38]:

- Inter-diffusion bonding (a): it happened as a result of the intermolecular interaction between the molecules of the fibers substrate and the resin.
- Electrostatic bonding (b):it happened as a result of the attraction between the opposite charges on the surfaces of the fibers and polymer matrix.
- Chemical bonding (c): it occurred as a result of chemical reactions between the substances, which create chemical bonds, including atomic and ionic bonds.
- Mechanical interlocking (d): it occurred as a result of interlocking between peaks and pores or other irregularities of the substrates.

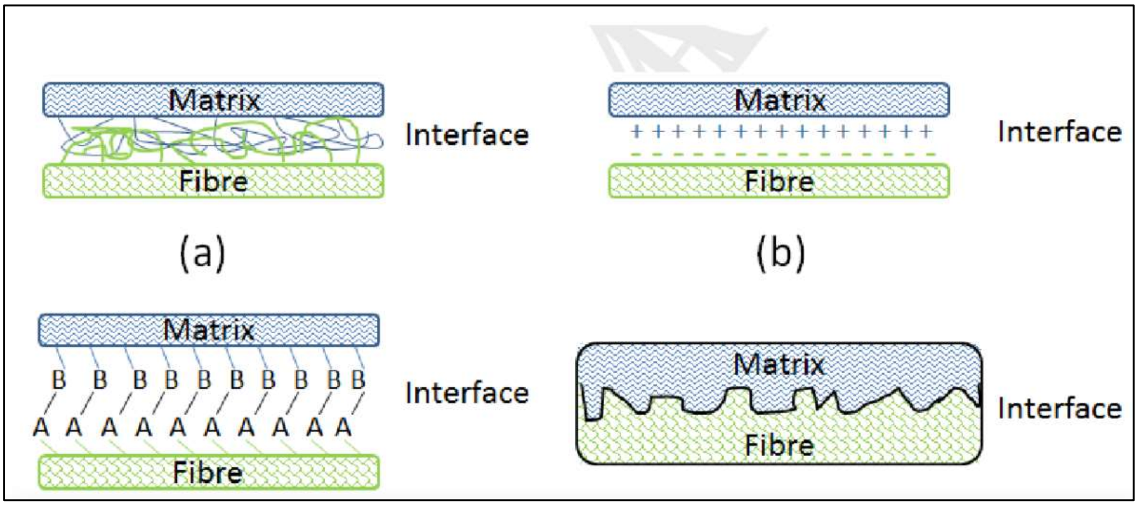

Figure 10: Bonding types [38].

To ensure good adhesion, at least one of these bonding mechanism must be achieved, using pressure, temperature, and different chemical and physical treatments; multiple bonds can occur at the same interface at the same time [39].

In processing of polymeric matrix composites generally and in polyethylene matrix composites especially, the question of good adhesion is still opened, and many efforts have been done to improve the adhesion between the matrix and the filler. These efforts include chemical and physical treatments of the matrix or the fillers. Chemical treatment is the most used technique to improve adhesion, including the use of coupling agents such as silane [40] and maleic anhydride grafted thermoplastics [41],[42] and /or surface treatment of fillers. The type of filler treatment depends mainly on the type of filler (natural or synthetic fibers). Different chemical treatments of natural fibers and particles have been applied to improve adhesion in natural fibers/polymer matrix compounds such as Alkaline treatment [43]–[47], Acetylation treatment [48], Silane treatment [49], Benzoylation treatment and Peroxide treatment [48],[50],[51]. Silane sizing is the most used for coating of the glass fibers to improve their adhesion to polymeric matrix [52]–[55]. On the other hand physical treatment which includes plasma, corona discharge, flame, UV/ozone became in the last few decades a green alternative of the chemical treatment [56].

1.3.2 Plasma treatment for adhesion improvement:

Low-temperature plasma treatment for adhesion improvement has recently attracted a great deal of attention as an environmentally friendly alternative to chemical treatment. This technique may be used for the surface treatment and modification of both matrices and reinforcements.

Plasma surface activation is used to improve wettability and adhesion to other materials by attaching free radicals and functional groups. The type of functional groups depends on the composition of the plasma. The working gases used in plasma treatment include noble gases (Ar, He), reactive gases (O2, air,N2/O2, H2/O2, NH3, CF4) and organic gases (HMDSO, TFE, PFO, acrylic acid). The functional groups generated on polymer's surface include carboxyl, hydroxyl, amine, or aldehyde groups [5].

J. Trejbal et al. [57] reported that oxygen plasma treatment of glass fibers increased their wettability by 25% when compared with untreated glass fibers. Argon plasma treatment of glass fibers improved its interfacial shear strength to polyester resin [58], in another study the effect of plasma treatment of glass fibers on the tensile strength of glass fibers/epoxy composite was studied, the fibers was treated using low-pressure radio frequency plasma with air and argon as a working gas. The results indicated a better tensile strength for samples prepared using treated glass fibers compared to untreated glass fibers, the best result was obtained when the fibers was treated with argon as working gas for 1 min [59]. Air-plasma and Ar-plasma were used to treat wood fibers, and the fibers then were used to prepare wood fibers-PP composites. The composites prepared with treated fibers showed better tensile strengths and modulus comparing with composite prepared from untreated fibers, the air-plasma improved the strengths more than Ar-plasma [60]. The low pressure plasma surface modification of the coir fibers, using air and oxygen as gases, improved their adhesion to thermoplastic starch and as a result both tensile strength and modulus improved compared to the untreated fibers composites ,oxygen plasma was more effective [61], similar trend was observed when flax fibers were treated with low pressure air plasma [62], plasma treatment successfully improved their adhesion to different matrixes [63]–[65].

Various industrial polymers such as polyether ether ketone (PEEK), polyester, polyethylene, polylactic acid, polydimethylsiloxane (PDMS), polyamide, Etc. have been successfully modified to have hydrophilic surfaces for improved adhesion properties using the plasma treatment process [66]–[70], the treatment was applied on the flat polymer substrates such as films and foils, fibers, textile, and membrane.

Despite their huge potential, the plasma treatment of powders has not found a lot of applications as modification of flat bulk polymers because of many complications connected with three-dimensional geometries of powders, their large surface area, the aggregation phenomenon and therefore the necessity of solid mixing of the treated powder. However, powder plasma treatment has finally been successfully applied and found application in many fields such as desperations and paints ,coating, composite materials and rotational molding [3].

Polyethylene is one of the most treated powders using plasma as a result of its simple structure and wide applications. Many researchers studied the different advantages of plasma treatment of polyethylene. M.Quitzau et al. [71], treated polyethylene powder in hollow cathode glow discharge after treatment polar functional groups were detected on the powder surface, causing an enhancement in wettability. H. Sourková and P. Spatenka [72], treated liner low density polyethylene in low-pressure oxygen plasma, an increase in wettability and O-atoms concentration were observed as a result of the treatment. The increase in oxygen content on the surface of HDPE powders after oxygen plasma treatment was also observed in a previous study conducted by S. H. Park [73]. As a result of the oxygen plasma treatment of polyethylene powder. Weberová et al. [74], reported a significant improvement in the adhesion of the treated powder to metal and glass substrates from 1.6 MPa (non-treated powder) to 11.0 MPa (plasma treated powder for 1200 s) for metal substrate and from 0.4 MPa (non-treated powder) to 7.1 MPa (plasma treated powder for 1200 s) for glass substrate .

Pavlatova et al. [5], reported better dispersion of ultra-high molecular weight polyethylene (UHMWPE) in water after plasma treatment, which allowed the use of the powder as a filler in a water-based paint, the varnish filled with treated material was easily applied to a sheet metal plate without agglomeration or air bubbles and was able to withstand 135 000 cycles using the hair brush tool without any wear, almost 100,000 cycles more than the pure varnish.

In the field of rotational molding, the use of plasma-treated polyethylene was reported in some studies only. M. Pavlatova et al. [5], treated different types of polyethylene suitable for rotational molding and the treated powder was sintered, and the surface energy was measured after sintering. The samples prepared from plasma treated powder have surface energy values about 10 mN/m higher than the samples prepared from untreated powder and this makes the samples sintered from treated material ready to be glued to the paint and to different inserts without any further treatment. Another application of plasma-treated polyethylene in rotational molding is multilayered products with improved bonding between layers. J. Sezemsky and P. Špatenka [75], studied the effect of plasma modification of polyethylene powder on its bonding ability with polyamide in a multilayer structure prepared by rotational molding. The results showed a significant improvement in the joint strength between polyamide and plasma treated polyethylene,(7.657 ± 1.024 N mm - 1) compared to untreated polyethylene (3.662 ± 0.430 N·mm−1).

1.3.3 Composites via rotational molding

The interest in preparing composites using the rotational molding technique has started since 1999 and increased in the last two decades [76] .The first article we could find in the field was written in 2003 in which HDPE was reinforced with different types of natura fibers to produce composites using rotational molding [77], since then many types of fibers (carbon fibers, different types of natural fibers) and fillers (calcium carbonate graphite, silica) were introduced as reinforcements for different types of matrices (LDPE, HDPE, polycarbonate, polyamides, etc.).

In contrast to other processing techniques like injection molding and pressure molding, the rotational molding process operates at atmospheric pressure; this means there is no pressure to ensure the mechanical interlocking between the matrix and the reinforcements, thus adhesion is the biggest problem, which makes reinforcement of the rotomolded product very difficult.

So far, natural fibers are the most tested in rotational molding. Torres et al. [77], made the first attempt to incorporate natural fibers into rotational molding, they tried different types of natural fibers, including jute, wood, cabuya, pecan, sisal, and different types of rice shell flour. The composites were prepared with a high-density polyethylene matrix. In an attempt to improve the adhesion, natural fibers, and flour (pecan and rice shell) were treated with coupling and dispersion agents. The percentage of fiber and flour was varied in the experiments between 0-15%. They first prepared single layer parts, but the examination of the inner surface showed that a large proportion of fibers stick out of the polymer matrix (Figure 11-A), in order to obtain better reinforcement efficiency and good internal surface finish, double layer parts were prepared, two layers parts showed better fiber distribution across the sample thickness (Figure11-B).The mechanical properties of the rotomolded cylinders characterized using compression mode, and in all cases, reinforced moldings showed higher compression forces than the unreinforced. In another study they focused their works on cabuya and sisal fibers, they produced composites with fibers content up to 7,5 wt.%, after performing different mechanical tests, the results showed decrease in compression strength and impact strength after adding the fibers, while the tensile strength was maintained at the same level as the pure polyethylene samples. Composites had thinner walls, smaller density, and higher bubble content compared to unforced samples [78].

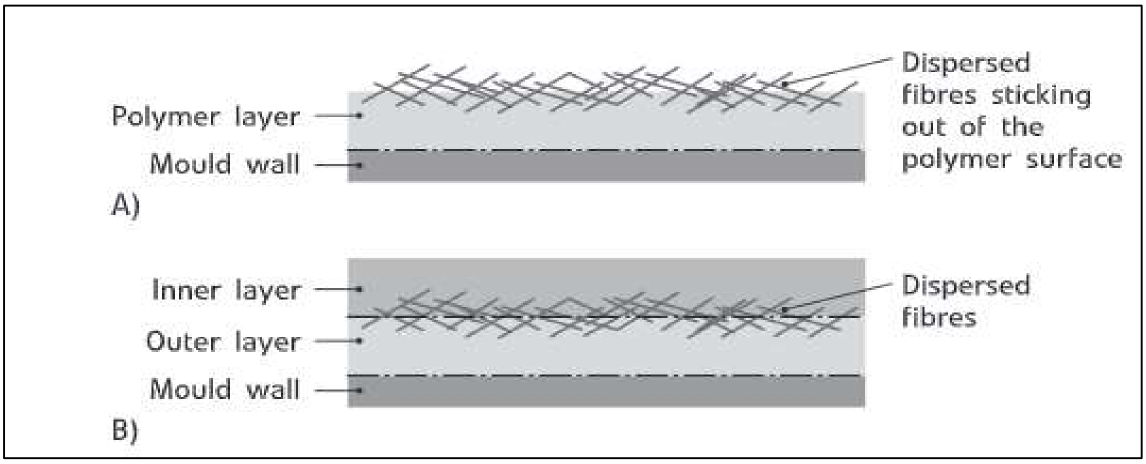

Figure 11: A) Single layer natural fiber reinforced rotomolded specimen, B) Double layer natural fiber reinforced rotomolded specimen [77].

Flax fibers were used as reinforcements for HDPE, linear low-density polyethylene (LDPE), and a mix of HDPE and LDPE to produce rotational-molded bio composites and the effects of silane, benzoylation, and peroxide treatments on mechanical and physical properties of composites were studied. Generally, the composites maintained tensile strength values similar to those of unfilled polyethylene; on the other hand impact strength slightly improved for the composites prepared using treated fibers compared to untreated fibers, water absorption of the treated fibers composites was less comparing with untreated fibers composites, which could indicate better adhesion and less bubbles, but there was no clear SEM image to support this theory; the treatment with silane in overall was the best in terms of improving mechanical properties and water absorption [79].

Ortega et al. [80], prepared rotational molding composites of polyethylene with banana and abaca fiber. Different methods were followed to produce two- and three-layer parts. Table 1 shows different formulations prepared for rotational molding.

Structure	*Types of fibers*	*Formulation*	*Short name*
Two Layers	*Virgin banana fibers*	*600g virgin PE/200g PE+5% fibers*	*1*
		200g virgin PE/600g PE +5%fibers	2
	Virgin abaca fibers	600g virgin PE/200g PE + 5% fibers	3
		200g virgin PE/600g PE +5% fibers	4
	NaOH treated abaca fibers	600g virgin PE/200g PE +5% fibers	5
		200g virgin PE/600g PE +5% fibers	6
Three Layers	Virgin banana fibers	400g virgin PE/200g PE +5% fiberss/200g virgin PE	7
	Virgin abaca fibers	400g virgin PE/200g PE+5% fibers/200g virgin PE	8
	NaOH treated abaca fibers	400g virgin PE/200g PE+5% fibers/200g virgin PE	9

Table 1: Composition of different banana and abaca composites [80].

To obtain the composites, the fibers were pulverized together with virgin PE pellets to produce a homogeneous powder material and then used as a raw material for the rotational molding process. The result of mechanical testing showed that the addition of banana and abaca fibers improved tensile and flexural modulus, while the tensile and impact strength decreased. NaOH treatment increased the thermal stability of the composites by 14% compared to composites prepared by untreated abaca fibers, but the mechanical properties were reduced.

Lopez et al. [81], used agave, coir, and pine as reinforcements for LMDPE, MAPE (maleic anhydride grafted polyethylene) was used to treat the fibers to improve the adhesion between the fibers and the matrix. Surface treatment helped to achieve better interfacial adhesion between the fibers and the polymer, which can be clearly seen in SEM images Figure 12, which caused an improvement in mechanical properties of LDPE composites prepared using rotational molding. Surface treatment was more effective for agave and coir fibers than for pine fibers because of their chemical composition. The study also indicated that the improvement of mechanical properties strongly depends on the fiber content. Composites with a lower fiber content(10%-20%) were found to have better morphological and mechanical properties than composites containing a higher fiber content. The improvement in tensile modulus obtained at 20% of the fiber content was approximately 262 MPa for treated agave compounds, 266 MPa for treated coir compounds, and 245 MPa for treated pine composites.

A comparative study between compression molding and the rotational molding process in the production of polylactic acid (PLA) and agave fiber bio composites was carried out by Lopez et al. [82]. The study showed that rotomolded composites showed higher porosity than compression-molded composites because the rotational molding process is carried out in the absence of any pressure. Compression-molded composites showed better interfacial adhesion between fibers and polymer than rotomolded composites. The mechanical properties of the rotomolded composites decreased as the fibers content increased.

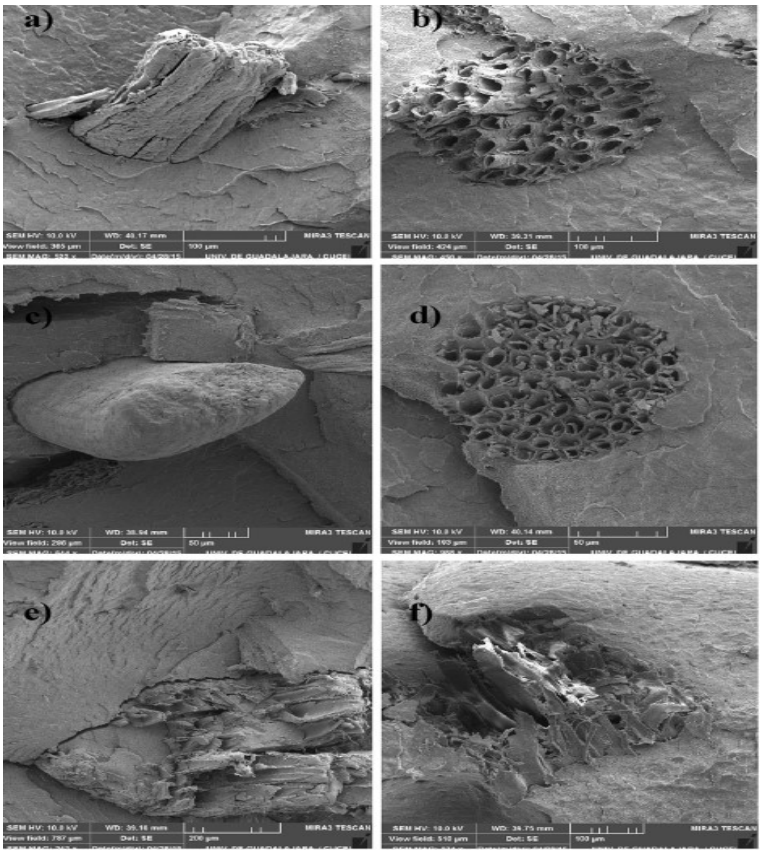

Figure 12: SEM images of adhesion between polyethylene matrix and different untreated and treated fibers, a) Untreated Agave fibers, b) Treated Agave fibers ,c) Untreated coir fibers, d) Treated coir fibers, e) Untreated pine fibers, f) Treated pine fibers [81].

Hanana et al. [83],[84], tried maple fibers as reinforcements for the LLDPE matrix and produced a composite using rotational molding. Maple fibers were treated with malleated polyethylene (MAPE) and the properties of the composites were compared to those prepared with untreated fibers. The tensile and flexural modulus increased for both composites prepared using treated and untreated fibers compared to the net samples. However, in all cases composites with treated fibers had higher values compared to the composites with untreated fibers. The tensile strength of the untreated fibers composites decreased with increasing fibers content compared to the unfilled samples, while the tensile strength of the treated fibers composites was close to or slightly above the unfilled samples. Impact strength decreased with increasing fibers content for all composites, with slightly higher values for treated fibers composites compared to untreated fibers composites. In addition to this study, they conducted another study in which they prepared self-hybrid composites using mixture of different sized maple fibers such as short (125-250 um), medium (250-355 um) and long (355-500 um) with different ratios (75/25, 50/50, 25/75), they analyzed the properties by varying the concentration (10, 20 and 30%), the results indicated better properties of self-hybrid composites compared with single size fibers composites. For example, a 75/25 ratio of medium/short or long/short fibers produced higher values of tensile modulus and tensile strength in the range of 13-33% compared to composites formulated with a single fiber size.

Barczweski et al. [85], studied the structure and properties of rotational molded polypropylene/wood floor composites. Composites were prepared using polypropylene copolymer (rPP) with 5 wt.% commercial grade of untreated wood flour (WF) and chemically treated wood flour (mWF). The natural filler was chemically modified by a silanization process using 3-aminopropyltriethoxysilane(3-APS). The addition of wood floors was found to cause the creation of the pores and decreased the overall mechanical properties of the composites despite the application of a preliminary drying and chemical treatment.

A study by Andrezjweski et al. [86], concluded that it is important to choose appropriate surface modification methods and matrix with appropriate properties to get composites with good mechanical properties. In the study, buckwheat husk was used as filler, which was waste material from agro-industry, PLA (polylactic acid) and PE (Polyethylene) used as a matrix. The properties of both composites were analyzed. Different sizes of particles were teste, particles with size less than 50µm, 50-200 µm particles and 200-500 µm particles. The study explained the importance of particle size in order to obtain better composites, it seems that smaller particles prevent individual granules from joining to solid material.

Another surface treated natural fiber composites were prepared using rotational molding by Robeldo-Ortiz et al. [87]. In their study, agave and coir fiber were used to make composites based on green polyethylene (LLDPE). The fiber surface was treated with maleated polyethylene (MAPE). The results of the study proved the importance of surface treatment for the manufacture of natural fiber composites. Composites having good morphology were obtained using surface treated fibers because porosity was decreased due to improved compatibility between fiber and matrix Figure13. The tensile properties of treated coir fiber composites were increased sufficiently compared to untreated fiber composite and neat Green PE. It was observed from the study that better mechanical properties were obtained with Green-PE natural fiber composites compared to petroleum-based rotomolded polyethylene.

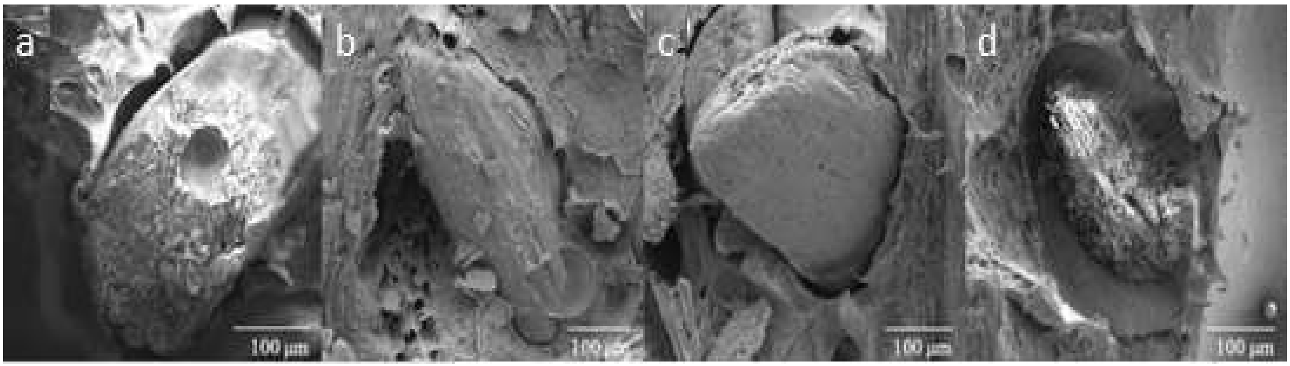

Figure 13: Micrographs of the fiber-matrix interfaces in the composites: a) Green-PE/agave fiber, b) Green-PE/treated agave fiber, c) Green-PE/untreated coir, d)Green-PE/treated coir [87].

In another study, two types of wood particles were used as a reinforcement for recycled high density polyethylene to produce composite by rotational molding, different particles content and process parameter were tested to optimize the process and the results showed that the best composites were obtained at 15% of wood particles with particles size between 297 µm and 500 µm, oven temperature of 320 ◦C, and heating time of 25 min for CPW and 28 min for PWP [88].

Another attempt has been made to incorporate coir fibers in rotational molding to produce PE / coir composites; the fibers were used in powder form with average particles size 125 µm, fibers content varied between 0 and 10wt%. The results showed a slight improvement in mechanical properties at fibers content up to 7 wt.% compared with un-filled polyethylene [89], this results correspond to the results obtained by Lopez et al [81].

Glass-reinforced composites have been successfully prepared using different techniques. However, in rotational molding only two studies reported the use of glass fibers to prepare composites. W, C. Chang et al. [90], used glass fibers to prepare rotomolded composites. He tried four different approaches to prepare the composites in order to optimize the mechanical properties of the resulted composites. The first approach was to sandwich the glass fibers between two layers of polyethylene, in the second approach, glass fibers and polyethylene were pre-compound and granulated into pellets, and were sandwiched between two layers of polyethylene to produce rotomolded part, the pellets were grounded into powder in the third approach and the powder was sandwiched between two layers of PE to produce another rotomolded part, the last approach was preparing one layer rotomolded composite using the pre-compound powder. The composition of different compounds is presented in Table 2.

Moulding	**Approach**	**GF Content (%)**	**1st Shot**	**2nd Shot**	**3rd Shot**
PE	-	N/A	3.6 kg PE		
7%GFE265	I	6.5	1.8 kg PE	250g GF	1.8 kg PE
3LPelE265	II	17.5	0.9 kg PE	1.8 kg pre-compounded pellets	0.9 kg PE
3LPowE265	III	17.5	0.9 kg PE	1.8 kg pre-compounded composite powder	0.9 kg PE
FWE265	IV	35	3.6 kg of pre-compounded composite powder		

Table 2: Composition of different glass fiber composites.

The results of mechanical tests showed an increase in the tensile and flexural modulus of all composites. However, a different level of enhancement was observed as a result of the different content of fibers in each approach. The composites prepared using pre-compound granulates and powder showed higher modulus enhancement compared to the composite prepared by the first approach (without pre-compounding), and the use of pre-compound powder showed even higher level of tensile and flexural modulus 33.1% and 69.1%, respectively, in malti-layers composites. A single-layer pre-compounded composite with the highest GF content (35% wt.) showed the higher raise in both modulus among all composites. In contrast to the modulus impact strength of all composites declined compared to the unfilled material [90].

Another attempt to incorporate glass fibers and carbon fibers in rotational molding was made by Hofler et al. [91], rotomolded parts were prepared using high-density polyethylene and different glass fibers and carbon fibers. The glass fibers were ultrathin glass fibers (UTGF) with diameter of 4 um, and another two types of glass fibers with 13 um diameter , silane sized, and aspect ratio of 6:1 and 12:1, respectively. Two types of carbon fibers had a diameter of 7 microns and an aspect ratio of 11: 1 and 21:1, carbon nanotubes (CNT) were also used. The fibers content ranged from 0.5 wt.% to 2 wt.% for all composites. The results showed that only carbon nanotubes at the lowest content (0,5 wt.%) improved the impact strength comparing with the net HDPE, for all other composites the impact strength was decreased by adding the fibers at all contents. Tensile strength and flexural strength showed only minor deviation (5%) by adding different types of fibers. The flexural modulus of glass fibers decreased at low fiber content (0,5 wt.% and 1wt.%) and slightly recovered to be equal to net HDPE flexural modulus at 2 wt.% of the fibers, while flexural modulus of carbon fibers showed a slight increase especially at 1wt.% of the fiber, SEM images in Figure 14 showed no adhesion between the glass fibers and the matrix .

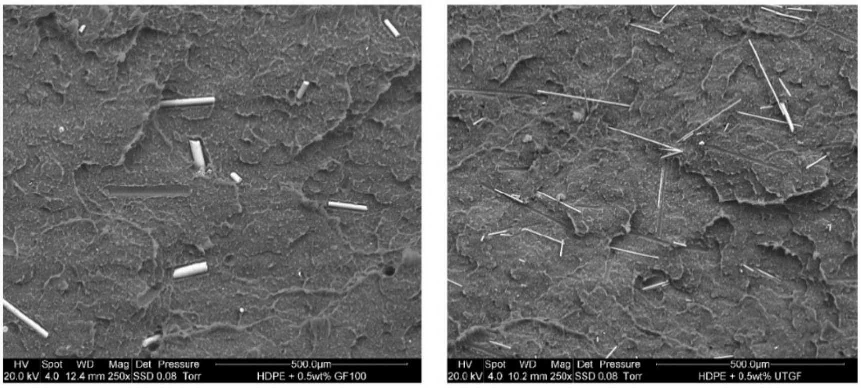

Figure 14: SEM pictures of HDPE/GF composites (left – GF100, right – UTGF) [91].

Particulate reinforcements are used mainly to improve stiffness and toughness while they are less effective in strengthening materials than fiber reinforcement. The main advantage of particle-reinforced composites is their low cost and ease of production [92]. In rotational molding, many types of particles were used.

To investigate the mechanical properties of particulate reinforced polyethylene in rotational molding process, Yan et.al, [93], used different mathematical models (Guth model, Halpin–Tsai–Nielsen, Verbeek model, Nielsen model, Nicolais–Narkis model) to predict the tensile properties; these models were previously used in other molding processes such as injection molding, compression molding to predict the tensile properties of particulate reinforced composites. To verify the theoretical models, different types and sizes of particles were used as a filler to prepare composites using rotational molding. The particles used in this research can be divided into two major groups by size, small (6.5 to 35 µm) and large (90 to 240 µm). MLDPE was mixed with the particles in two different ways, direct mixing and melt compounding. The comparison between theoretical models and experimental methods showed that the Halpin-Tsai-Nielsen, Nicolais-Narkis models could successfully predict the tensile properties of the particulate reinforced composites produced by the rotational molding process when a uniform reinforcement distribution is achieved. Mechanical tests and SEM images showed that in the direct mixing method, the size of the particles plays a significant role. The uniform distribution can be achieved using large particles, because it is easier to cover a larger particle with molten polymer; additionally, smaller particles tend to agglomerate and form a cluster inside the matrix. The tensile modulus for all compounds prepared using large particles tends to increase with increasing the particle content up to 10%. However, at higher content the modulus remained stable or started to decrease, this is may be as a result of agglomeration of the particles at higher particles content as it is shown in Figure 15, zones of agglomeration can be noticed in samples with higher particles content. For the small particles, the modulus starts to decrease at lower content of particles. The tensile strength for all composites decreased with increasing the particles content. Composites prepared using melt compounding showed higher mechanical properties compared to direct mixing in general and it was recommended to be used specially to prepare composites with small particles.

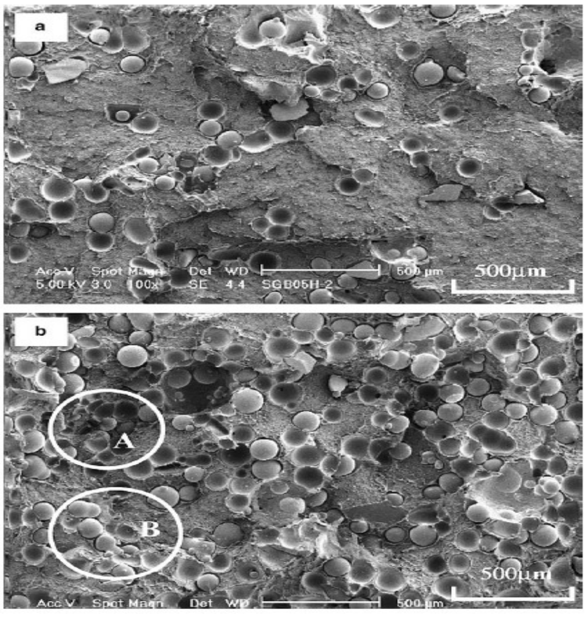

Figure 15: SEM micrographs of the impact fracture surfaces of samples produced by direct mixing method: (a) with 5 vol% Spherical glass and (b) with 15 vol% Spherical glass , Zone A: a particulate cluster, Zone B: a particulate chain [93] .

In another study by W. Yan et al. [94], spherical glass beads (SGB) and irregular shape particles (RGP) with average size 100, 240, respectively, were used as a reinforcement for rotomolded linear medium density polyethylene. The impact strength increased by almost 11% at 10 vol% of both types of particles, further increasing of the particles content decreased the impact strength .Tensile modulus increased by adding the particles, while the tensile strength decreases with the addition of the particles.

Calcium carbonate also introduced to the process by Baumera et al. [95], linear medium density polyethylene, different percentage of CaCO3 (2.0, 5.0 and 10.0wt%),with and without erucamide (Crodamide ER Powder - Croda Brazil) slip agent was mixed together, extruded, and granulated. The granulates were then micronized and used to produce composites using rotational molding. SEM and optical microscopy images showed that porosity in composites cross section of composites increased with increasing CaCO3 fraction. The same behavior was noticed in many other composites prepared by rotational molding; this indicates that filler hinders the diffusion of the bubbles through the part, and longer heating time at molding temperature could help with reducing the bubbles. SEM images also revealed poor adhesion between the matrix and the particles. Mechanical properties generally were decreased for all composite comparing with the net polyethylene, this is due to poor adhesion and high level of porosity, and the addition of erucamide did not affect the mechanical properties of any sample.

Polymeric nanocomposites have recently attracted a great deal of attention in both research and industry fields because of their ability to significantly improve polymer properties even at very low filler loadings. They have already been applied in the many fields, especially in automotive and packaging industries [96]. Many types of nanoparticles have already been tested in rotational molding, in an attempt to change mechanical , electrical, and thermal properties of the rotomolded parts.

Polyamide-6 were mixed with organic modified montmorillonite nanoparticles (omMMT) and prepared by melt-compounding then used to produce a rotomolded composite, the aim of adding omMMT nanoparticles was to prepare nanocomposites with improved mechanical properties and flame retardancy properties suitable for the production of fuel tanks by rotational molding. Composites with 5 wt.% of the nanoparticles with and without the H321 heat stabilizer were prepared. The testing results showed very poor thermal stability of the rotomolded nanocomposites prepared without a heat stabilizer, making them unsuitable for rotational molding. The addition of a heat stabilizer improved the thermal stability, making both PA6 and PA6 nanocomposites possible candidates for rotational molding. Mechanical testing showed that tensile modulus of rotational molded PA6 nanocomposite is much higher than that of neat PA6, while their tensile strength was lower [97].

Chandran et al. [96], prepared LLDPE – Fumed Silica (FS) nanocomposites using rotational molding. Composites were prepared by melting LLDPE with 4% of FS, cooling and grinding the resulted mix into fine powder and then the powder was used to produce composites by rotational molding. Adding 4 wt.% of FS improved the tensile modulus from 750.43 MPa for net LLDPE to 1882.52 MPa for the composites, creep resistance of nanocomposites also increased by 14% compared to net material.

In order to achieve cost-effective and antistatic graphite compounds suitable for rotational molding. Graphite nanoplatelets with an average particle size of 13 μm and an estimated flake thickness of approximately 76 nm were also used to prepare the rotomolded composite. Two types of polymers were used as matrix linear low-density polyethylene (LLDPE) and poly (ethylene-co-vinyl acetate). The particle content varied from 0 to 2 wt.%, the LLDPE composite were mixed in two different ways before molding, dry blending and melt compounding, and the poly (ethylene-co-vinyl acetate) compounds were prepared only using dry blending. The surface resistivities of the composites prepared by dry mixing were within the static dissipation range at a filler content of 0.25 wt.% , the surface resistivity decreased into the conductive range at a higher content, while the composite prepared by poly(ethylene-co-vinyl acetate) were already in the conductive range at a graphite content of 0.25 wt.%, the tensile and impact strength decreased for all composites [98].

G.Hofler [99], conducted research with rotationally molded polyethylene halloysite nanocomposites. Halloysite is a natural, nano-size, mineral clay. Two grades of medium-density linear polyethylene and one grade of high-density polyethylene were used as a matrix. The composites were prepared using both dry blending and melt compounding approaches. The pre-compounding of the material prior to molding improved the mechanical properties of the rotomolded part compared to the parts prepared by dry blending. Tensile modulus increased by 15% with the addition of 5 wt.% of HNT which dry mixed with powder in a high speed mixer, and at 10 wt.% if compounded. The composites also showed a slight improvement in flexural modulus at the same particle content. The impact strength decreased for all composites even at very low particles content and regardless of the mixing method.

Carbon nanocomposites were prepared by rotational molding. Different content of untreated and plasma treated carbon nanofibers (0, 0.01, 0.1, and 1.0 wt.%) were dry-blended with polyethylene and used to prepare rotomolded parts. SEM images showed that the treated carbon fiber showed a better distribution inside the matrix as a result of good adhesion and fibers wetting. Mechanical testing showed that plasma treated nanofibers increased impact strength comparing with net polyethylene and composites prepared by untreated nanofibers. The tensile modulus and tensile strength also increased by 20% and 8%, respectively, as a result of plasma-treated nanofibers, while untreated fibers did not show significant effect on the tensile properties of composites comparing with the net matrix [100].

The literature review showed that only few articles that investigated preparing foam sandwiches in rotational molding were found. These articles mainly studied polyethylene foam, and they did not investigate the adhesion between sandwich layers. Although polyurethane foam is widely used in rotational molding products such as insulation containers , buoys, and refrigerator components, it is not studied in the literature.

In the field of rotational molding of composites, the majority of the research investigated preparing natural fibers composites. The literature elaborated the significance of the surface treatment of the fillers and the powder in order to achieve a proper adhesion between the matrix and the filler. Mostly chemical treatment methods were the most used, and only few articles reported using of plasma treatment as an alternative method for adhesion improvement and it proved to be effective.

Only two articles were found that investigated the possibility of producing glass fibers composites by rotational molding, these articles did not study the composites thoroughly and they did not investigate the effect of any type of surface treatment of the matrix or the fibers on the resulted composites, which left the door open for more investigation.

Based on the current state of art and because importance of the sandwich structure and glass fiber composites in many industries we decided to conduct this research to study in depth the properties of polyethylene- polyurethane foam sandwiches and polyethylene/ glass fibers composites prepared in rotational modeling, and to investigate the effect of plasma treatment of polyethylene powder and glass fibers on the properties of the resulted sandwiches and composites.

Chapter 2:Thesis Goals

The main aim of thesis is to study application of plasma treated polyethylene powder and plasma treated glass fibers in composites and sandwiches prepared via rotational molding.

The main objectives set to achieve this aim are as follows:

- To optimize the rotational molding process of plasma treated polyethylene samples. by preparing samples from treated polyethylene and untreated polyethylene via rotational molding at different peak internal air temperature (PIAT) and testing them .
- To determine the effect of using plasma treated polyethylene on the adhesion between the Polyethylene and polyurethane foam in sandwiches structures, by preparing sandwiches consisting of two plates of polyethylene (skin material) and polyurethane (core), and then comparing the force needed to de-bond the sandwich when untreated and treated polyethylene are used to prepare PE plates, and visually inspecting the bonding surface after testing to evaluate the PU residual on the bonding surface, which is an indicator of better adhesion.
- To determine the effect of using plasma treated polyethylene and glass fibers on the mechanical properties of the composites prepared via rotational molding and on the adhesion between the fibers and the matrix. By preparing composites using different mixture of untreated and treated powder and fibers, trying different plasma treatment time of both the powder and the glass fibers, and optimizing the rotational molding heating process, then conducting different mechanical tests and SEM analysis of the composites and analyze the results.
- To demonstrate the possibility of the application of the developed materials in the selected industrial applications.

Chapter 3: Materials and experiments

3.1 Materials:

For laboratory experiments the following materials were used

- Linear low density polyethylene ‘DOWLEXTM 2629UE’, with density 0.935 g/cm3 and melt flow index (MFI) 4 g/10min from Dow Chemical Company, (Michigan ,US); Plasma modification of PE powder was processed by Surface Treat, a.s. (Turnov, Czech Republic).
- Short, milled glass fibers with an average length of 0.19 mm and an average diameter of 14 μm by LanXESS Company (Cologne, Germany).
- Fisher International single-component polyurethane foam with density 25 to 35 kg/m3,from Fisher international (North Carolina, US).
- Release Agent Rotorelease® MKX-17-014 from Münch Chemie International GmbH (Weinheim, Germany).

For industrial experiments the following materials were used:

- Linear low-density polyethylene Clearflex 50 U, with density 0.936 g/cm3 and melt flow index 7 g/10 min from Versalis (San Donato Milanese, Italy) .
- Two-component polyurethane foam system designed for the insulation of commercial refrigerators and cooling units. VORATECTM SC 474 Polyol / VORATEC SD 100 Isocyanate (Maryland, US).

3.2 Plasma treatment process:

For preliminary experiments industrial grade of plasma treated dowlex 2629EU were used. The treatment was proceeded in industrial pilot plant LA650 (Surface treat company) (Figure 16-a) ,the reactor is based on vacuum process, working gas was air with flow 540-630 sccm, pressure was standard 100 Pa, Plasma was generated by two microwave sources operating in pulse mode with a total power of up to 2 kW, the treatment time was 9 min. Depending mainly on the particle diameter, up to 15 kg of powder can be treated in one batch.

Figure 16: a)The pilot plant LA650 ,b) laboratory equipment LA400.

For other experiments, Dowlex powders were treated in a laboratory device LA 400 (Surface Treat, a.s., Czech Republic) (Figure 16,b) with vacuum working chamber and microwave discharge (1 kW, pulse mode, 0.25 kg powder),pressure 100 Pa, working gas was oxygen with flow 100 sccm, the powder was treated for different treatment times (1 min, 3 min, 5 min, 10 min). Glass fibers were also treated in LA 400 for different times (20,40,60 min) under the same conditions.

For the industrial experiments original material that is used in Olivo company Clearflex 50 U was treated in the in industrial pilot plant LA650 under the same conditions that was used for industrial grade dowlex powder.

3.3 Samples preparation :

3.3.1 Rotational molding samples preparation:

To study the effect of plasma treatment and PIAT temperature on the mechanical properties of the final rotomolded products, samples from untreated dowlex and industrial grade plasma treated dowlex were prepared via rotational molding machine.

The samples were prepared using a laboratory-scale ‘rock and roll’ rotational molding machine with electrical heating, which is shown in Figure 17,a. The machine is designed to undergo full 360 ° rotation motion of the mold around one axis (rolling) and swinging action of the oven around a perpendicular axis (rocking). The oven is heated using four electric resistance heaters placed at the bottom of the oven. The cooling is carried out using a fan installed under the oven. The temperature inside the oven and the molds are monitored using two sensors; one is fixed in the oven to measure the oven temperature, and the other is inserted inside the mold after the mold is placed in the oven, which measures the internal air temperature of the mold (PIAT). The rotation speed was fixed at 10 rmp for all experiments, the swing angle was 45 °.

The mold was a rectangular aluminum box with dimensions 250 mm x 95 mm x 95 mm that is presented in Figure 17,b .

Before loading the material into the mold, the release agent was applied to the inner surface of the mold.

The weight of the material used to produce each sample was 400 g to produce samples with wall thickness 4 mm.

The samples were prepared by loading the powder in the mold, putting the mold in the cold oven, and then heating the oven to temperature 250 ° C and holding it at this temperature until the PIAT temperature reached a certain temperature, when this PIAT temperatures was reached, the heating was stopped, and cooling was started. The PIAT temperatures that were tested were 180 ° C,200 ° C, 220 ° C, 240 ° C.

Figure 17: a)"Rock-and -roll" Rotational molding machine, b) Aluminum mold .

3.3.2 PE/PU sandwiches Preparation:

To study the effect of using plasma treated polyethylene on the adhesion between the polyethylene and the polyurethane foam. Sandwiches containing different percentages of plasma treated polyethylene were prepared. The used powder was treated for different periods, 0.5, 1, 3, 5 min, and the percentage of the treated powder on the plates was varied from 0 to 100 wt.%.

In the first step rectangular PE plates with dimension of 83 mm x 45 mm x 4 mm. were prepared using a rubber mold presented in (Figure 18, a) at temperature 160 ° C for 25 min. After the plates were sintered, removed from the oven, and cooled , a hole with a diameter of 8 mm was drilled in the middle of each plate, and each 2 plates were placed in a special form prepared especially for this experiment (Figure18,b), and polyurethan foam was injected between the polyethylene plates (Figure 18,c) and left to cure for 24 hours, then the excess foam was removed, and the samples were ready for testing.

Figure 18: Sandwich preparation : a) Mold used to prepared rectangular plates, b) Form used to prepare the PE/PU sandwiches, c) Samples foaming.

In the second step instead of preparing the polyethylene plates using the rubber mold in the oven , the plates were taken from the walls of boxes that prepared using a rotational molding machine, and then sandwiches were prepared in the special mold similarly to the first step.

3.3.3 Glass fiber composites preparation

A preliminary experiment was conducted first. Industrial grade of plasma treated dowlex 2629EU treated in industrial pilot plant LA650 for 9 min was mixed with different percentages of glass fibers (5 wt.%,10 wt.%,15 wt.%,20 wt.%). The mixture was placed in the mold inside the cold oven and then heated until the oven temperature reached 250 ° C and held at this temperature until the PIAT temperature reached 200 ° C, the heating was stopped, and cooling was started.

After that, a detailed study was conducted to evaluate the effect of different parameters on the properties of the final products. The first step was to study the effect of the plasma treatment time of polyethylene powder. Polyethylene powder was treated for 1,3,5 and 10 min. The selected treatment times were chosen according to the findings of Sorkouva and Spatenka [72]. The treated powder was mixed with 10% of untreated glass fibers and then used to prepare the composites. The material was heated to an oven temperature of 250 ° C and held at that temperature until the PIAT temperature reached 220 ° C, the heating was stopped, and cooling was started .

In the second step, we studied the effect of the heating process on the final properties of the composites. Two different temperatures were tested. Instead of using the PIAT temperature to determine when to stop heating and start cooling. The oven was heated to 250 ° C or 220 ° C and held at those temperatures for different periods and then cooling started at the end of holding period. The holding time at the oven max temperature was 15 min,30 min , 45 min and 60 min. Composites were prepared using 5 min treated powder and 10% untreated fibers.

In the third step, untreated and treated polyethylene wax was mixed with 5 min treated polyethylene powder in an attempt to incorporate a greater number of smaller particles into the powder. Untreated wax was added in two different percentages (3 wt.% and 20 wt.%), while 5 different percentages of plasma-treated wax was tested (3 wt.%, 5 wt. %, 10wt.%, 15 wt.%, 20 wt.%). Polyethylene wax was treated by plasma under the same conditions as treated polyethylene for 3 min. The composites were prepared at oven temperature 220 ° C and holding time 30 min.

In the fourth step, the effect of plasma treatment of glass fibers was studied. Glass fibers were treated for 20,40 and 60 min and then mixed with untreated powder and 10 min plasma treated powder. The composites were prepared at oven temperature 220 ° C and holding time 3o min.

Finally, the effect of different fibers content was studied by preparing composites using 10 min treated powder mixed with 10,15 and 20 wt.% of 40 min treated glass fibers. The oven temperature was 220 ° C with a holding time of 30 min.

The weight of the material used to produce each sample was 300 g of pure PE powder or PE powder / glass fiber mixture to produce samples with wall thicknesses between 3 and 4 mm. Powder and fibers were mixed before molding for 5 to 10 minutes using a kitchen mixer to insure proper distribution of the fibers in the matrix.

3.3.4 Industrial samples preparation:

To study the applicability of our new materials in the industrial field, samples were prepared in Olivo cold logistic company, which is a leading company for producing insulated containers for food distribution, catering and food trade, transport and storage of dry ice, healthcare logistics, the company is located in France and has international partners and distributors around the world. The company produces different shapes and sizes of containers which are made from hollow rotomolded polyethylene parts filled by polyurethane foam for insulation.

The reason the company wanted to test our materials is that their products which are made using untreated polyethylene had air swellings between the PE and the PU as a result of the instance separation between the polyethylene and the polyurethane after production, which deform the products.

To test the materials. The lids of one of the original company products were produced using different combinations of materials and compared to the original lids.

The rotomolded samples were prepared in a carousel rotational molding machine, which is presented in Figure 19. The machine consists of a heating chamber and a cooling chamber, up to 4 molds can be fixed on a straight arm and the molds are then put into the oven and when the heating is finished, the molds are then moved into the cooling chamber.

Figure 19: Carousel rotational molding machine.

To prepare the samples, the oven was previously heated to 265 ° C, and then the mold was placed in the oven for 12 min, then the mold was moved to the cooling chamber for 25 min, and then the product was demolded. Rotation speed of the main axes is 7 rpm, the speed ratio of the two axes is 6/1.4.

The lids were rotomolded using 5 different combinations of materials:

- Original product of the company made from untreated Clearflex 50 U polyethylene, weight of used polyethylene was (3kg) and resulted wall thickness was (5mm).
- Mixture of 50/50 untreated/treated Clearflex 50 U polyethylene without fibers, weight of used mixture was (3kg) and resulted wall thickness was (5mm).
- Mixture of 50/50 untreated/treated Clearflex 50 U polyethylene with 10% glass fibers, weight of the mixture was 3 kg (2,7 kg of polyethylene mixture+0.3 kg of glass fibers) the resulted wall thickness was (5 mm).
- Mixture of 50/50 untreated/treated Clearflex 50 U polyethylene with 10% glass fibers, weight of the mixture was 2,4 kg (2.16 kg of polyethylene mixture+ 0.24 kg of glass fibers) the resulted wall thickness was (4 mm) with 20% reduction in weight and wall thickness.
- Mixture of 50/50 untreated/treated Clearflex 50 U polyethylene with 10% glass fibers, weight of the mixture was 2.1 kg (1.89 kg of polyethylene mixture+ 0.21 kg of glass fibers) the resulted wall thickness was (3.5 mm) with 30% reduction in weight and wall thickness.

After the rotomolded parts were finished, the parts were moved into special molds which are presented in Figure 20, to be filled with two parts polyurethane foam, then left for 60 min to solidify, the foam was previously mixed, mixing ratio was 154 (isocyanate)/100 (polyol).

Figure 20 : Customized polyurethane injection molds.

The shape of final products is presented in Figure 21

Figure 21: Shape of the lid.

Samples for two different tests were cut from the led.

Specimens presented in Figure 22 with dimension of 83 mm x 45 mm x 70 mm were cut to be used in de-bonding force test.

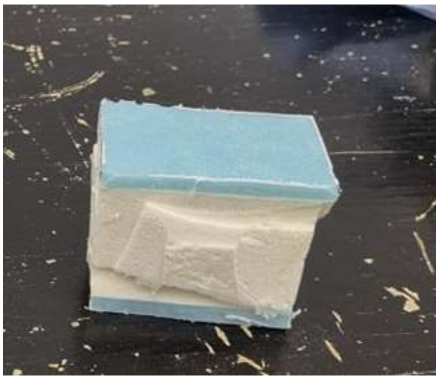

Figure 22: Samples for de-bonding force.

For falling hammer test specimens that are presented in Figure 23 with dimension of 150 mm x150 mm x70 mm were used.

Figure 23: Specimens for falling weight testing before the test.

3.4 Testing methods:

3.4.1 Tensile test:

Tensile properties were measured according to ASTMD 638 using the universal testing machine TINUS OLSEN H50KT (Figure 24) at a gauge length of 60 mm and a speed of 50 mm per minute at room temperature. Reported values are the average of at least five specimens.

The tensile strength (stress) was calculated by dividing tensile force by the cross-sectional area of the samples before deformation:

$$\text{Tensile strength } R = F/A \ (MPa) \qquad \text{Equation 1}$$

The tensile modulus was calculated by dividing tensile stress by tensile strain, which is a relative deformation, and it is calculated by dividing the change in length ($Ln - L0$) by the original length, L_0 :

$$\text{Young's modulus } E = stress/strain = (FL0)/A(Ln - L0)\ [MPa] \qquad \text{Equation 2}$$

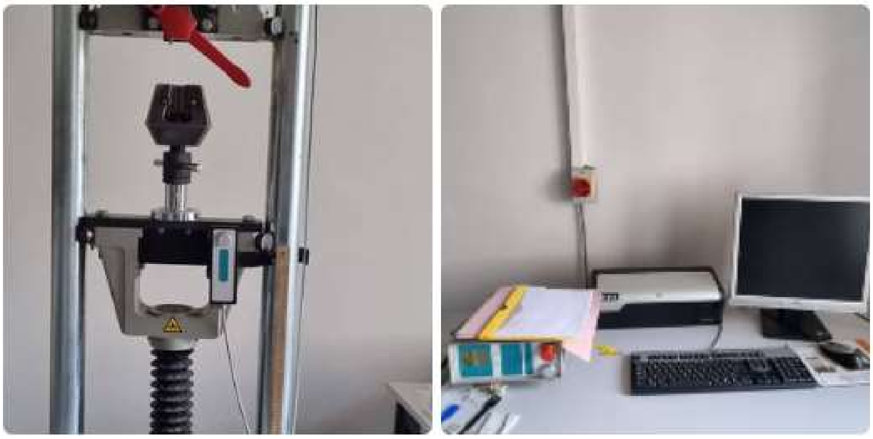

Figure 24: Tensile test machine.

3.4.2 Flexural Test:

Three point bending test was performed according to ASTM D790 using MTS Exceed E42 bending machine (Figure 25, a) ,shape of the samples is presented in (Figure 25, b) testing speed was 10 mm/min, distance between supports was calculated using the following equation:

$$L=16 \cdot h\ [mm]$$ Equation 3

Flexural modulus was calculated using the following equation:

$$Ef=F\cdot \mathbf{L}^3/48\cdot I\cdot d\ [MPa]$$ Equation 4

$$I = b.h^3/12$$ Equation 5

Where:

- F: Applied force [N].
- I: Moment of inertia [mm^4].
- L: Span length [mm].
- d: Deflection [mm].
- b: sample width [mm].
- h: sample thickness [mm].

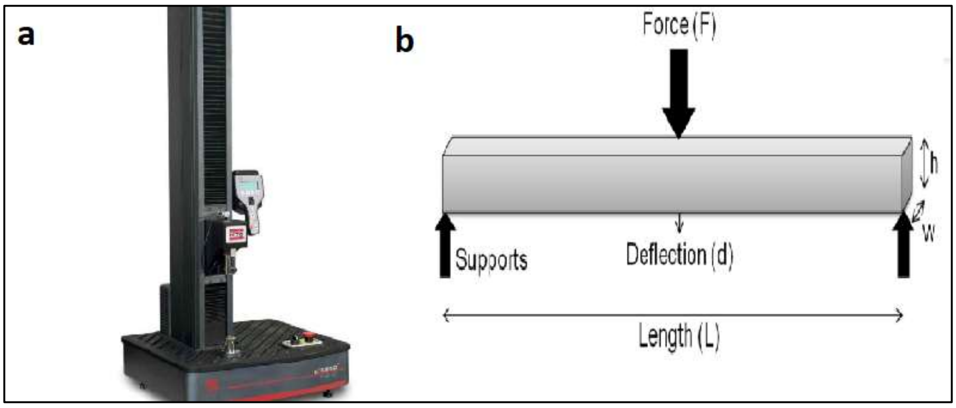

Figure 25: Flexural test:a) Testing machine,b) samples shape.

3.4.3 Impact Test :

Charpy impact tests were performed using impact testing machine CEAST 7.5 J presented in Figure 26 according to ASTM D 6110 . The samples were notched with a notch of 1.5 ± 0.2 mm. The tests were performed at room temperature 23 ± 2 ° C.

Impact strength was calculated by dividing the absorbed energy by the cross section of the sample at the notch.

Figure 26: Impact testing machine.

3.4.4 Falling hammer test:

This test was applied only on the industrial samples prepared in France. Gravity falling hammer is presented in Figure 27, the hammer weight is 11.6 kg and with a line height of 3500 mm (hammer is completely at the top). The impact energy was changed by changing the height of the ram from 20 to 1200 cm, and samples were observed to determine whether separation between the polyurethane and polyethylene sheet will occur or whether the polyethylene sheet will break at higher impact energy.

Figure 27: Gravity falling hammer.

The shape of the hammer head is cylinder which is presented in Figure 28 with 5 cm diameter and 8 cm length.

Figure 28:Hammer head.

The impact energy was calculated by the following:

$$E = m * g * h$$

Where:

E: Impact energy J.

m : Mass of the hammer kg.

g: Gravitational acceleration, 9.8 m/s2.

h: falling height m.

The impact energy of the hammer falling from different heights is presented in Table 3:

Height m	Energy J
0.2	22.75
0.4	45.50
0.6	68.25
0.8	91
1	113.75
1.2	136.5

Table 3: The impact energy resulted from the hammer falling from different heights.

At least 4 specimens were tested for each combination. Each specimen was hit by the hammer many times, each time the hammer was set to fall from different height (20,40,60,80,100,120) cm.

3.4.5 De-bonding Test:

De-bonding test for PE/PU sandwiches was performed using a customized testing machine, which is presented in Figure 29, the test was performed at room temperature, the applied force was 20 N/s, the rate of force increase was 2 N/s

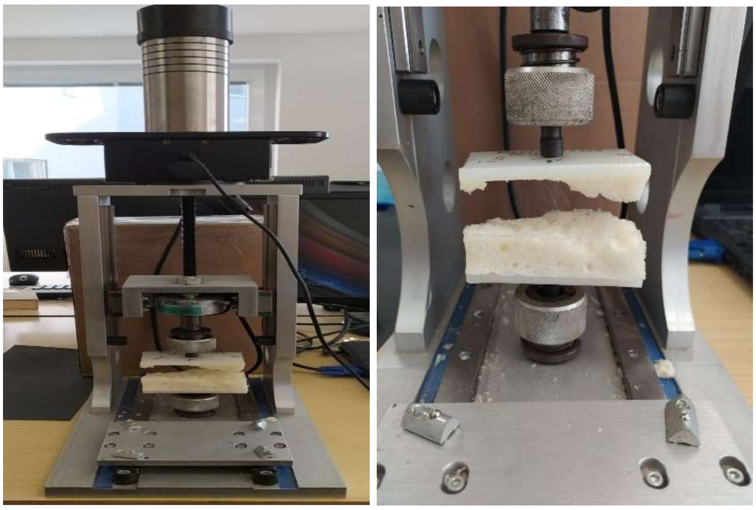

Figure 29:De-Bonding testing machine.

3.4.6 Optical Microscopy:

Optical microscopy (OM) images were performed using a Nikon SMZ 1500 stereomicroscope equipped with a CCD camera, which is presented in Figure 30.

Figure 30: Optical microscopy.

3.4.7 Scanning Electron Microscopy:

Scanning electron microscope JSM-7600F (JEOL, JP) Figure (31,a) in the faculty of mechanical engineering – Czech Technical University in Prague and scanning electron microscope (Lyra3, Tescan) Figure (31,b) in the Faculty of Electrical Engineering and Communication, Brno.

The samples were broken using liquid nitrogen and the fracture surface was coated by chromium or carbon to improve its conductivity and prevent surface charging.

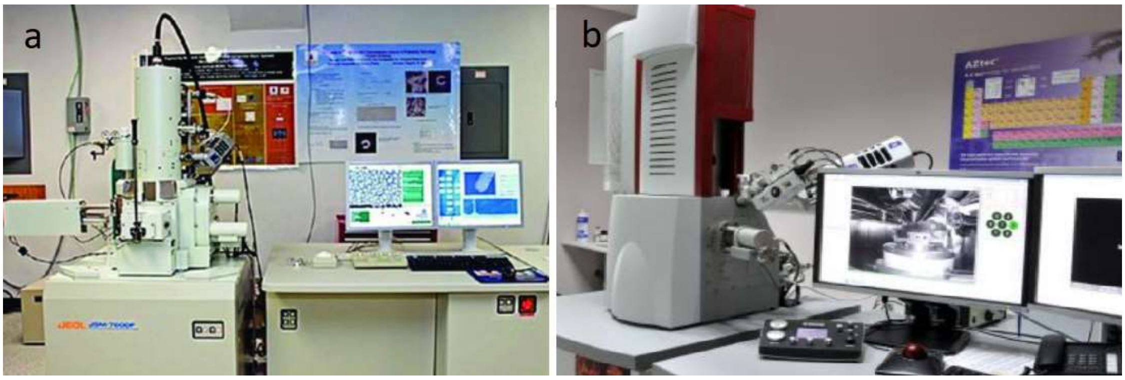

Figure 31: a) Scanning Electron microscope JSM-7600F (JEOL, JP),b) Scanning electron microscope (Lyra3, Tescan).

3.4.8 Differential scanning calorimetry (DSC):

Differential scanning calorimetry (Netzsch STA 409PG LUXX)(Figure 32) was used to study the thermal behavior of untreated and plasma-treated powder. Samples were measured in a protective atmosphere of nitrogen (N2). The heating rate was 10 ° C per min to 300 ° C with a duration of 5 min. The cooling rate was on average 5 ° C.min-1 with non-isothermal crystallization.

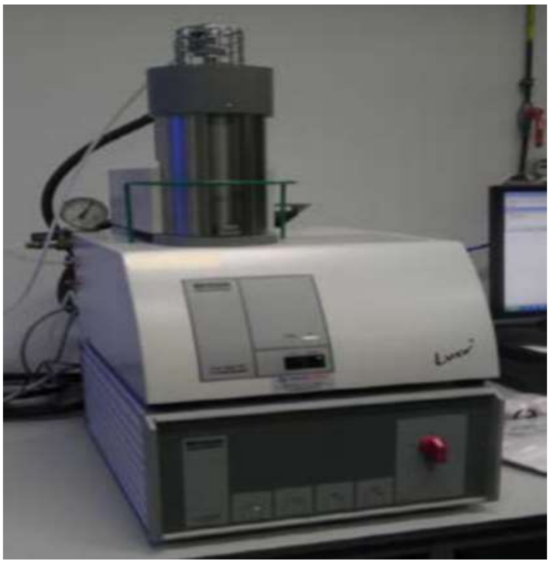

Figure 32:Differential scanning calorimetry (Netzsch STA 409PG LUXX).

Chapter 4: Results and discussion

4.1 Characterization of Plasma treated polyethylene powder:

4.1.1 SEM of PE particles before and after treatment :

Plasma treatment is surface modification techniques, using the correct processing conditions should not affect the shape or the structure of the power particles. Figure 33 shows SEM images of polyethylene powder before (a) and after (b) plasma treatment, no difference can be noticed in the shape of the powder [101].

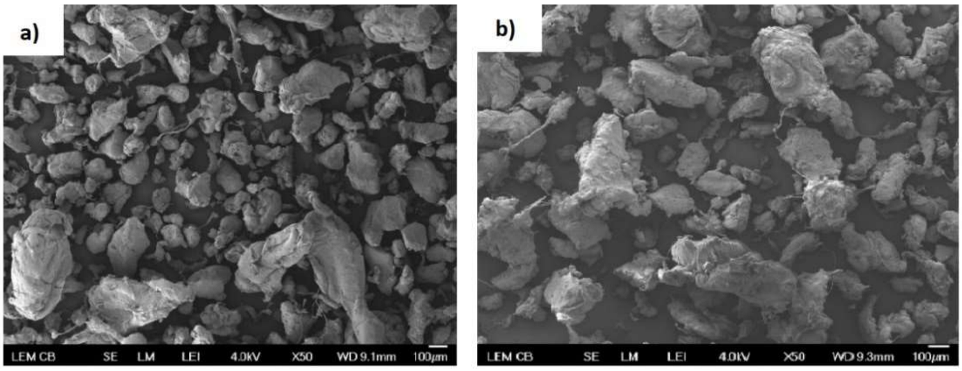

Figure 33: SEM images of untreated (a) and treated (b) polyethylene particles [101].

4.1.2 Differential Scanning Calorimetry (DSC) measurements:

DSC measurements were previously conducted by our team on untreated and treated polyethylene powder to observe melting temperature and crystallization temperature of the material before and after treatment. The resulted DSC curves are presented in Figure 34 showed that treated and untreated powder have the same crystallization temperature of 113 ± 1 ° C and approximately the same melting point, 128 ± 1 ° C for untreated PE and 127 ± 1 ° C for treated PE, so plasma treatment does not affect the thermal behavior of polyethylene and both untreated and treated polyethylene can be prepared using the same regime [102].

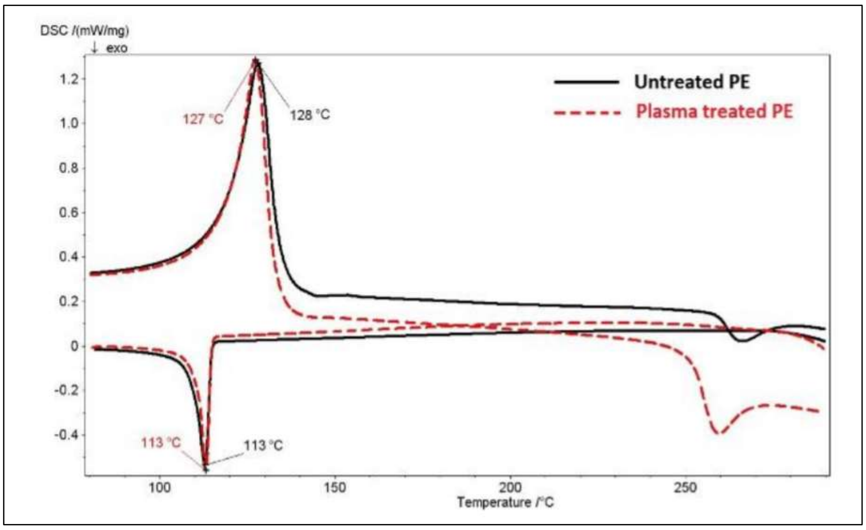

Figure 34: DSC measurement of untreated and treated powder [102].

4.1.3 Surface characterization of plasma treated PE :

The effect of plasma treatment on the wettability and O group concentration of PE powder was studied and reported by Sorkouva and Spatenka [72]. Their results are presented in Figure 35. They demonstrated that a significant increase in wettability can be observed up to 10 minutes treatment time, while the concertation of the oxygen groups continues to increase with increasing treatment time.

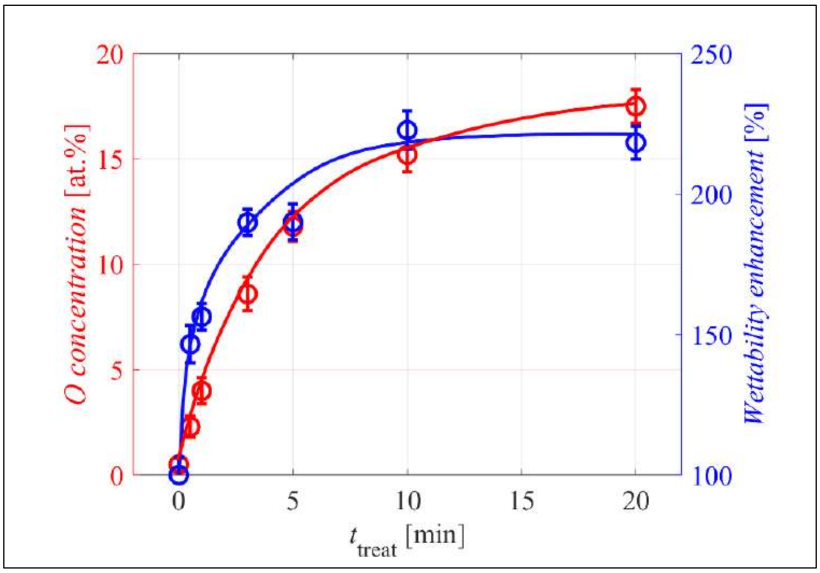

Figure 35: Effect of powder treatment time on the wettability and O group concentration [72] .

4.1.4 Properties of rotational molding samples prepared by untreated, and plasma treated PE

The maximum internal air temperature PIAT is a critical temperature in the rotational molding process. If the PIAT temperature is very low, the powder will not have enough time to sinter properly and more air buckets will be trapped in the melt, resulting in undercooked products with a bigger number of bubbles ,while very high PIAT resulted in overcooked products where the material starts to degrade due to exposure to high temperature for a long time. Table 4 showed heating time needed to reach each PIAT temperature for both untreated and plasma treated powder :

PIAT, ° C	Heating time	
	UTPE	TPE
180	36	36
200	40	40
220	44	44
240	48	48

Table 4: Heating time to reach different PIAT temperature.

The same time was needed to heat both untreated and treated powder; this proved that plasma treatment does not change thermal behavior of the samples, and this corresponds to the results obtained from DSC measurements.

4.1.4.1 Visual inspection and optical microscopy:

Visual inspection showed that samples prepared with treated materials have yellow color compared with samples prepared by untreated powder Figure 36

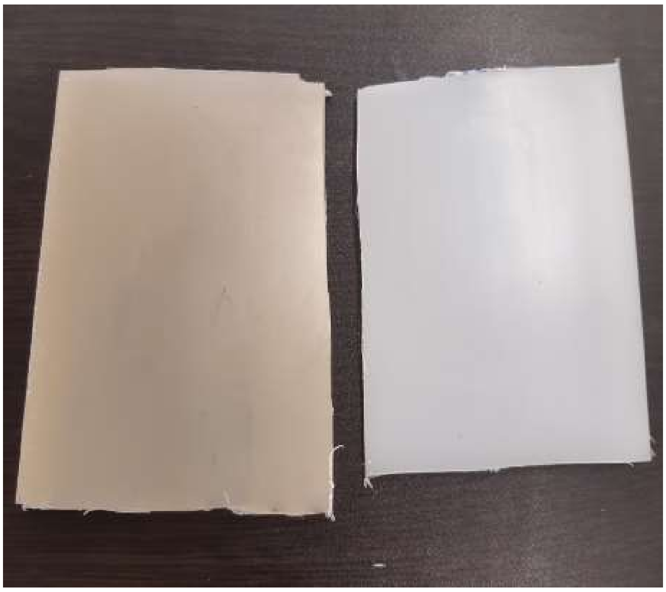

Figure 36**:** Color changing of sample prepared using treated powder (To the left) comparing with samples prepared using untreated powder (to the right) **.**

This yellow color is caused by oxidation and subsequent reactions resulting from the presence of functional groups after treatment, and it should not be confused with the color change that occurs as a sign of sample degradation, as it can be seen in Figure 37 the yellow color resulted from degradation is accompanied with glossy inner surface in addition to burning smells.

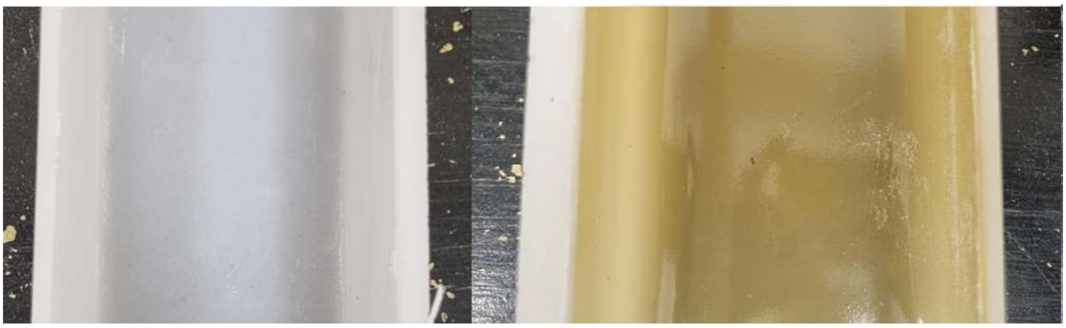

Figure 37 : Color changing as a result of sample degradation : to the left normal sample with no sign of degradation, to the right degraded sample.

Optical microscope images of the outer surface of samples prepared at two different PIAT temperatures are presented in Figure 38, in the samples prepared at PIAT temperature 180 ° C a lot of small bubbles can be noticed on the outer surface of the samples (Figure 38,a) while the bubbles disappear with increasing PIAT temperature to 220 ° C (Figure 38,b), which indicate better quality products.

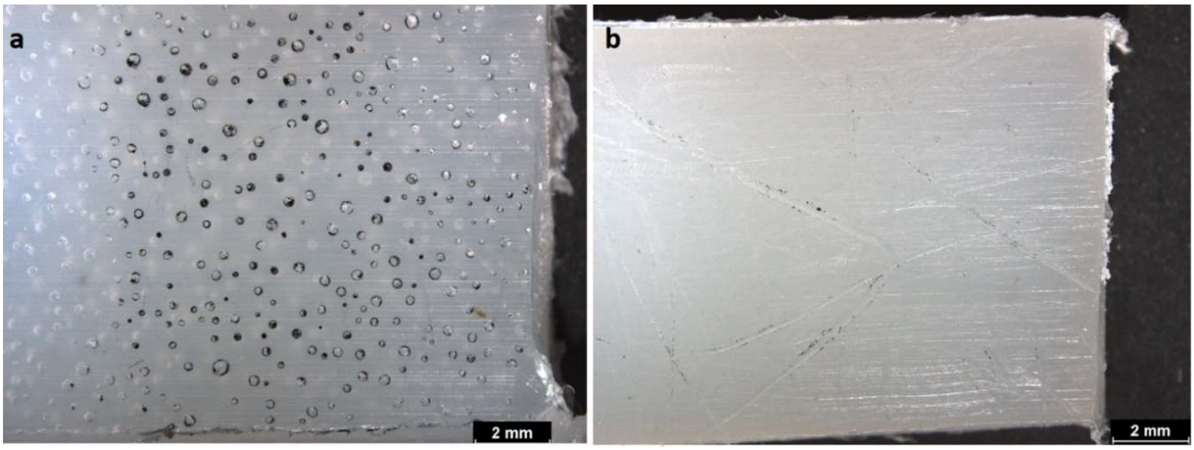

Figure 38: Optical microscope of samples' outer surface: a) Samples prepared at PIAT temperature 180 ° C, b) Samples prepared at PIAT temperature 220 ° C.

4.1.4.2 Mechanical properties:

The tensile strength of untreated and plasma-treated polyethylene which is prepared at different PIAT temperatures is presented in Figure 39. The lowest value of tensile strength is this of samples prepared from untreated powder at PIAT temperature 180 ° C this could be as a result of more bubble remaining in the samples prepared at this temperature. The differences between tensile strength values of the samples prepared using treated and untreated powder at different PIAT temperatures are very small less than 5%.

The tensile modulus is presented in Figure 40, the tensile modulus of the samples prepared from the untreated powder remains the same at different PIAT temperatures, while a very slight decrease up to 6% can be observed for the treated samples prepared at PIAT 220 ° C and 240 ° C compared to the treated samples prepared at 180 ° C and 200 ° C.

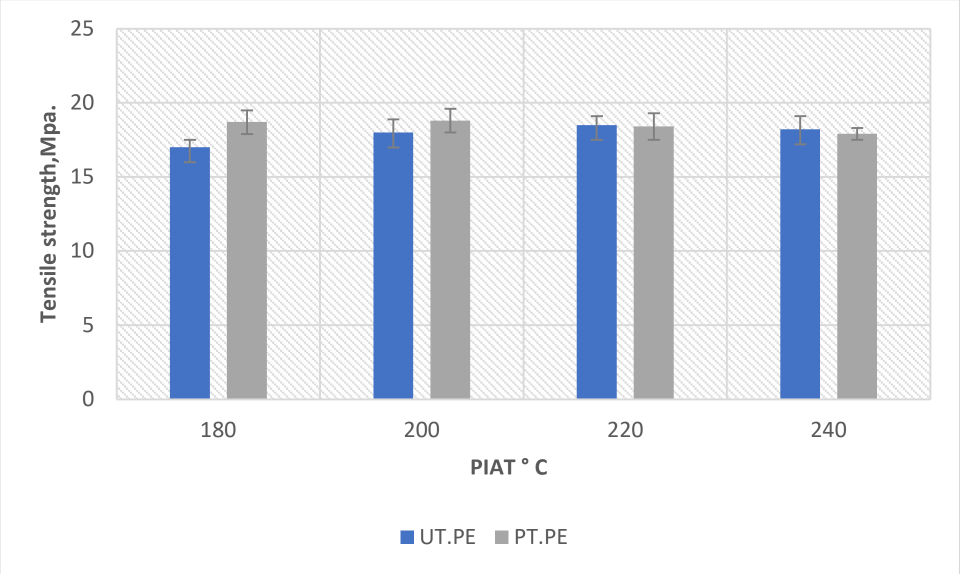

Figure 39: Tensile strength of rotomolded samples prepared using untreated and treated PE at different PIAT temperature.

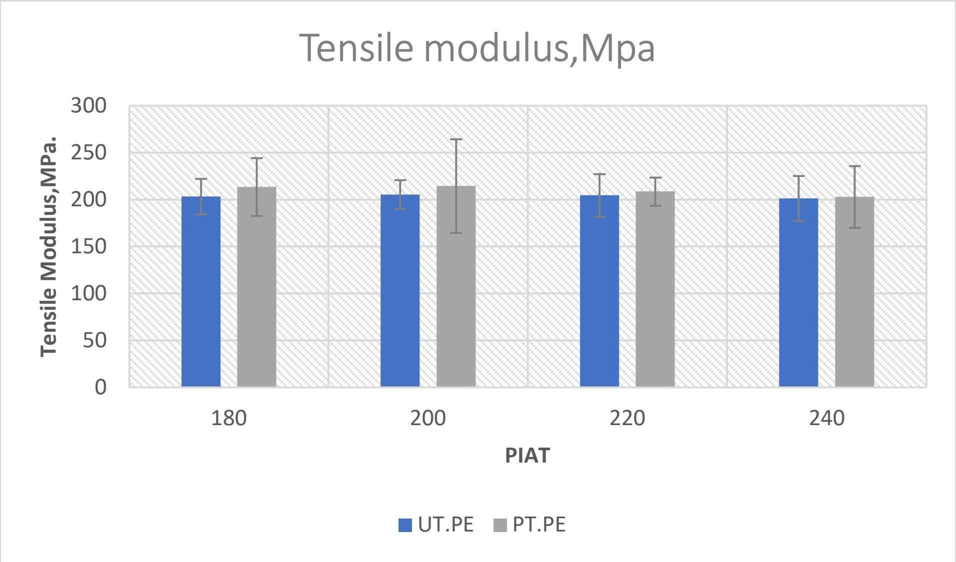

Figure 40: Tensile modulus of rotomolded samples prepared using untreated and treated PE at different PIAT temperature.

Impact test results are presented in Figure 41,impact strength tends to slightly increase with increasing PIAT temperature to reach the highest value at PIAT temperature 240 ° C, this could be as a result of fewer bubbles in samples prepared at higher PIAT temperature. No difference between samples prepared with untreated and treated powder can be observed, except for samples prepared at PIAT temperature 200 ° C the impact strength of treated samples was 10% higher than that of untreated samples.

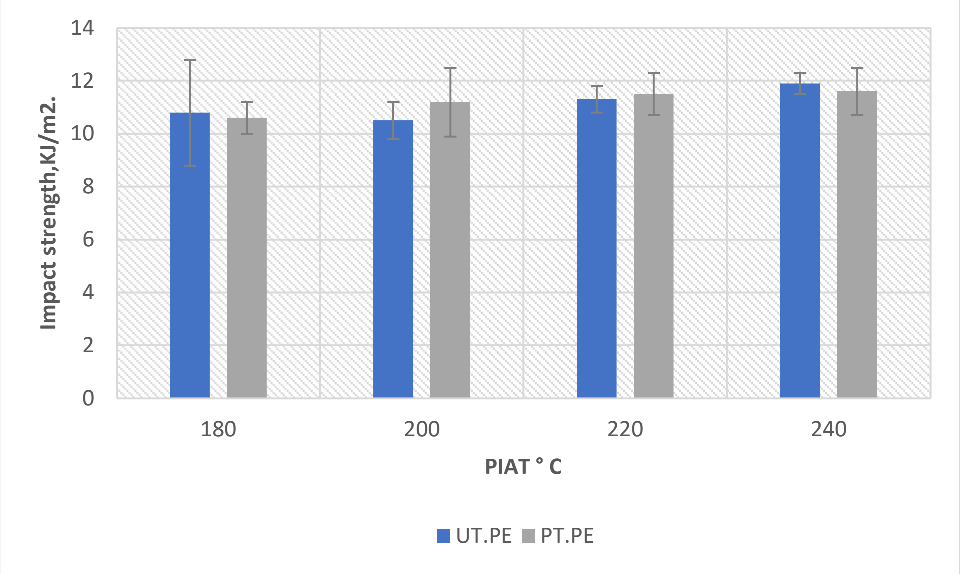

Figure 41:Impact strength of rotomolded samples prepared using untreated and treated PE at different PIAT temperature.

4.2: PE/PU sandwiches

4.2.1 Effect of plasma treated powder content

The effect of the percentage of 1 min treated powder in the PE plates prepared in the oven on their bond to polyurethane foam is presented in Figure 42. It can be seen that increasing the amount of treated powder in the mixture increases the force needed to separate them from polyurethan foam; the force increased from 22,79 N for samples prepared using untreated powder to 188.86 N for samples prepared using a mixture of 25/57 untreated powder/treated powder. Even with using only 15% of treated powder in the mixture de-bonding force increased almost by 279% comparing with samples prepared using untreated powder, this is because the treated powder kept the high surface energy resulted from the plasma treatment of the powder even after sintering of the powder into plates. Using of 100% of treated powder for preparing PE plates is not needed as no further increasement in the de-bonding force was noticed when using 100% of treated powder, this could be because the highest surface energy of the samples was already reached when 75% of the treated powder was used.

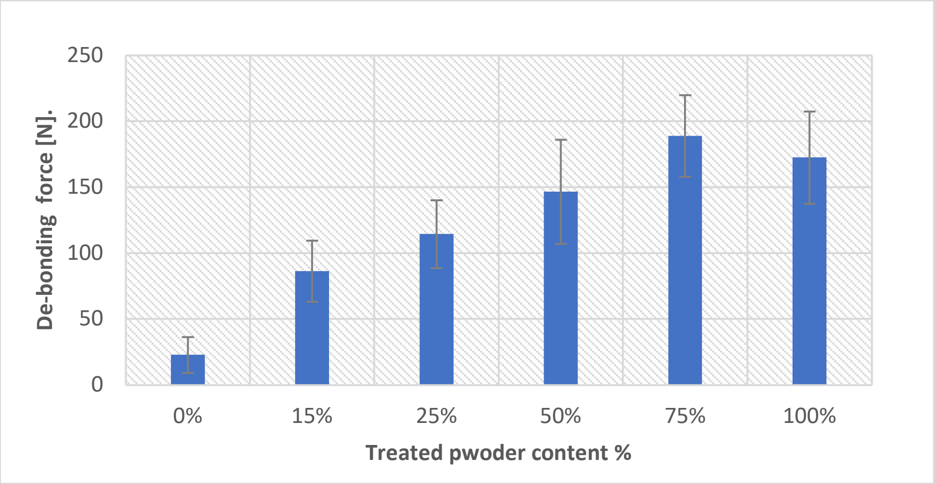

Figure 42: Effect of 1 min treated powder content in polyethylene plates on the force needed to de-pond PE/PU sandwiches.

After testing it was noticed that in all cases, the debonding occurred on the upper plate that was fixed to the moving jaw of the testing machine. The amount of PU residue on the surface of upper PE plates with different treated powder content was estimated by visual inspection and presented in Figure 43, it was determined on a scale from 0 to 100% where 0% means no residue trace, 5% means very small amount mainly on the edges and 100% foam is covering all the surface of upper plate.

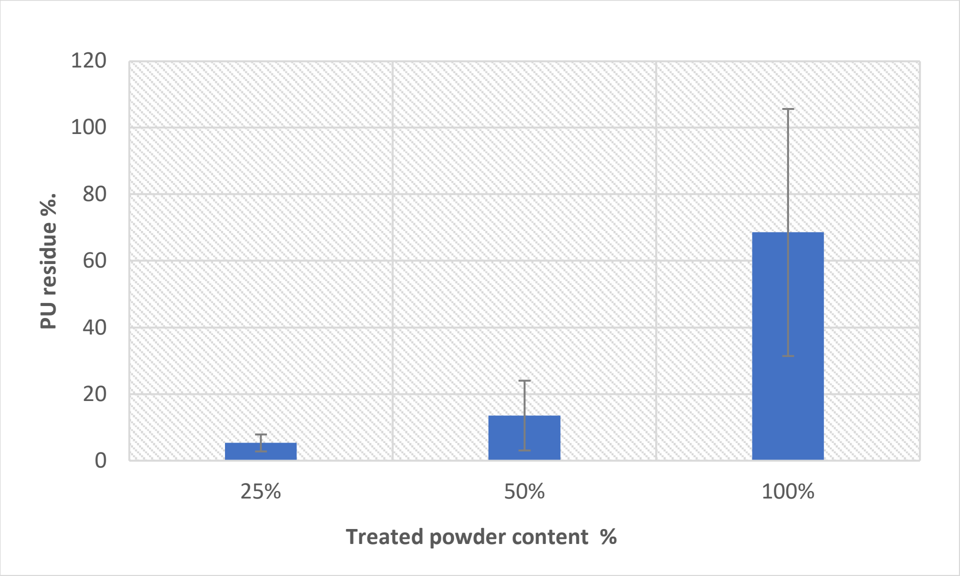

Figure 43: Effect of 1 min treated powder content in polyethylene plates on the PU residue on the bonding surface of the upper plates after testing.

In all sandwiches prepared using untreated PE plates the samples were ripped off without any foam left on the bonding surface, and this was also the case in most of the sandwiches prepared using PE plates that contain 15 % treated powder, while as shown in Figure 43 a trace of PU residues (around 5%) started to appear on the bonding surface of upper plates that contain 25% treated powder, the residual amount increased to 14% on the surface of PE plates that contain 50% of treated powder and to 69% on the surface of the plates that contain 100% treated powder. Figure 44 shows images of the amount of PU residues on the bonding surface of the upper PE plates prepared with different percentages of treated powder after testing.

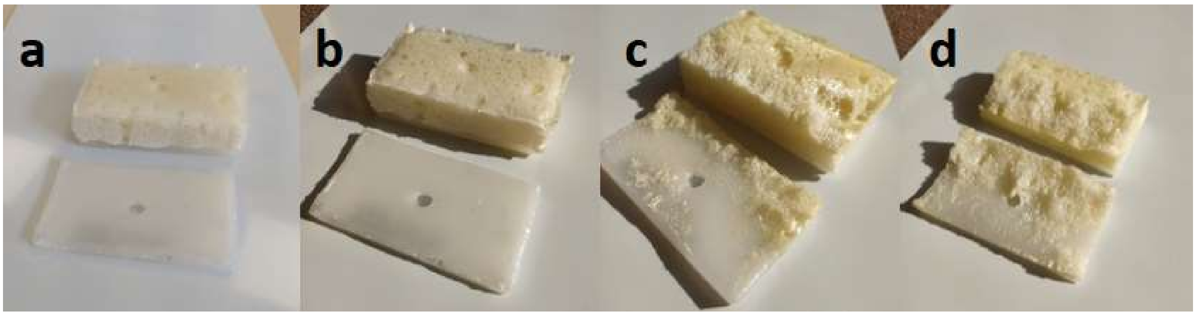

Figure 44: PU residue on the upper plate bonding surface after testing: a) sample prepared with untreated powder, b) samples contain 15% of 1 min treated powder, c) samples contain 50% of 1 min treated powder, d) samples contain 100 % of 1 min treated powder.

4.2.2 Effect of the presence of incision in PU foam

It was noticed during tests that de-ponding of the sandwiches was always happening near the upper plate (which is connected to the movable jaw). An incision with depth of o.5 cm was made in different positions in the foam to demonstrate its effect on the debonding behavior (foam tearing) of the sandwiches. Three incision patterns were tested, the first in which the incision was made near the upper plate, the second in which the incision was made near the lower plate, and the third in which two incisions were made, one near the upper plate and the other near the lower plate. The results of the tests are presented in Figure 45. The presence of incisions did not change the tearing behavior, the foam tearing continued on the upper bonding surface and did not start from the incisions, independently of the incision site. The reason could be that the debonding force acts directly on the upper plate which is connected to the moving jaw of the testing machine, which distributes the force hence the stress on the bonding surface between the upper PE plate and polyurethane and causes the tear to start near the upper bonding surface. The force needed to tear the foam did not change much for the samples with incision near the upper plate and for the samples have two incisions compared to the sample having no incision, while a slightly larger force was needed to tear the samples that had incision near the lower surface. A very small amount of PU residue was observed on all samples after testing, with a maximum amount of 23% that was detected on the surfaces of samples that had an incision near the lower surface.

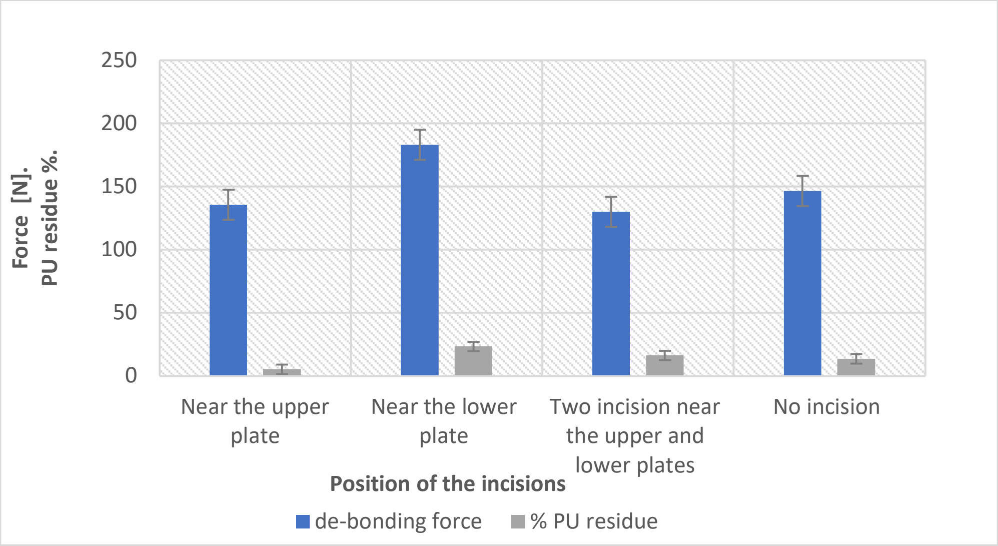

Figure 45: Effect of incisions in foam on de-bonding force and PU residue on bonding surface.

4.2.3 Effect of treatment time:

The comparison between the debonign force and the PU residue of the samples prepared using 1 min and 3 min treated pwoder is shown in Figures 46 and 47, respectivaley

De-bonding force inceased with increasing treatement time, and this is because increasing powder treatement time increases the wettability and concentration of the O groups as it was demonstreted by Hana et.al [72]. De-bonding force increased by 96% when 25% of the 3 min treated powder was used compared to the same percentage of 1 min treated powder, at 50% the increase in bonding force was only 19% compared to the 1 min treated powder. This indicates that at low percentages of treated powder, the treatment time has a significant effect on the debonding force, while this effect decreases at higher content of treated powder. This can be explained that when the content of treated powder in the polyethylene plates is low, a longer treatment is required to provide a greater number of active groups on the surface of the blates after sintering, while a higher content of treated powder provides the required number of these fuctional groups without the need for a longer treatment time. The amount of PU residue also increased by increasing treatement time, and the effect was significant with a lower content (25%) of treated powder, it increased from 5% for plates containing 1 min treated powder to 88% for plates that conatin 3 min treated powder.

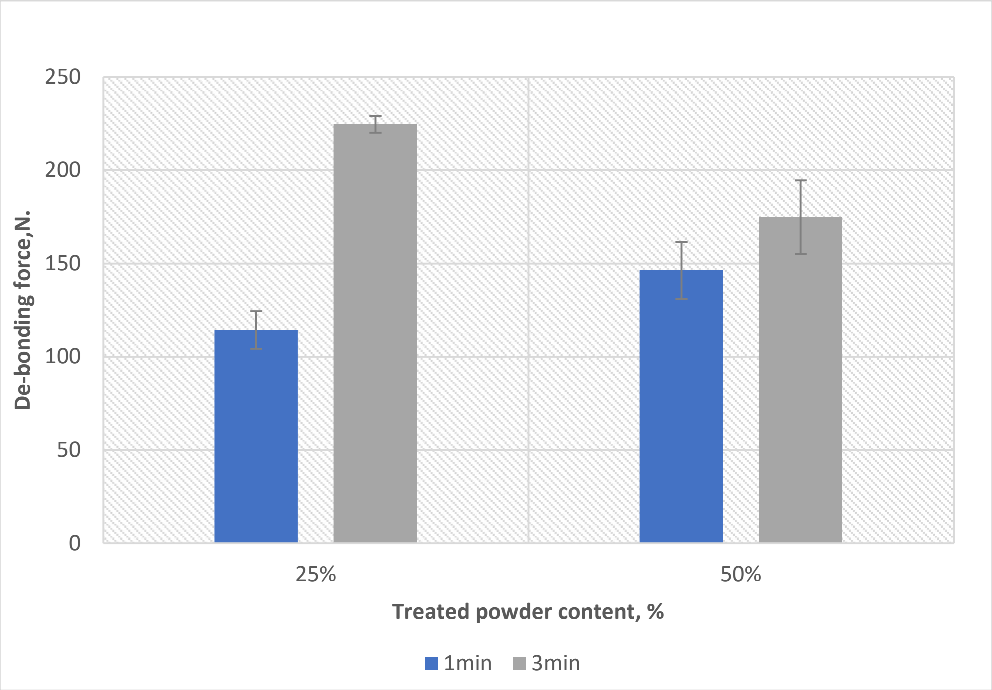

Figure 46: Effect of powder treatment time on de-boding force needed to tear the sandwiches.

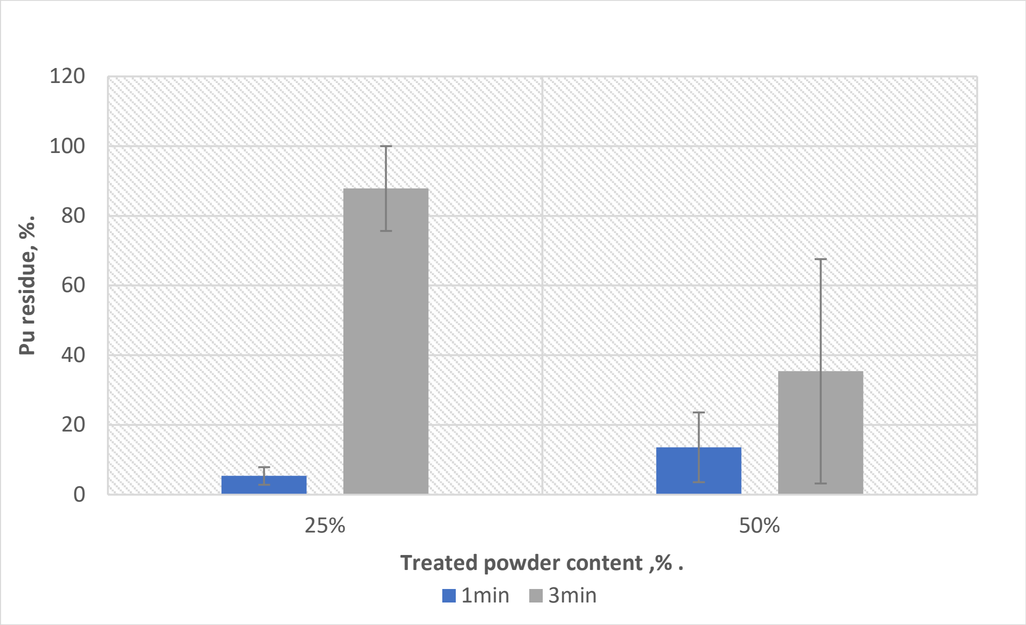

Figure 47: Effect of powder treatment time on PU residue on the bonding surface.

De-bonding force and PU residue of the samples contains 25% of powder treated for different time is presented in Figure 48 , It shows that de-bonding force and PU resdidue increased with increasing treatment time from 0,5 min up to 3 min, and decreased when using 5 min treated powder. This maybe because the sufrace of the plates was already saturated by functional groups at 25% of 3 min treated powder, and longer treatement time was not needed.

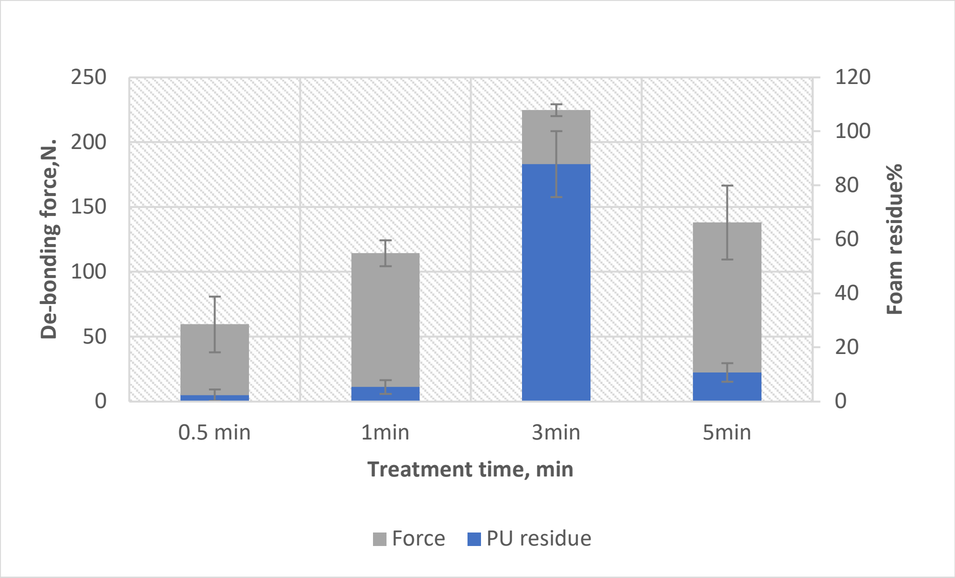

Figure 48: Effect of different treatment time on de-bonding force and PU residue on bonding surface in sandwiches contain 25% of treated powder.

4.2.4 Application in rotational molding

To test if using plasma treated powder in rotational molding will have the same positive effect on the adhesion between polyethylene and polyurethane, polyethylene boxes containing different percentage of treated powder were prepared in rotational molding and rectangular plates were cut from rotomolded boxes walls and the plates then were used to prepare sandwiches.

Figure 49 shows the effect of 1 min treated powder content on the de-bonding force of sandwiches consist of polyethylene plate that were prepared by rotational molding.

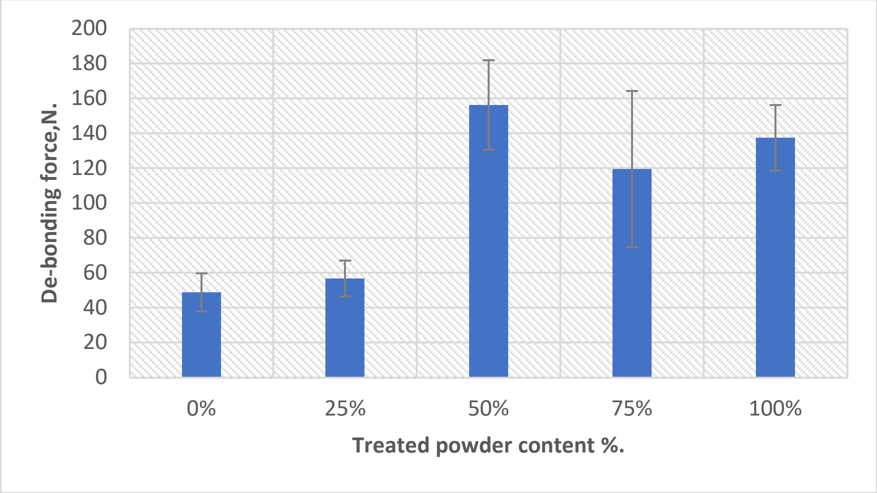

Figure 49: Effect of treated powder content in PE plates prepared using rotational molding on de-bonding force needed to tear PE/PU sandwiches prepared using the plates.

De-bonding force increased by increasing the treated powder content in the plates, the maximum force was reached at 50% of treated powder in the plates.

The PU residue left on the upper plate is plotted in Figure 50, the PU residue on the upper plate after tests kept increasing with increasing treated powder content, from 0% for plate prepared with untreated powder to 100% for samples prepared with 1min treated powder.

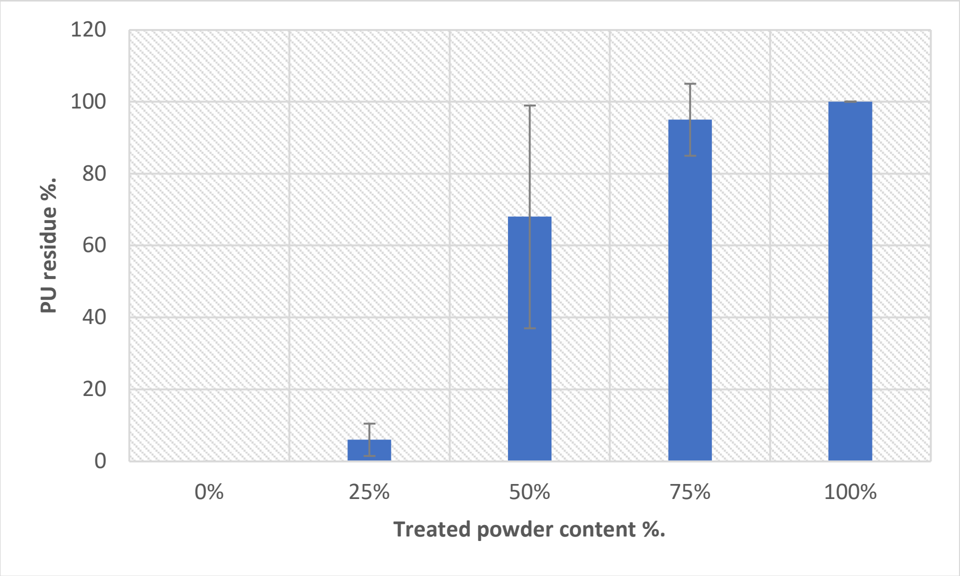

Figure 50: Effect of treated powder content in PE plates prepared using rotational molding on the PU residue on the bonding surface after testing.

Figure 51 shows surface of upper plate after testing, as it can be clearly seen no PE residue on the surface of plate prepared from untreated powder while PU residue totally covers the surface of plate prepared from 1 min treated powder.

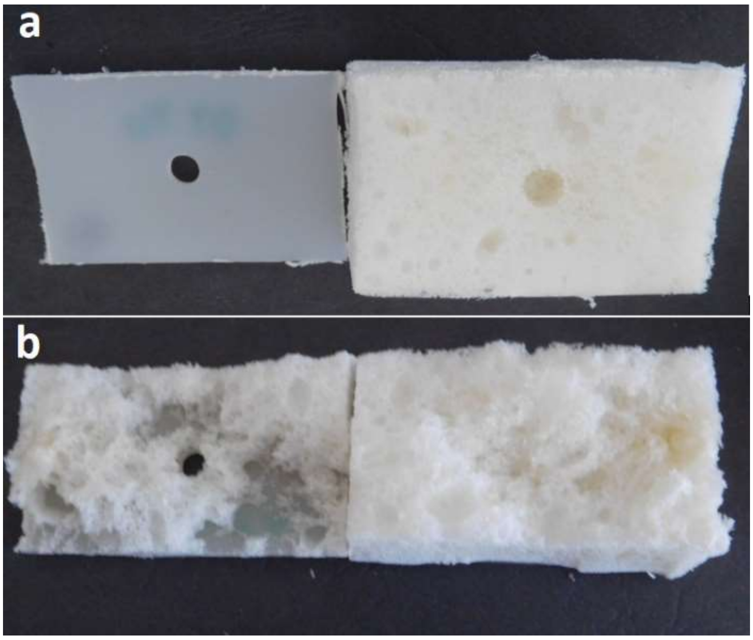

Figure 51: PU residue: a) Plates prepared from untreated powder, b) Plates prepared from 1 min treated powder.

Effect of higher treatment time is presented in Figure 52, the samples are prepared using totally treated powder, higher treatment time did not have significant effect on the force needed to tear the bond between the polyethylene plate and polyurethane. Similar to plates prepared by 1 min treated powder the upper surface of plate prepared using 3 min and 5 min treated powder were totally covered with PU residue after testing Figure 53.

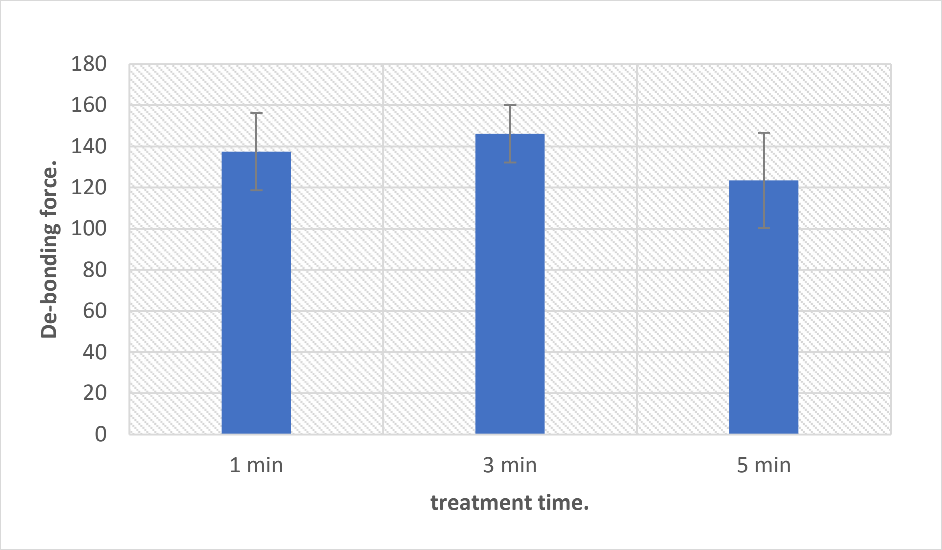

Figure 52: Effect of treatment time of polyethylene on de-bonding force of plates prepared using rotational molding.

Figure 53: PU residue: a) Plates prepared from 3 min treated powder, b) Plates prepared from 5 min treated powder.

4.3 Glass fiber composites

4.3.1 Preliminary Results:

Preliminary experiments have been done using untreated powder and industrial grade plasma treated powder, which was treated in the industrial pilot plant LA650 for 9 min. Composites with different glass fiber content ranging from 5wt% to 20wt% were prepared at oven temperature 250 ° C and cooling started when the PIAT temperature reached 200 °C [103].

The tensile strength of the composites prepared using untreated and plasma treated powder with different glass fiber content is presented in Figure 54. The tensile strength of the composites prepared using untreated and treated powder with low glass fiber content (5 wt.%) was maintained at the same value as the pure PE samples and started to decline with the addition of more fibers to reach the lowest values at 20 wt.% of glass fiber content; this could be a result of poor adhesion, the presence of a higher number of bubbles and fiber agglomeration at higher fiber content. No significant improvement as a result of plasma treatment is noticed. The only improvement that could be observed was in samples containing 15 wt.% fibers, where composite materials prepared with treated powder showed an improvement of 17% compared to composite materials prepared from untreated powder [103].

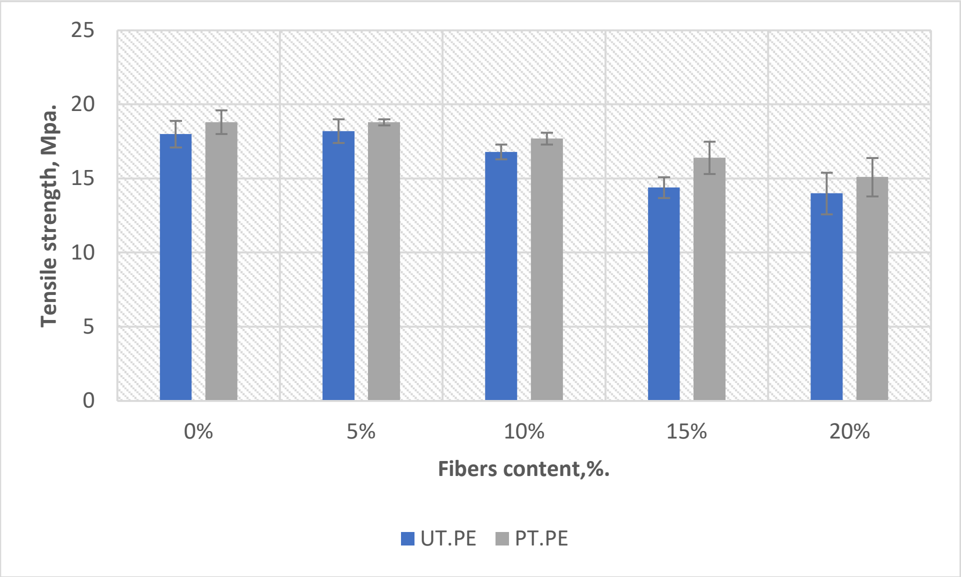

Figure 54: Tensile strength of composites prepared using untreated and treated powder with different content of glass fibers.

The tensile modulus presented in Figure 55 increased by increasing fiber content compared to the net polyethylene ,this is the result of the presence of rigid fibers that have significantly higher tensile modulus than PE powder. Tensile modulus increased by 46% and 48% for untreated and treated composites, respectively, compared with unfilled samples. No significant differences in the values between treated and untreated powder in all cases [103].

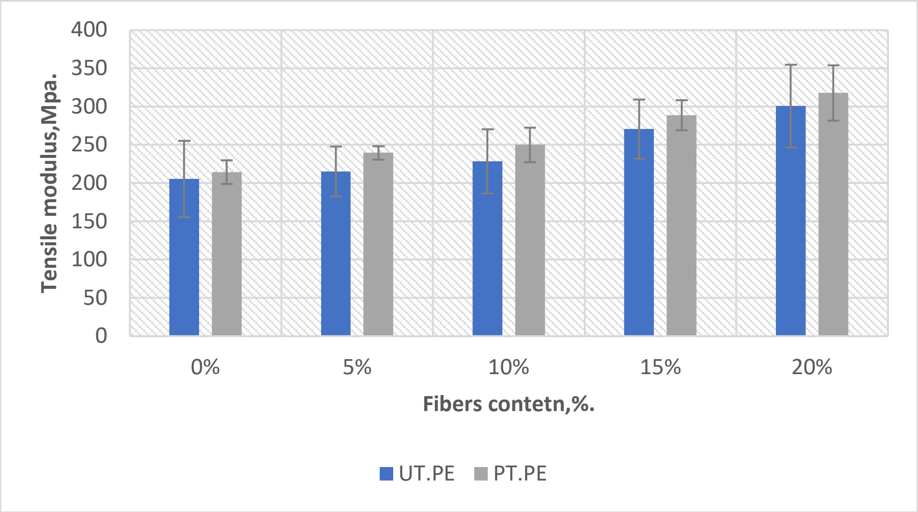

Figure 55: Tensile modulus of composites prepared using untreated and treated powder with different content of glass fibers.

In contrast to the tensile modulus, impact strength testing results which are presented in Figure 56 showed decalin in the impact strength values with increasing fiber content, the reason could be that the presence of rigid glass fibers decreases the mobility of the polymer chain, therefore decreasing its ability to absorb impact energy [103].

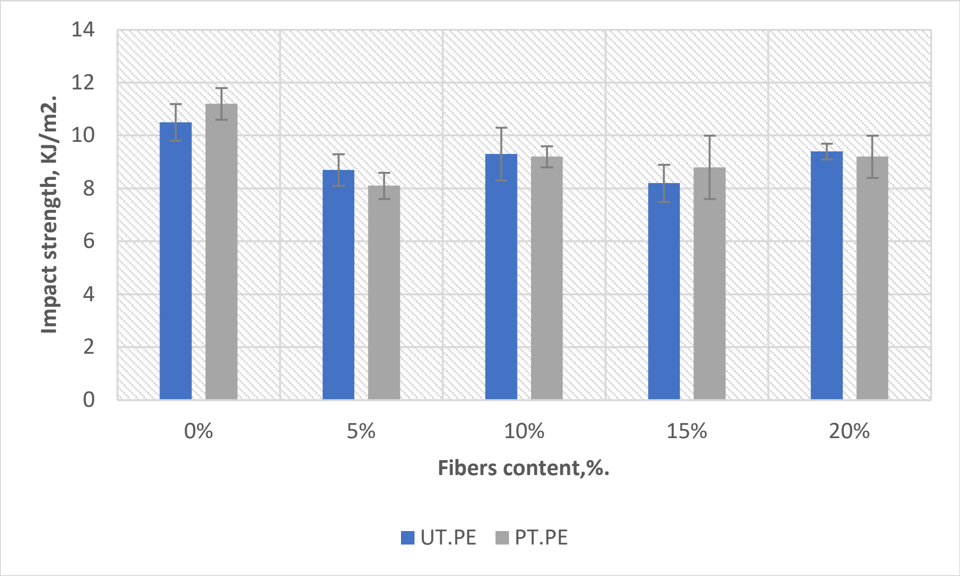

Figure 56:Impact strength of glass fiber composites prepared using untreated and treated powder with different content of glass fibers.

The results of mechanical testing indicated that there was no practical difference between composites prepared with untreated and treated powder in most cases. SEM images of the fracture surface of composite prepared with untreated and treated powder are presented in Figure 57; there was no improvement in the adhesion between the matrix and the fibers.

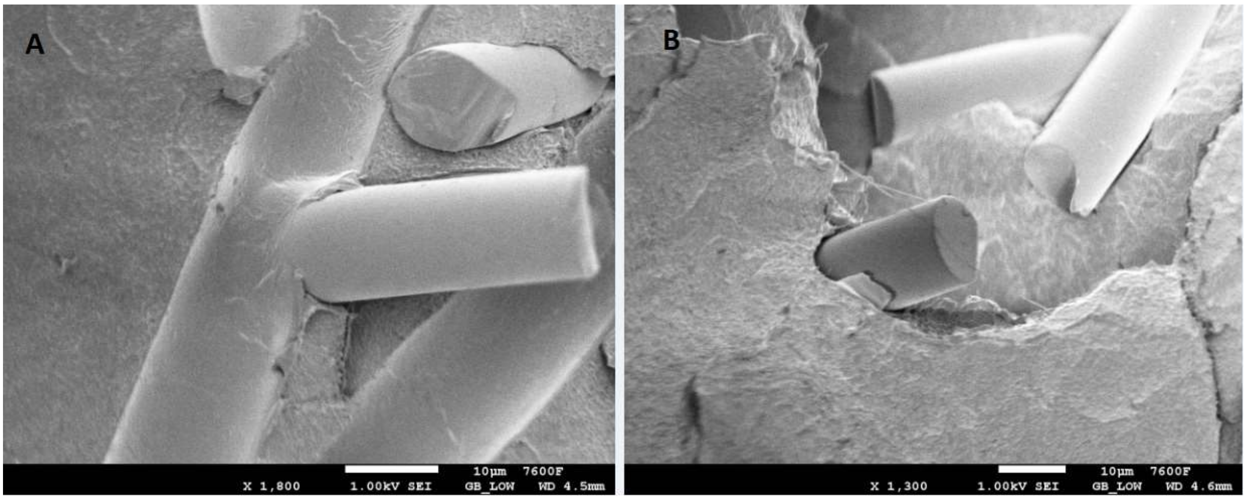

Figure 57:SEM images of composites fracture surface: a) Composites with untreated PE , b)Composites with plasma treated PE.

The reason for the bad adhesion even after plasma treatments could be many reasons. One of the reasons could be the short treatment time. Zuzana et al. [74], investigated the effect of different plasma treatment times of the same dowlex powder on their joint strength to glass rods, the lowest treatment time they tested is 30 seconds, practically this treatment time is equal to the treatment time of the powder we used to carry out our preliminary experiments (9 min treatment of 15 kg of powder in the LA650 machine is equal to 30 second treatment of 250 g of powder in the L400 machine, a larger amount of powder requires longer treatment time), Zuzana’s results showed that for a short treatment time less than 3 min, the sintering behavior of treated and untreated powder was identical, all samples failed at the rod-polymer interface, a completely clean surface without trace of plastic residue was observed in all samples prepared using powder treated for short time, while plastic residue was noticed on the surface of glass rods when powder with longer treatment time were used (from 3 to 20 min), the surface of glass rods at short and long treatment time are shown in Figure 58.

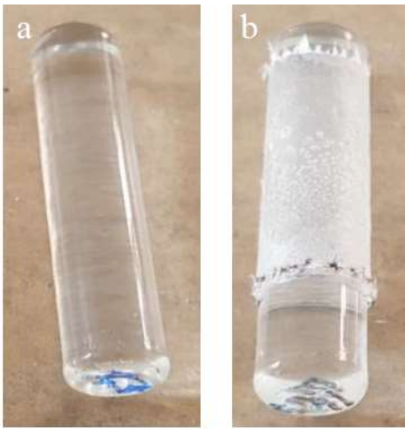

Figure 58*:* Glass substrates after strength test: a) powder treated for less than 3 min ,b) powder treated for more than 3 min [74].

However, in the mentioned study the strength of the joint to glass rods of samples prepared with treated powder increased compared to the strength of the joint prepared with untreated powder even at the lowest treatment time, and this was not the case in our experiments, and this could be the result of the difference in sintering behavior in both cases, in the mentioned study the powder was sintered on the large surface of the glass rod in an oven , while in rotational molding we are trying to sinter a big particle of powder on the surface of short fibers with very small diameter comparing with the particle diameter which could make the wetting of the fiber by the powder hard in the absence of additional pressure. We think that to have a good wetting of the fiber by the powder, the fibers should at least have three contact points with three powder particles. To calculate the minimum fiber dimeter that is needed to fulfill this condition, we assumed three identical spherical particles with the same diameter 280 µm (equal to the average diameter of our powder) are in contact together as it is shown in Figure 59, and we also assumed an ideal situation where the fiber will be located exactly in the center of the free space between three particles and has one contact point with each powder particle; a simple equation was used to calculate the needed fiber diameter as follows:

$$\cos 3 = \frac{\sqrt{3}}{2} = \frac{R}{R+r} \quad \Longrightarrow \quad r = \frac{(2-\sqrt{3})}{\sqrt{3}} R \qquad \text{Equation 6}$$

From this equation, the diameter needed to have at least three contact points with the powder is calculated, and it is 43,3 µm, while the real diameter of the fibers used in the experiments is 17 µm.

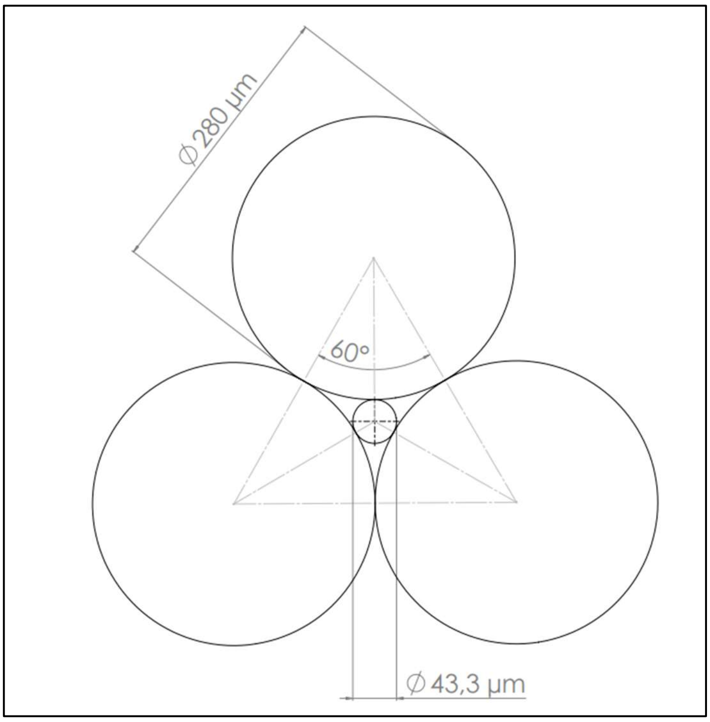

Figure 59: The contact between PE particles and one glass fiber.

The effect of reinforcements size on the mechanical properties of composites prepared using rotational molding was reported in other studies. W. Yan et al. [93], reported that in particulate reinforced rotationally molded polyethylene composites, particle size played an important role in the composite's property when polyethylene powder and glass particles were dry mixed together and used to prepare the composites via rotational molding, better distribution was achieved when the largest particle size (90–240 µm) was used . Another study also indicated the importance of particle size in preparing composites by rotational molding when dry mixing is used to mix the filler with the matrix, the study reported that it was not possible to prepare a proper composite by rotational molding when buckwheat husk filler with particle size less than 50 um was used as filler for both polyethylene and PLA [86]. Hanan et al. [83], found that maple with particles size 355-500 µm used with polyethylene to prepare the composite through rotational molding prevents the formation of empty spaces or bubbles in the material between the fibers and the matrix.

In previous study conducted by S. Panikkassery Sasidharan et al. [104], the same plasma treated polyethylene was used with coir fibers that had an average diameter of 100 µm to prepare composites via rotational molding, and the treatment successfully improved the adhesion between the fiber and the matrix which can be clearly noticed in Figure 60.

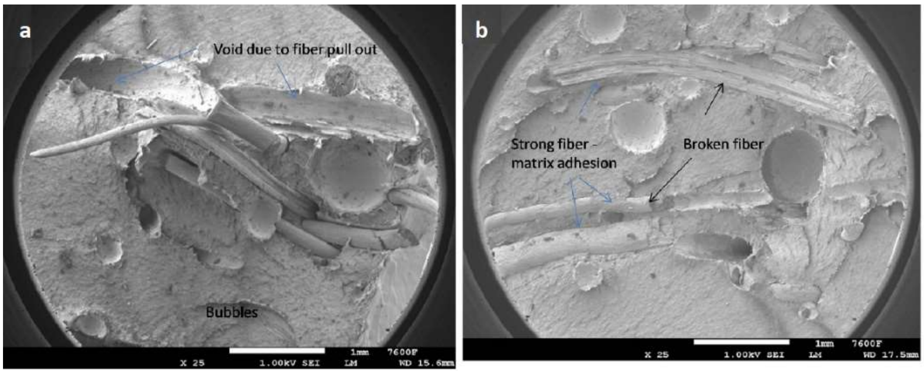

Figure 60: SEM images of coir fibers composites fracture surface: a) Composites with untreated powder ,b) composites with plasma treated powder [104].

The same plasma-treated powder and glass fibers were also used by Vojtech et al. [102], to prepare composites in small mold in the oven, no pressure was added to the process, which makes its sintering conditions similar to rotational molding conditions, the results demonstrated that composites prepared using smaller powder size up to 100 µm had the best mechanical properties and showed very good adhesion to glass fibers, as it can be noticed in Figure 61. These results proved the importance of the convergence between the powder particles size and the diameter of the fibers to achieve good adhesion.

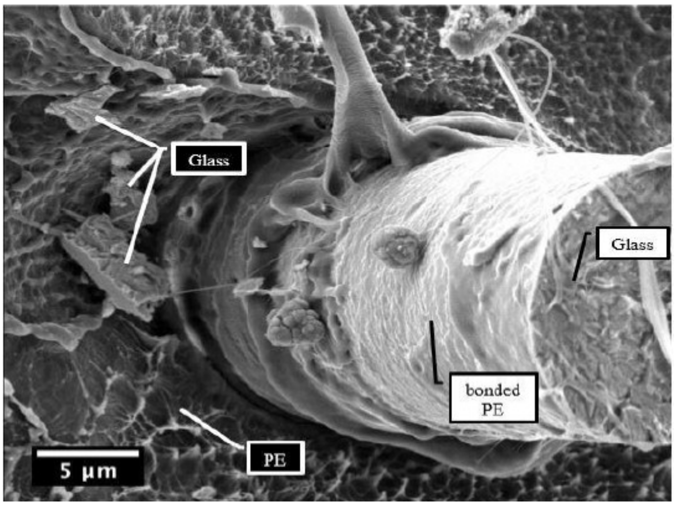

Figure 61: SEM images shows the adhesion between glass fiber and plasma treated PE in composites prepared using pressure-less technique [102].

4.3.2 Effect of different factors on mechanical properties of glass fibers composites prepared by rotational molding

4.3.2.1 Effect of treatment time :

The tensile strength of the composites prepared using powder treated for different times is presented in Figure 62, The tensile strength of the composites prepared using untreated powder maintained almost the same values as the net polyethylene samples. Increasing the plasma treatment time of the powder slightly increased the tensile strength. Composites prepared using 10-min treated powder had a tensile strength 7% higher than the tensile strength of pure polyethylene and 9% higher than composites prepared using untreated powder [105].

The reason that significant improvement in the tensile strength was not achieved as a result of different treatment times could be that at short treatment times (1 and 3 min) the treatment was not yet sufficient to improve the adhesion between the fiber and the matrix, while at long treatment times (5 and 10 min) the reason could be an increased number of bubbles on the outer surface of the samples and uneven inner surface indicating agglomeration of the fiber.

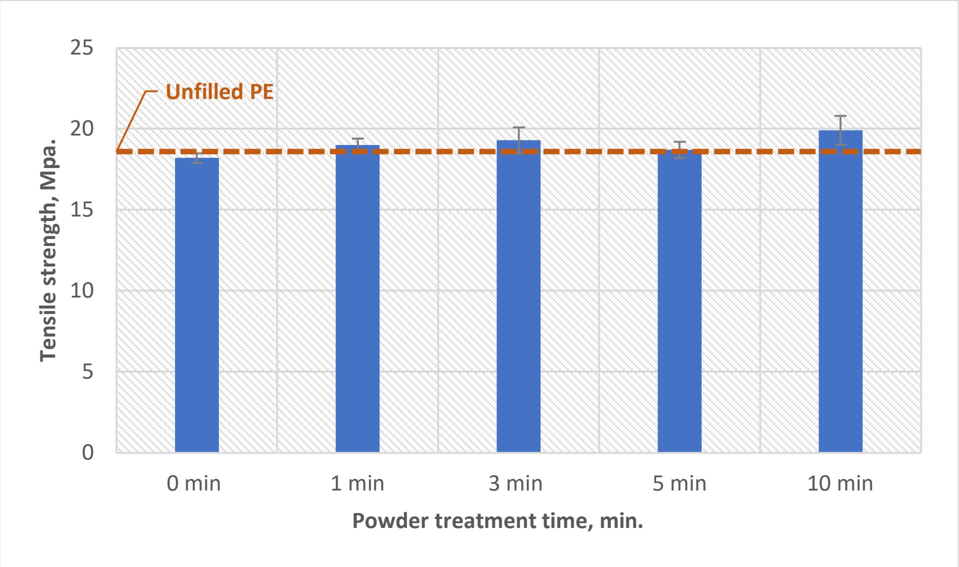

Figure 62: The effect of PE powder treatment time on the tensile strength of the composites produced using treated powder and 10 wt.% untreated glass fibers [105].

The tensile modulus of the composites is presented in Figure 63. All composites showed higher modulus than pure polyethylene, the tensile modulus of the composites increased from 272.2 MPa for composites prepared with untreated powder to 343.8 MPa for composites prepared using 3-min treated powder. The reason for this increase is the presence of rigid fibers in the matrix. However, the modulus decreased when using 5-min and 10-min treated powder; this decrease resulted from the higher bubble content in the composites and uneven inner surface [105].

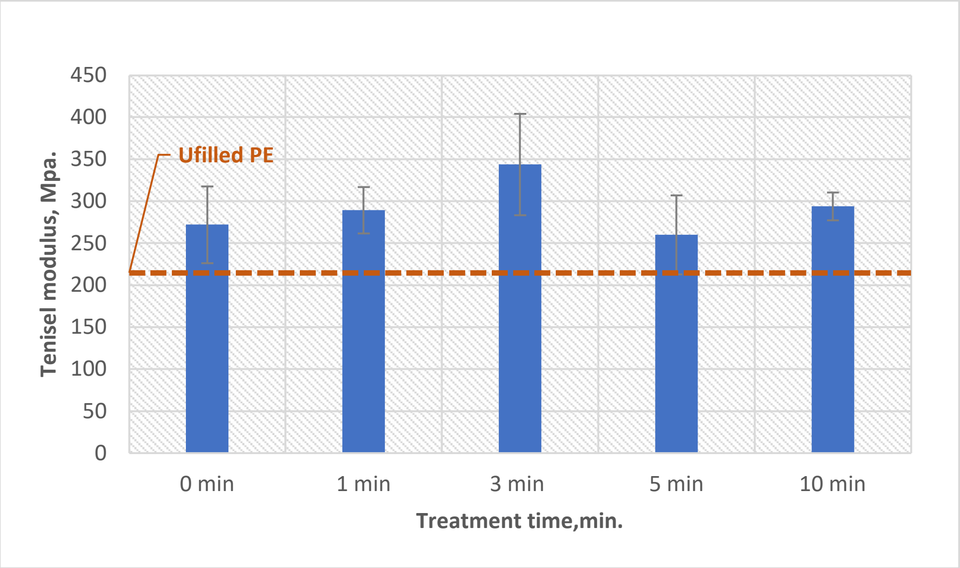

Figure 63: The effect of the PE powder treatment time on the tensile modulus of the composites produced using treated powder and 10 wt.% untreated glass fibers [105].

The flexural modulus presented in Figure 64, showed a similar trend to the tensile modulus. The composites showed a higher modulus than the net polyethylene in all cases, and the highest modulus was reached when 1-min treated powder was used to prepare the composites which was 47% higher compared to the modulus of net polyethylene. Also similar to the tensile modulus a slight decline can be noticed in the modulus when using longer time treated powder, but this decline appeared earlier in the case of flexural modulus where 10% decrease in the modulus can be noticed when using 3-min treated powder compared to composites prepared using 1-min treated powder. However, composites modulus was still higher than the modulus of net polyethylene, in all cases [105].

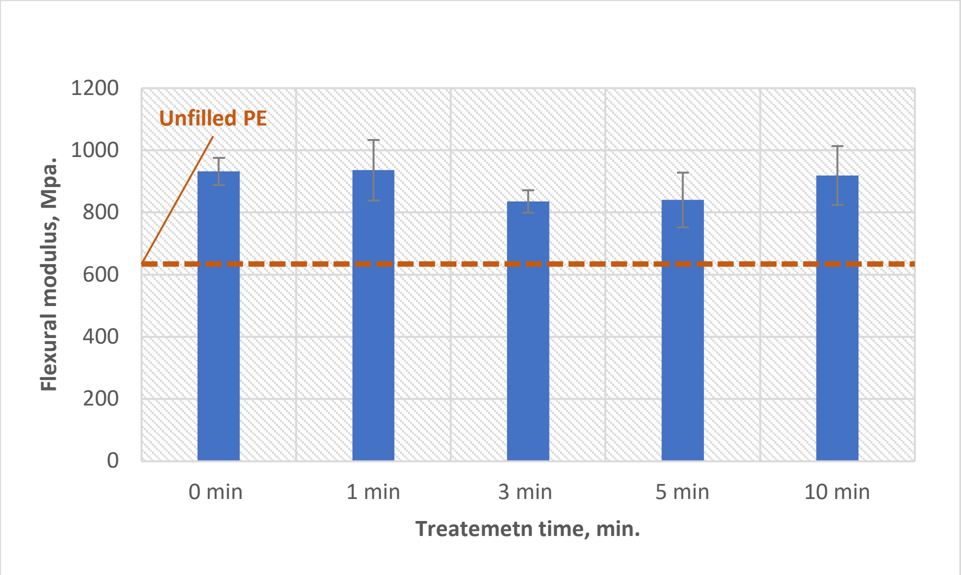

Figure 64: The effect of the PE powder treatment time on the flexural modulus of the composites produced using treated powder and 10 wt.% untreated glass fibers [105].

W. Chang et al. [90] and Höfler et al. [91], also reported the improvement of both tensile and flexural modulus of the samples prepared via rotational molding as a result of incorporation of different types of glass fibers to the polyethylene compared to unfilled samples. S. Panikkassery Sasidharan et al. [104], reported the improvement of tensile modulus of coir fibers/plasma treated polyethylene composites prepared via rotational molding comparing with unfilled samples and with composites prepared using untreated powder. Improvements in tensile modulus and flexural modulus of other natural fiber composites prepared by rotational molding compared to unfilled samples were also reported in other studies [81],[84],[87] .

The impact strength of the composites is presented in Figure 65 [105], all composites showed lower impact strength than those of unfilled samples; this is a result of the presence of hard phase in the mixture. Increasing the treatment time also contributed to a further reduction of impact strength, which as mentioned previously, is a result of a higher number of bubbles on the surface of composites prepared using powder treated for more than 1 min. The highest reduction in impact strength was observed for composites prepared using 5-min treated powder where the reduction reached 21% compared to unfilled samples, while a recovery can be observed when a 10 min powder was used. However, the impact strength of the composites was still less than this of net polyethylene. Similar reductions in impact strength were observed in references as a result of the use of short glass fibers as reinforcement in rotational molding [90], [91]. Contrary to glass fiber, some of the natural fibers composites have been shown to be more effective in improving the impact strength of the composites prepared by rotational molding [87],[104], this could be because longer fibers are more effective in mechanical energy dissipation as a result of a longer fiber pullout distance and possible fiber–fiber interaction (entanglements) as long as no fiber breakup occurs [104]. Also contrary to glass fibers Sumesh. K. R. et al. [106], reported an improvement in impact strength of rotomolded composites prepared from plasma treated polyethylene with recycled carbon fibers comparing with net polyethylene samples and with composites prepared untreated polyethylene.

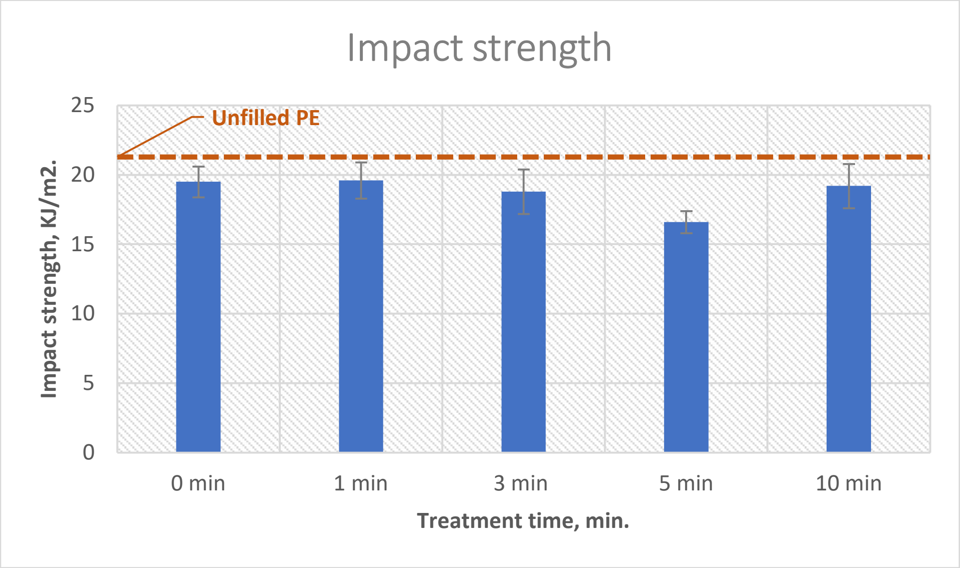

Figure 65: The effect of the PE powder treatment time on the impact strength of the composites produced using treated powder and 10 wt.% untreated glass fibers [105].

OM images of the outer surface of samples prepared using different treated powders are presented in Figure 66, an increase in the bubble's numbers can be noticed with increasing treatment time.

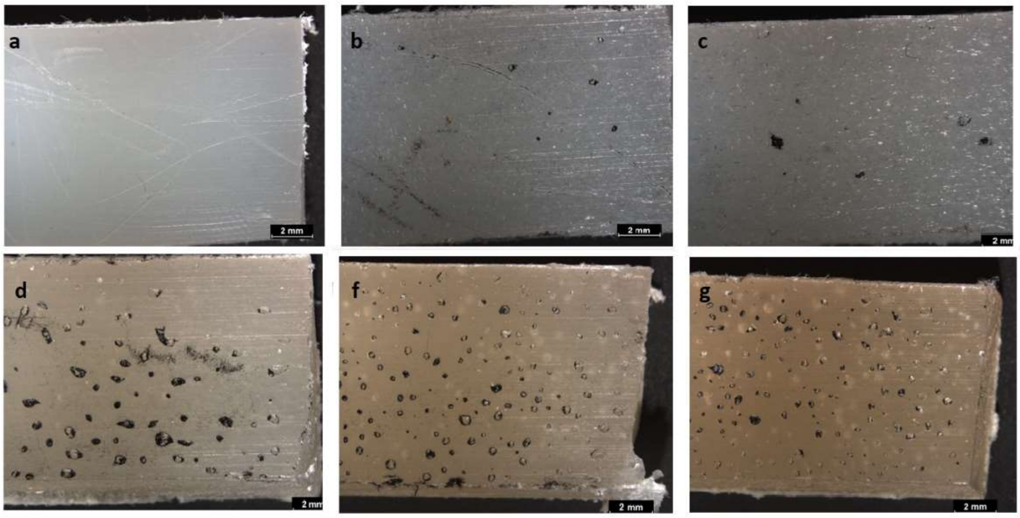

Figure 66: Optical microscope images of the samples' outer surfaces: a) unfilled PE, b) composites prepared using untreated powder, c) Composites prepared with 1 min treated powder, d) composites prepared using 3 min treated powder, f) composites prepared using 5 min treated powder, g) composites prepared using 10 min treated powder [105].

This behavior can be explained by the fact that the powder treated for longer time needs longer sintering time to achieve proper even layer [74]. In this step of the experiment the holding time at maximum oven temperature (250 °C) was only 5 min, and this could not be enough for proper sintering of the mixture of glass fiber and powder treated for a longer time.

4.3.2.2 Effect of oven temperature and holding time:

The tensile strength of the composites prepared at different temperatures and different holding time is presented in Figure 67 [105].

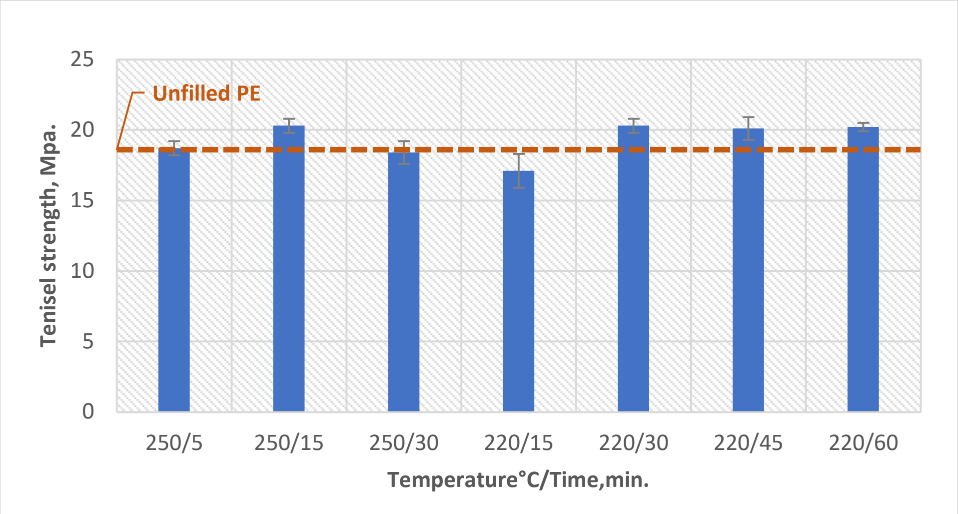

Figure 67: The effect of oven temperature and holding time on the tensile strength of the composites prepared using 5-min treated powder and 10 wt.% untreated fibers [105].

Preparation of the composites at oven temperature of 250 ° C for 15-min holding time improved the tensile strength by 9% compared with composites prepared at oven temperature of 250 ° C and PIAT 220 ° C (holding time in this case was only 5 min). However, 30-min holding time at 250 °C decreased the tensile strength again to 18.4 MPa and the samples showed degradation signs, this is why longer holding times at this temperature were not tested, instead a lower temperature of 220 ° C was tested for different holding times. Composites prepared at 220 ° C for 15 min had the lowest tensile strength, and visual inspection showed a lot of bubbles on the outer surface and uneven inner surface. Increasing the holding time to 30 min at the same temperature increased the tensile strength to a value similar to that of the composites prepared at a temperature of 250 ° C with a holding time of 15 min. Further increase in holding time did not cause any further improvement in tensile strength. The improvement of tensile strength as a result of longer holding time could be explained by better sintering of the samples. No bubbles were noticed on the outer surface, and the inner surface was smooth and even, which indicates better sintering of the powder and better distribution of the fibers in the matrix.

The effect of different temperature and holding time on the tensile modulus is presented in Figure 68, the highest value of tensile modulus was obtained for the composite prepared at oven temperature 220 ° C for 30 min, it was16% higher compared to our original composites prepared at oven temperature 250 ° C with 5 min holding time, and this resulted from less bubbles and smoother inner surface [105].

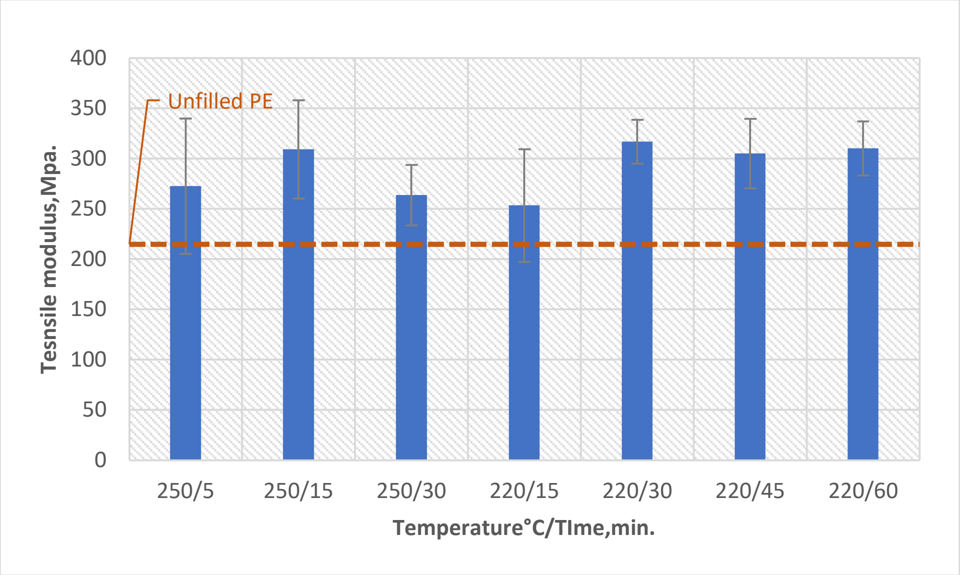

Figure 68: The effect of oven temperature and holding time on the tensile modulus of the composites prepared using 5-min treated powder and 10 wt.% untreated fibers [105].

Similarly, it was found that the flexural modulus of composites prepared at oven temperature 220 ° C for a holding time of 30 min is the best, which is 26% better than composites prepared at oven temperature 250 ° C and holding time 5 min (Figure 69) [105].

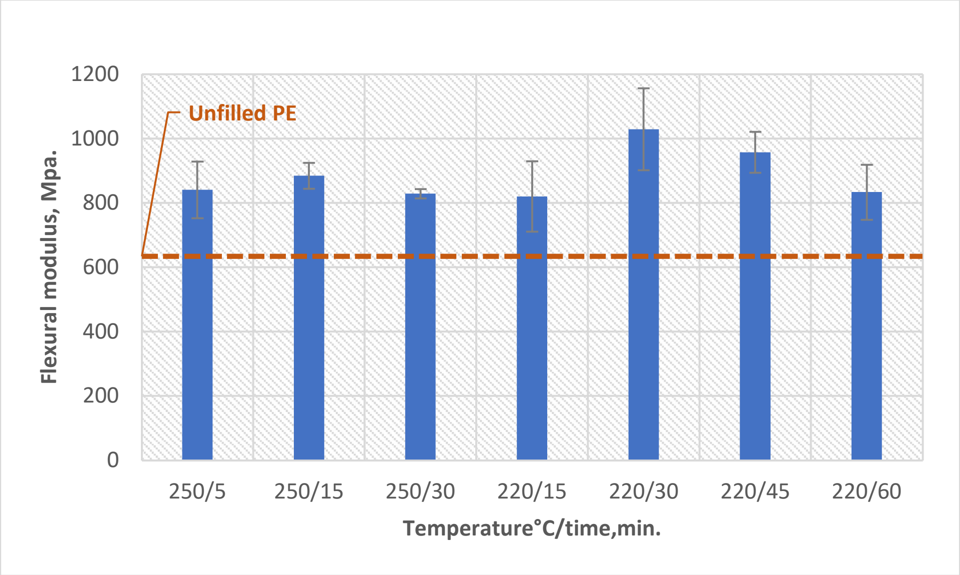

Figure 69: The effect of oven temperature and holding time on the flexural modulus of the composites prepared using 5-min treated powder and 10 wt.% untreated fibers [105].

The effect of different temperature and holding time on the impact strength of the composites is presented in Figure 70, different temperature and longer holding time at the peak temperature of the oven helped to increase the impact strength a little as a result of decreasing of bubbles number, but the impact strength in all cases stayed less than the impact strength of unfilled samples [105].

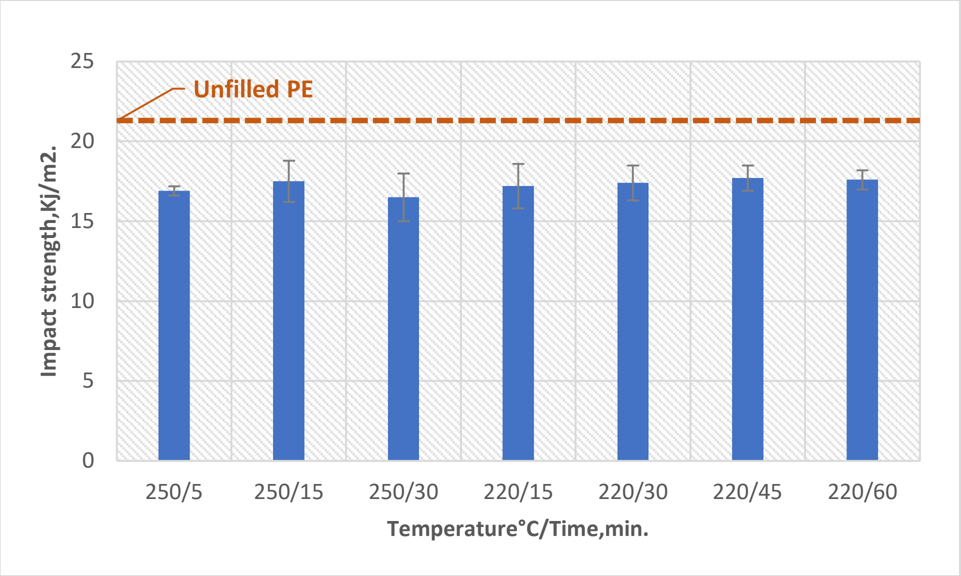

Figure 70: The effect of oven temperature and holding time on the impact strength of the composites prepared using 5-min treated powder and 10 wt.% untreated fibers [105].

Figure 71 shows the optical microscopy images of the outer surface of samples prepared at oven temperature 220 ° C for 30 min, no bubbles can be noticed. This indicates that longer heating time is needed to prepare composites using powder treated for longer time.

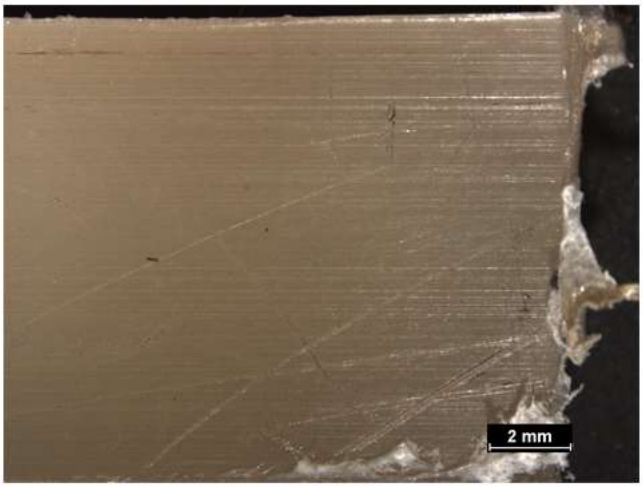

Figure 71:Optical image of the outer surface of samples prepared at oven temperature 220 ° C and 30 min holding time [105].

4.3.2.3 Effect of a mixture of polyethylene waxes:

Untreated and treated polyethylene wax was mixed with polyethylene powder in an attempt to incorporate larger numbers of smaller particles into the powder; it is known that the smaller particles melt before large particles. We assumed that wax particles will melt first and cover the fibers to form a sizing layer on the fibers surface and after that the larger polyethylene particles will melt and merge with the wax layer on the surface of the glass fiber which will improve the adhesion between the fibers and the polyethylene matrix, treated polyethylene for 5 min was used for these experiments, untreated and treated wax was mixed with polyethylene powder at different percentages, all samples were prepared at oven temperature 220 ° C for 30 min holding time. Figure 72 shows the results of the tensile strength tests. Adding 3 wt.% untreated and treated wax to the composites decreased the tensile strength for the composites from 20.2 MPa of composite prepared without wax to 18 MPa for the composites prepared with untreated wax and to 17.4 MPa for composites prepared with treated wax. This could be a result of the low tensile strength of the wax, which affected the tensile strength of the whole composite even at this low percentage. However, a higher wax content did not have a dramatic effect on tensile strength; the reason for this behavior is not clear.

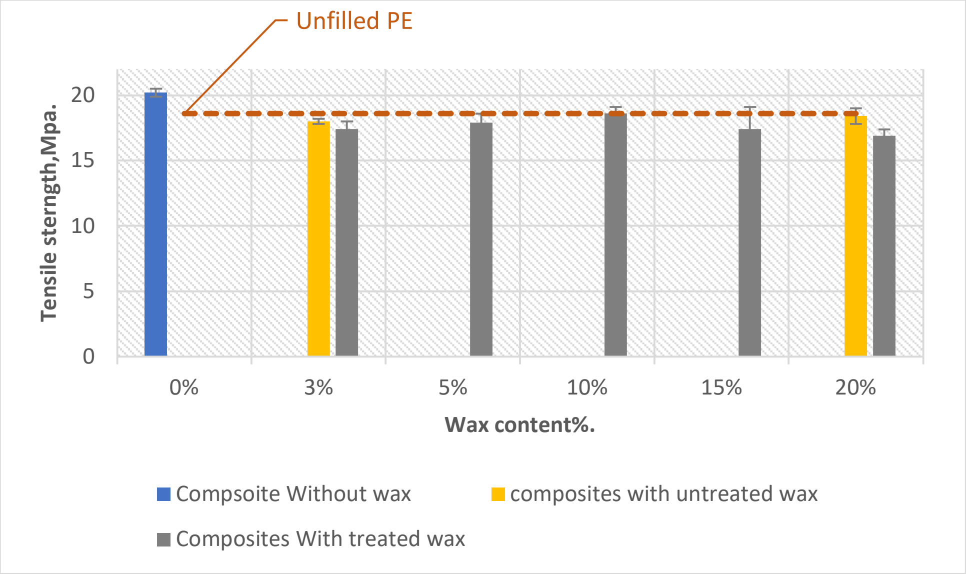

Figure 72: The effect of wax content on the tensile strength of the composites.

The effect of adding different content of untreated wax and plasma treated wax on the tensile modulus of composites is presented in Figure 73, tensile modulus of composites prepared with 20 wt.% untreated wax decreased by 15% .In the case of treated wax, adding 3 wt.% decreased the modulus by 10% and no further significant decrease was observed with increasing wax content. However, in all cases the modulus of the composite was still higher than the modulus of net polyethylene.

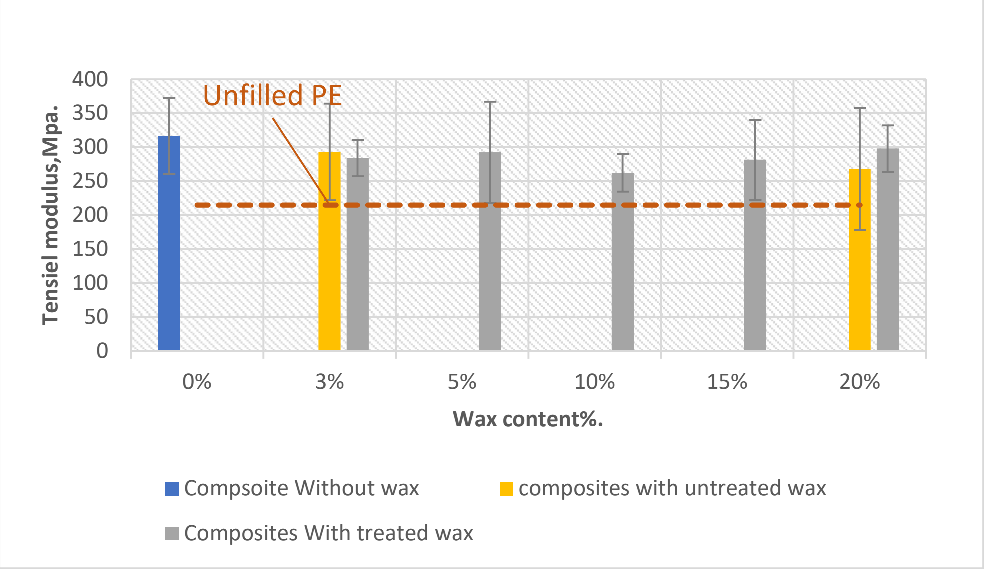

Figure 73: The effect of wax content on the tensile modulus of the composites.

The flexural modulus of wax composites is presented in Figure 74, adding the wax also decreased the flexural modulus of all composites compared to composites prepared without adding wax, the decline in the flexural modulus is bigger than the tensile modulus, at 3 wt.% of wax the modulus decreased by 21% for untreated wax and 16% for treated wax, and the decrease reached 27% and 24% for composites contain 20% of untreated and treated wax respectively.

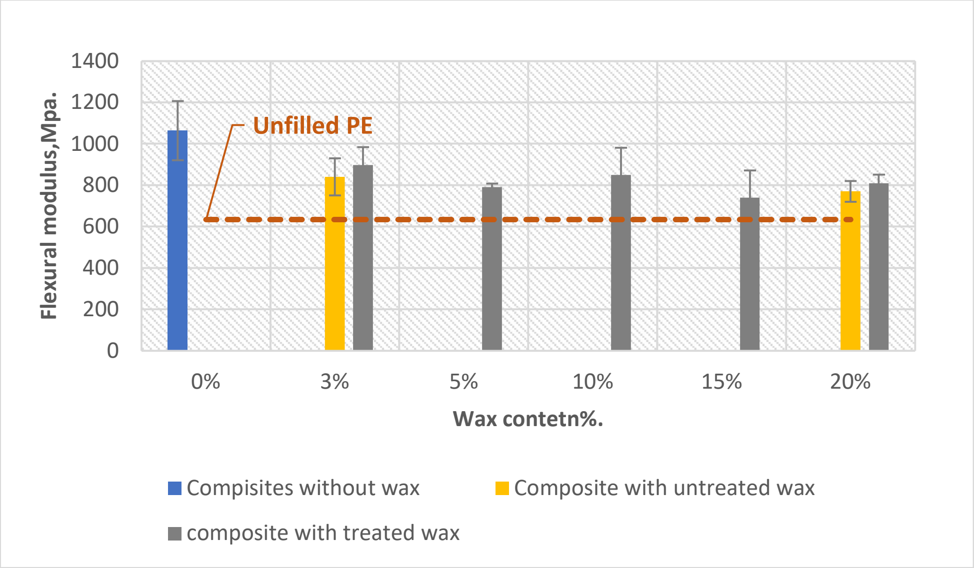

Figure 74: The effect of the wax content on the flexural modulus of the composites.

Figure 75 shows the results of the impact tests of wax composites, the impact strength of the composites dramatically decreased by increasing wax content. Impact strength of the composites contain 3 wt.% of untreated and 3 wt.% of treated wax decreased by 30% and 15% respectively comparing with composites prepared without wax, and by 43% and 31% compared to pure polyethylene samples, the decline continued with adding more wax and reached 46% for composites contain 20 wt.% of both untreated and treated wax comparing with composites without wax and 56% comparing with pure polyethylene samples. This dramatic decrease is a result of the brittle nature of wax.

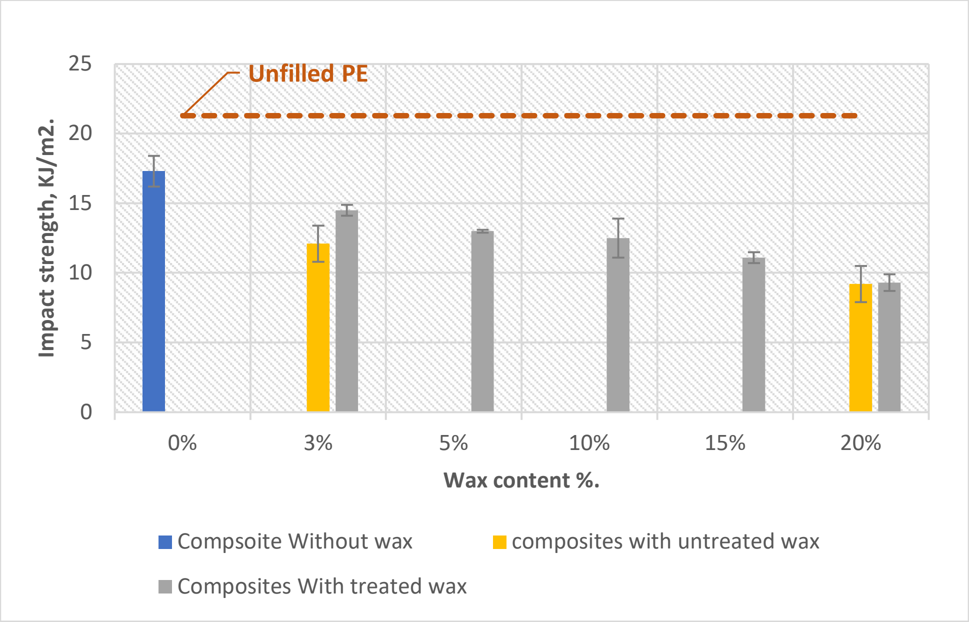

Figure 75:The effect of wax contains on the impact strength of the composites.

4.3.2.4 Effect of plasma treatment of glass fibers

The tensile strength of the composites prepared using treated and untreated glass fibers is presented in Figure76 [105]. Tensile strength of composites prepared using a mixture of untreated powder with plasma treated fibers had almost the same tensile strength as the composites prepared using untreated powder and untreated fibers. On the other hand, composites prepared using mixture of treated powder and treated fibers had higher tensile strength values compared with composites prepared using untreated fibers. Using both treated powder and treated fibers increased the tensile strength to 21.8 MPa for composites prepared using 10-min treated powder and 40-min treated fibers, which is 17% higher than un-filled PE and 15% higher than composites prepared using untreated powder and untreated fibers. The reason for this increase could be that the treatment of glass fibers added oxygen groups to the fiber surfaces and increased their surface energy with respect to the surface energy of the powder, increasing their wettability, and hence the adhesion between the matrix and the fibers. As is well known, for optimal wetting of any substrate by a liquid, the surface energy of the liquid should be higher than the surface energy of the substrate. Plasma treatment of polyethylene powder increases not only the concentration of the active groups on the powder surface but also the surface energy of the powder to values which could become close or even higher to the glass fibers surface energy, which could decrease the wettability. Therefore, treatment of the fibers was necessary to ensure that their surface energy was higher in relation to the powder surface energy. A. Haji et al. [59], reported improvement of the tensile strength of epoxy/glass fibers composites as a result of the plasma treatment of the glass fibers when compared with composites prepared from untreated fibers .

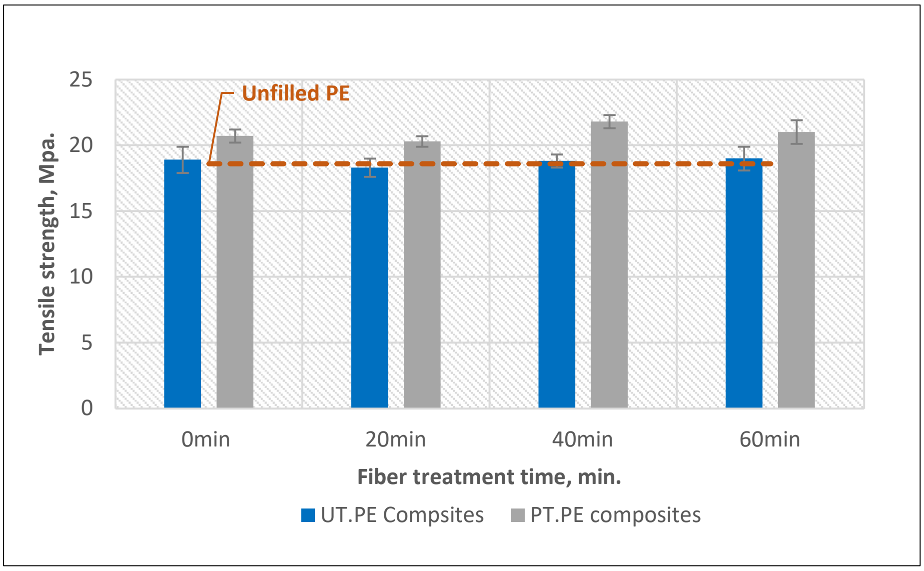

Figure 76: The effect of glass fiber treatment time on the tensile strength of the composites prepared using untreated and 10-min treated PE with 10 wt.% untreated and plasma-treated glass fibers [105].

Plasma treatment of the fibers did not significantly affect the tensile modulus (Figure 77) [105]. Composites prepared using untreated powder with treated glass fibers had almost the same values as composites prepared using untreated powder and untreated glass fibers. A very small decline less than 5% can be observed for composites prepared using untreated powder with 20-min treated fibers. Similarly, a minor decline of all composites prepared using treated powder and fibers was noticed when compared with composites prepared with untreated fibers.

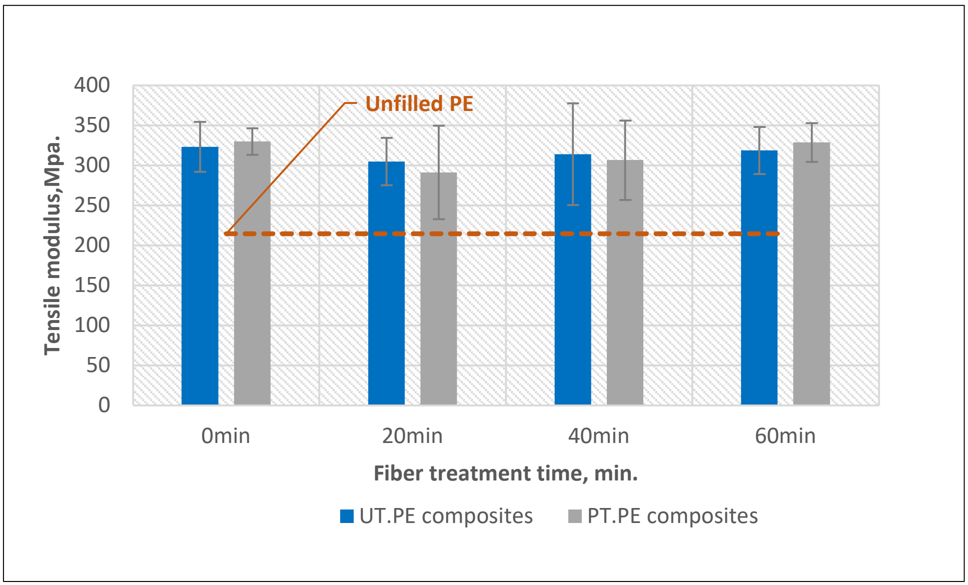

Figure 77: The effect of glass fiber treatment time on the tensile modulus of the composites prepared using untreated and 10-min treated PE with 10 wt.% untreated and plasma-treated glass fibers [105].

Figure 78 presents the flexural modulus of composites prepared using treated glass fibers. The flexural modulus of composites prepared using untreated powder and 20-min treated fibers improved by around 10% compared to composites prepared by untreated powder with untreated fibers; no further improvement was observed as a result of using treated glass fibers treated for 40 and 60 min. The composites prepared with treated powder and treated fibers maintained almost the same values as the composites prepared using untreated components, regardless of the fiber's treatment time [105].

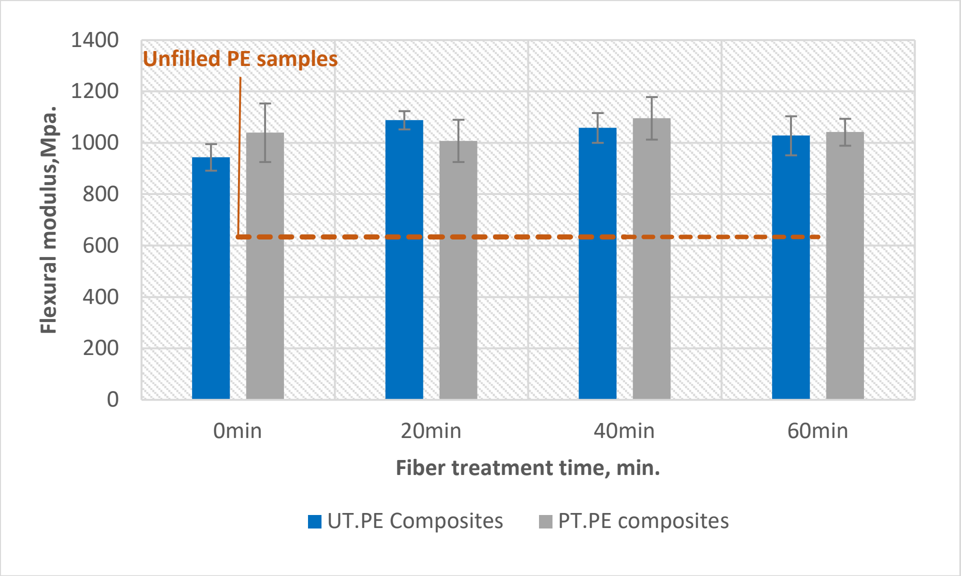

Figure 78: The effect of glass fiber treatment time on the flexural modulus of the composites prepared using untreated and 10 min treated PE with 10 wt.% of untreated and plasma-treated glass fibers [105].

Figure 79 presents the effect of plasma treatment of glass fibers on the impact strength of composites. Composites with treated powder and treated fibers maintained the same impact strength compared to those of untreated components. Similar behavior was also noticed for composites prepared with both treated powder and glass fibers; the only exception was minor decline by 7 % was noticed for composites contained 20 min treated fibers. Fibers treatment did not help to increase the impact strength to values higher than net polyethylene values [105].

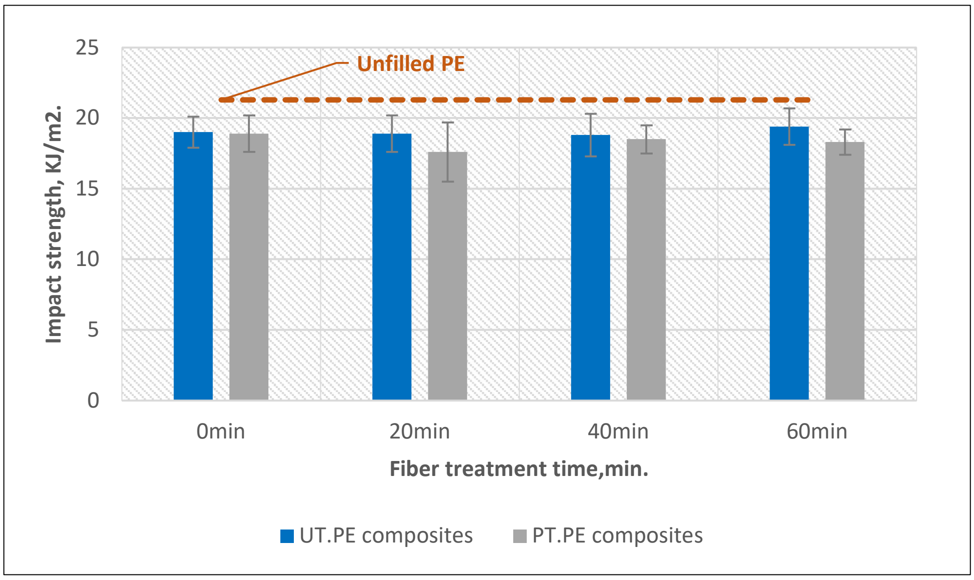

Figure 79: The effect of glass fiber treatment time on the impact strength of the composites prepared using untreated and 10-min treated PE with 10 wt.% of untreated and plasma-treated glass fibers [105].

4.3.2.5 Effect of fibers content:

The effect of fibers content on the tensile strength of the composite is presented in Figure 80. The composites were prepared using 10-min treated powder and 40-min treated glass fibers at oven temperature 220 °C and 30-min holding time. The tensile strength of composites increased by increasing fiber content up to 20 percent. Tensile strength of composites containing 20 wt.% fibers increased by 20% compared to net polyethylene. This resulted from optimizing the process conditions and using both treated powder and treated glass fibers, which improved the adhesion between the fibers and the matrix [105].

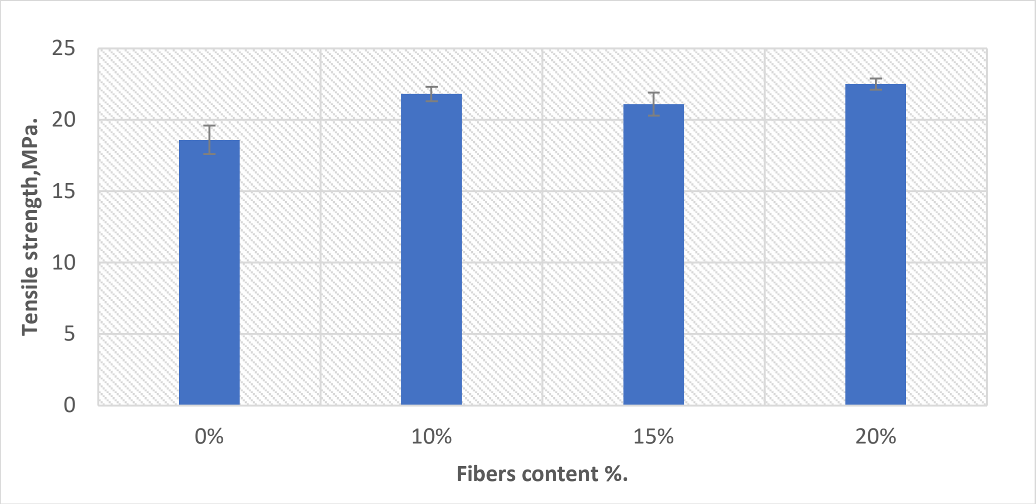

Figure 80: The effect of fiber content on the tensile strength of the composites prepared using 10-min treated powder and 40-min treated fibers [105].

The effect of fiber content on the tensile and flexural modulus of composites prepared using 10 min treated powder and 40 min treated fibers are presented in Figures 81 and 82 respectively. Both moduli increased with the addition of a higher content of fibers, which is the result of the incorporation of a greater number of rigid fibers in the matrix. The tensile modulus increased by 82% for composites containing 20% fibers, while flexural modulus increased by 99% for the same composites compared to unfilled PE samples [105].

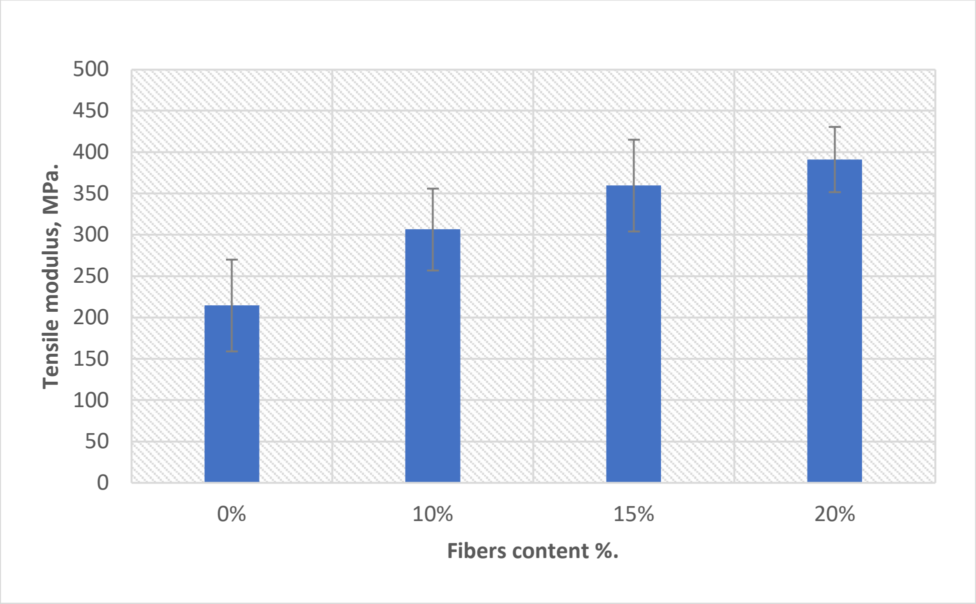

Figure 81: The effect of fiber content on the tensile modulus of the composites prepared using 10-min treated powder and 40-min treated fibers [105].

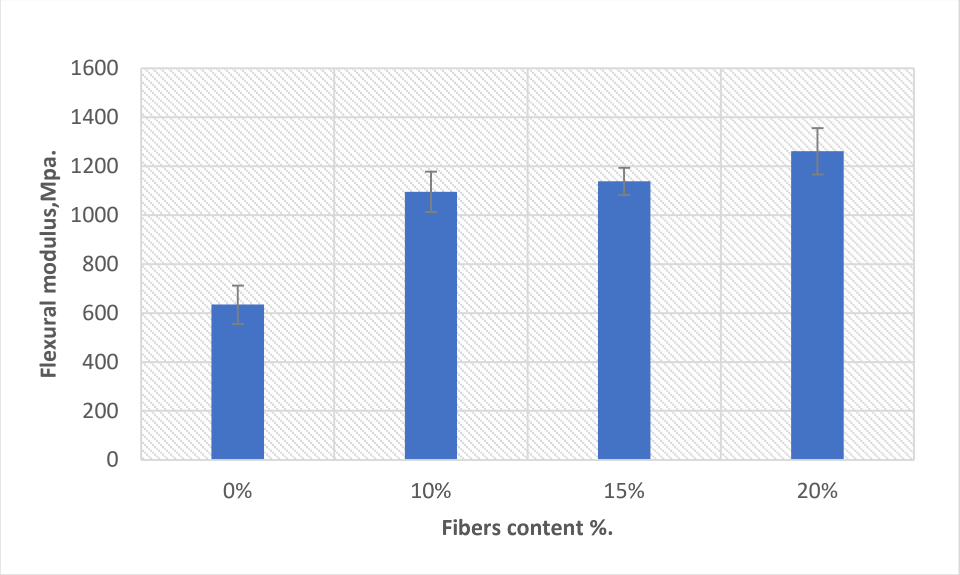

Figure 82: The effect of fiber content on the flexural modulus of the composites prepared using 10-min treated powder and 40-min treated fibers [105].

The results of higher content of glass fibers on the impact strength is presented in Figure 83. As shown, the impact strength kept decreasing with increasing fibers content to reach 38% reduction at 20 wt.% glass fibers content when compared with unfilled samples. This is a result of the presence of bigger number of brittle fibers ,which decreases the ability to absorb and transfer impact energy [105].

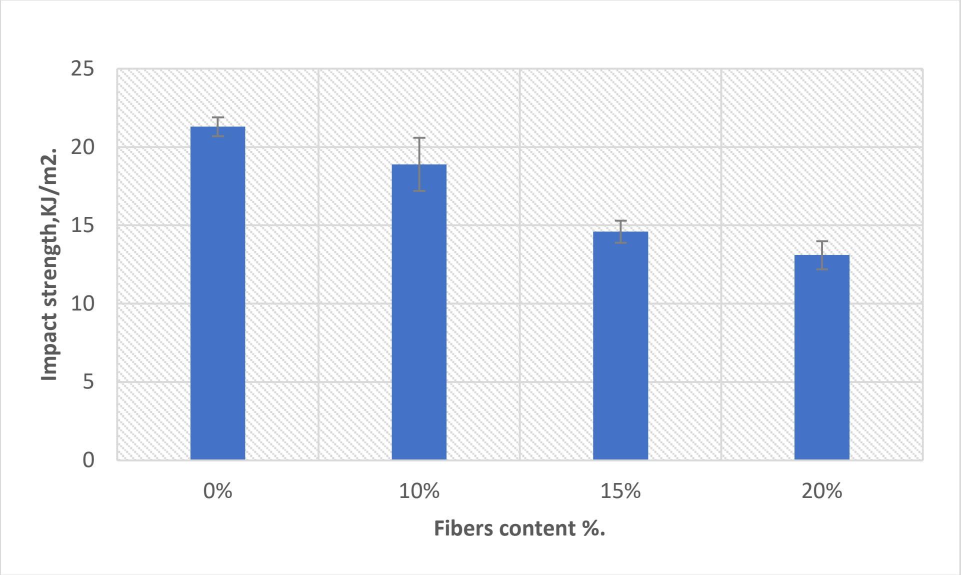

Figure 83: The effect of fiber content on the impact strength of the composites prepared using 10-min treated powder and 40-min treated fibers [105].

4.3.3 The Effect of Plasma Treatment of the Powder and the Fibers on the Stress-Strain Behavior of the Composites

Stress–Strain diagram obtained from the tensile test is presented in Figure 84. The stress–strain diagram of composites prepared from untreated powder and fibers was identical to that of the unfilled samples diagram, while treatment of the powder for 10 min changed the behavior of the composites. As it can be noticed, the composites prepared using the treated powder endured higher stress and showed less deformation under the stress compared to unfilled samples and to the composites prepared with untreated components. This indicated that the plasma treatment was successful in creating adhesion between the powder and the fibers, leading to efficient reinforcement of the polyethylene by the fibers and subsequently better tensile behavior of the composites. Further improvement in the tensile behavior can be noticed as a result of the treatment of the glass fibers and the increase of fiber content to 20% [105].

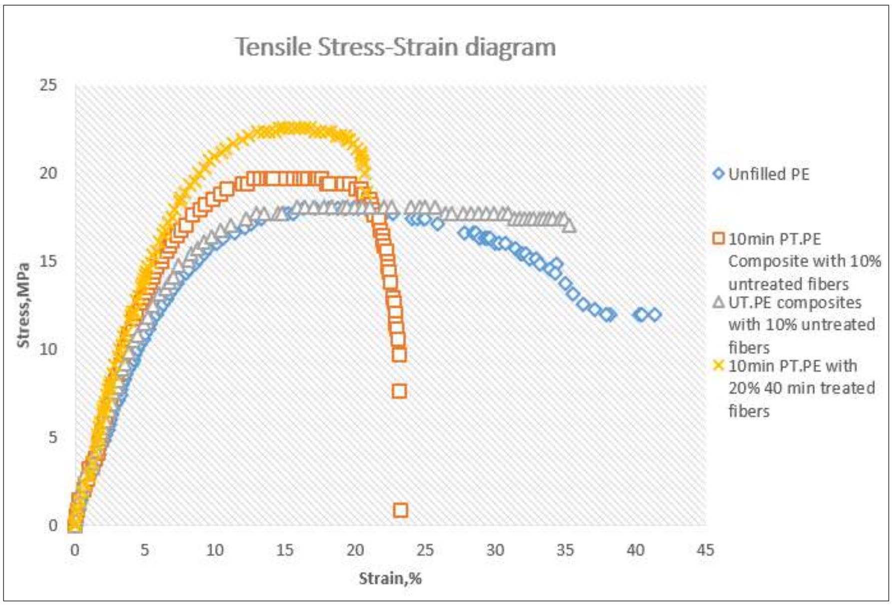

Figure 84: Examples of tensile stress–strain diagrams of different combinations of the rotomolded samples [105].

Figure 85 presents stress–strain diagram of flexural properties. Similar to tensile behavior, incorporation of fibers to the polyethylene changed its bending behavior. The composites tolerated higher stress with less deformation compared to unfilled samples. The plasma treatment and the higher fibers content also had a positive effect on the values of maximum stresses [105].

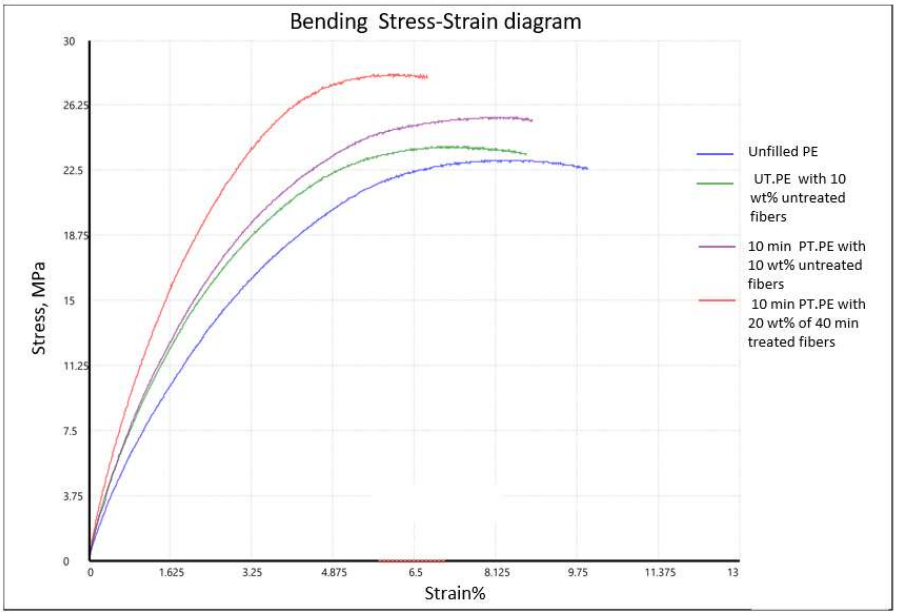

Figure 85: Examples of bending stress–strain diagrams of different combinations of the rotomolded samples [105].

4.3.4 Morphology analysis:

SEM images of fractured surfaces of composites prepared using powder treated for different time are presented in Figure 86. The surface of composites prepared using the untreated power Figure (86,a) shows no adhesion between the fibers and the matrix; a gap between them can be clearly seen. For composites prepared using the 1 min treated powder Figure (86,b), the gap between the matrix and the fibers can still be seen and no trace of polyethylene is shown on the fibers surface. With increasing treatment time to 3 min Figure (86,c) the gap disappeared, and little trace of polyethylene can be seen on the fibers surface. Evidence of better adhesion can be seen in Figure (86 d,e), which presents the fracture surface of samples prepared using 5 min and 10 min treated powders, respectively. The images show that there is no gap between the fibers and the PE matrix, and the amount of polyethylene residue left on the fibers surface after breaking was increased; this indicates good adhesion between the fibers and the matrix. These results are consistent with Zuzana et al [74] results on the adhesion between treated PE and a glass rod.

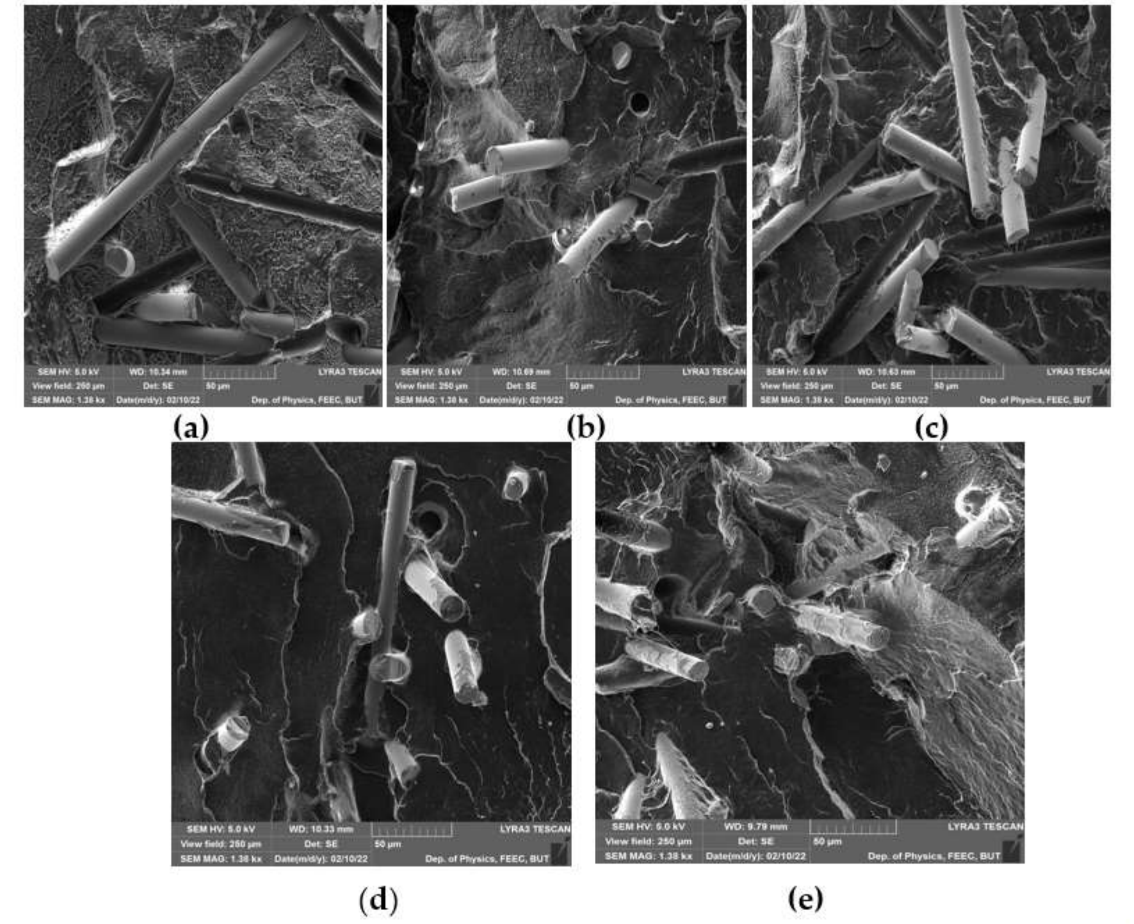

Figure 86: SEM images of fracture surface of composites prepared using untreated and plasma treated polyethylene: a) composites with untreated PE, b) composites with 1 min plasma treated PE, c) composites with 3 min plasma treated PE, d) composites with 5 min plasma treated PE, e) composites with 10 min plasma treated PE [105].

SEM images taken from different locations on the fracture surface of the composite prepared using 10 min treated powder with 40 min treated fibers and presented in Figure 87. The improved adhesion between the powder and the fibers as a result of the use of treated powder together with treated fibers can be clearly seen. Figure (87, c) shows a broken fiber totally covered with polyethylene which indicates very good adhesion between the fiber and the matrix; other broken fibers can be seen in Figure (87 a, b) [105] .

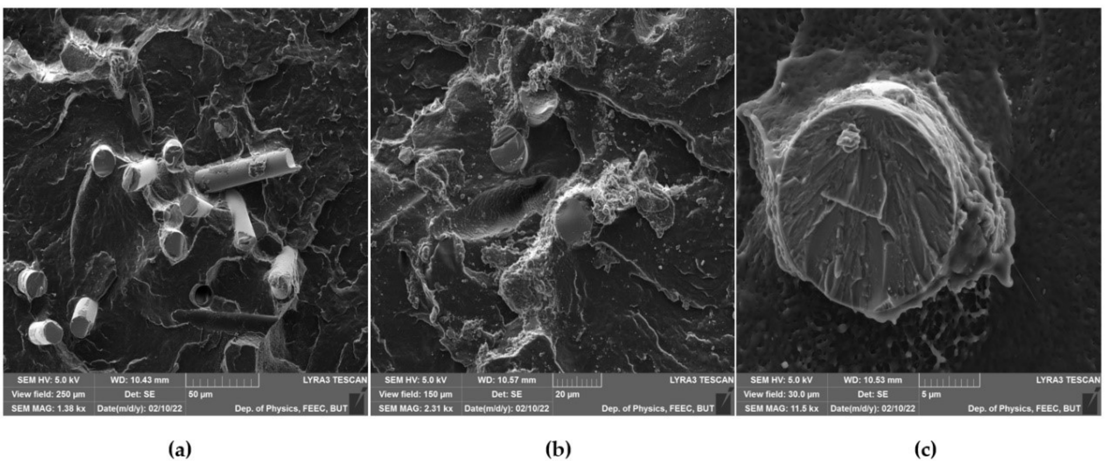

Figure 87: SEM images with different magnification taken from different places of the fracture surface of the composites prepared using 10-min treated powder and 40-min treated fibers: a) SEM Mag: 1.3 Kx, b)SEM Mag:2.31 Kx, C) SEM Mag:11.5 Kx[105].

SEM images with higher magnification of the interface between the fiber and the matrix are presented in Figure 88. Figure (88, a) shows the interface between untreated powder and untreated glass fiber , we can clearly see a gap between the fiber and the matrix due to poor adhesion between two nonpolar surfaces, and the fiber surface is totally clean, no polyethylene is left. Figure(88, b) shows the interface between 10 min plasma treated powder and 40min plasma treated fibers, it is clearly observed that the fiber surface is covered by polymer matrix, which indicates that treatment of both powder and glass fibers is necessary to achieve sufficient adhesion between the fibers and the matrix [105]. A similar good adhesion was not achieved in the literature where short glass fibers were used as reinforcements for composites prepared by rotational molding [90],[91].

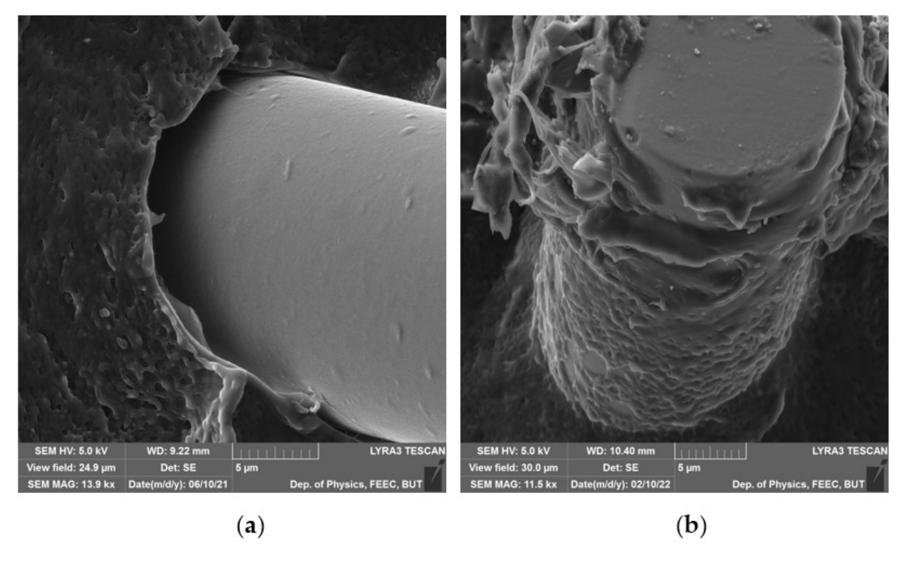

Figure 88: SEM images show the adhesion between PE and glass fibers :a) untreated PE and untreated fiber, b) 10 min plasma treated PE and 40 min plasma treated glass fibers [105].

4.4 Industrial results:

4.4.1 Effect of plasma treatment on the adhesion between the polyethylene and two-component polyurethane.

De-boding test was performed of the specimen that was taken from the industrial samples prepared in France. Industrial samples were prepared in different combination with and without glass fibers and compared to the original company product which is made from pure untreated polyethylene. Mixture of 50% treated powder and 50% untreated powder was chosen to be used for all treated samples.

It was not possible to test the samples prepared from untreated pure polyethylene (original products of the company) because there was no adhesion between the polyethylene and the polyurethane foam, and the separation happened during sample cutting. Images of the specimen are presented in Figure 89 .

Figure 89:Sandwich prepared using untreated powder before testing.

The perfect adhesion between the polyethylene and polyurethane in specimen contained 50% of treated powder can be seen very clear in the Figure 90.

Figure 90:Sandwiches prepared using treated powder before testing.

The results of de-bonding tests of the samples prepared using mixture of untreated polyethylene and treated polyethylene with and without fibers are presented in Figure 91.

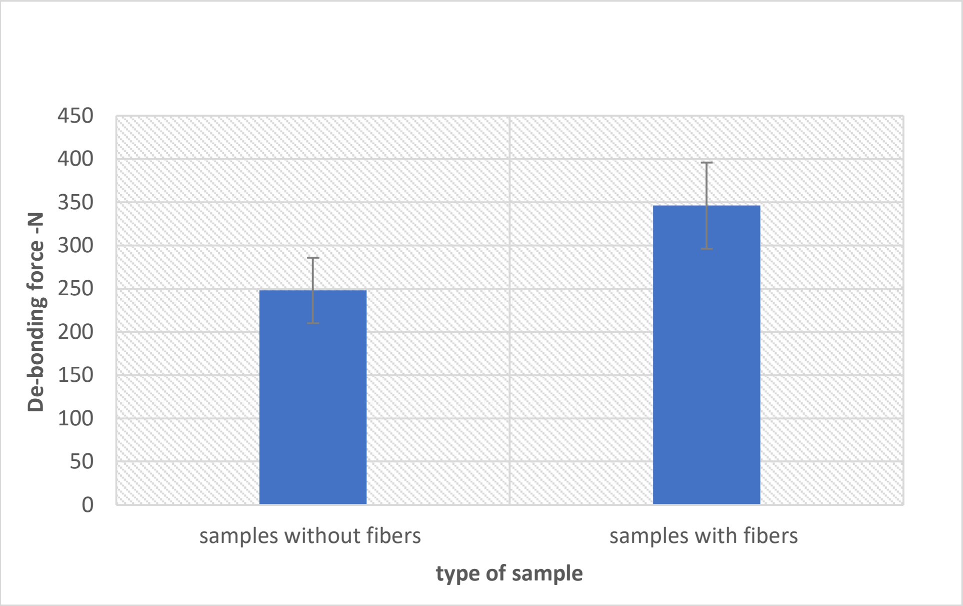

Figure 91: The effect of using glass fiber composites on the de-bonding force.

It can be noticed that the de-bonding force of samples prepared using composites contained 10% of glass fibers, increased by 40% compared to de-bonding force of samples prepared using pure polyethylene mixture. This could be because of the roughness of the inner surface of the composites, which add the mechanical interlocking to the chemical bonding in forming the interface between the polyethylene and polyurethane, and this create stronger adhesion.

Images of the samples after testing are presented in Figure 92. Similar to our samples prepared in the laboratory the tear of the samples happened near to the upper plate which was connected to the moving jaw of the testing machine. The contact surface of the specimen contained glass fibers, which is presented in Figure (92,b) was totally covered by polyethylene residue, which indicated better adhesion with the polyurethane foam compared to samples prepared using unfilled polyethylene figure (92,a).

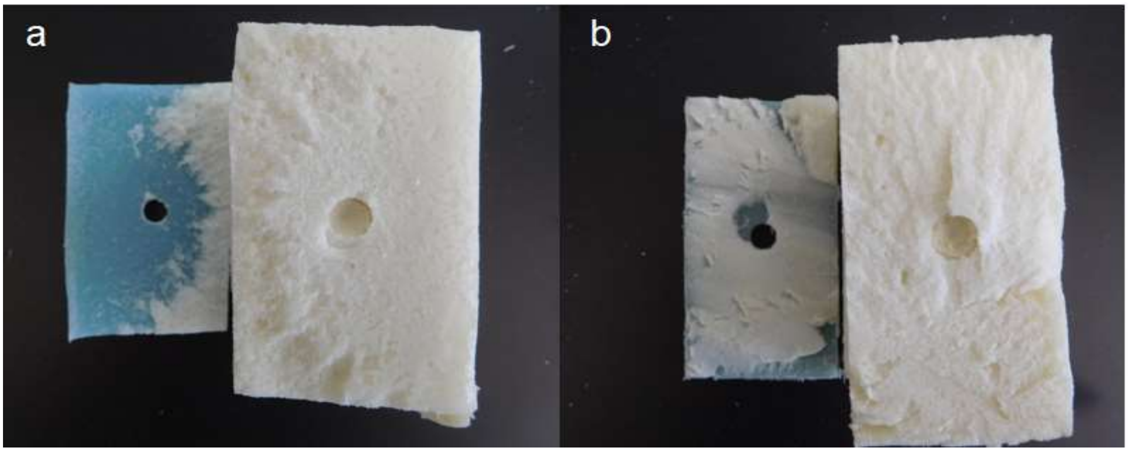

Figure 92:The effect of using glass fiber composites on the PU residue after testing: a) Samples prepared using treated powder without powder, b) Samples prepared using treated powder with 10% glass fibers.

4.4.2 Falling weight test results

Images of specimen after falling weight test are presented in Figure 93. As mentioned before each specimen was hit by the hammer falling from different heights. Figure (93,a) shows the samples prepared using pure polyethylene treated mixture without fibers, and no separation between the polyethylene sheets and the polyurethane can be noticed after the tests, as well no breakage in polyurethane sheets. Composites with different wall thicknesses that containing 10 wt.% of glass Figure (93,b,c,d) showed identical behavior to the behavior of unfilled samples, even at the highest impact energy, which was 136,5 J no separation or breakage can be noticed, and the amount of deformation of all samples independently of wall thickness was almost the same as the unfilled samples, as it can be noticed in Figure 93.

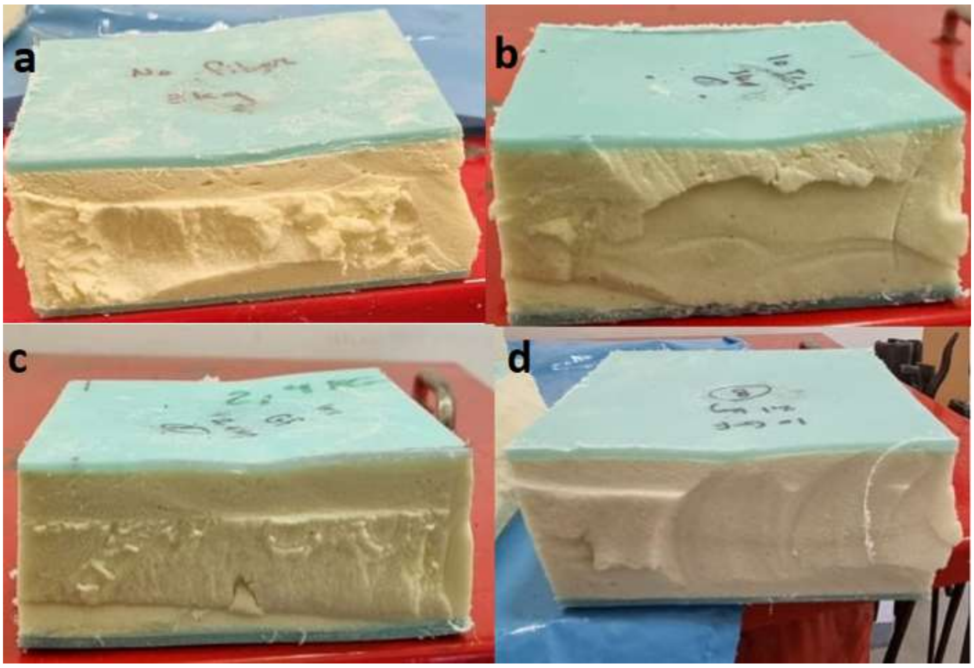

Figure 93: The deformation of the samples after falling weight test: a) Samples prepared using treated powder without fibers with wall thickness 5 mm, b) samples contain 10% of glass fibers with wall thickness 5 mm, c) Samples contain 10 of glass fibers with wall thickness 4 mm, d) Samples contain 10% of glass fibers with wall thickness 3,5 mm.

Another possible application of our glass fiber composites in the industrial field was preparing a kayak from plasma treated polyethylene with 10% of glass fiber. The powder was treated in the industrial pilot plant LA650 for 16 min, and the glass fibers was treated in the laboratory device LA400 for 40 min. It was prepared at Zelezny kayaks & canoes company (Jíloviště, Czech Republic), in Rock and roll rotational molding machine, the kayak was prepared by heating the powder from room temperature to temperature 240 °C and it was held at this temperature for 30 min and then cooled. Using glass fibers, we manage to decrease the weight of the kayak from 21 kg of the original kayak made by the company to 17.4 kg of kayak made from the composites.

Chapter 5.Conclusions and future work

This thesis investigated the possible application of plasma treated polyethylene powder and glass fibers in composites and sandwiches prepared by rotational molding.

To achieve the thesis goals and objectives, scanning electrons microscopy, differential scanning calorimetry and many another testing methods were used to investigate the effect of plasma treatment of the polyethylene on its thermal and surface properties and on the mechanical properties of its samples prepared via rotational molding technique comparing with those of untreated polyethylene prepared in the same technique. De-bonding force and visual inspection of PU residue on PE plates after de-bonding test were used to evaluate the PE/PU sandwiches. PE plates were prepared in two ways, via special mold in the oven and via rotational moldings and contained different percentage of plasma treated powder (treated for different periods). Composites with untreated and treated polyethene and glass fibers, were prepared via rotational molding. The effect of different parameters such as the treatment time of PE powder and glass fibers, the process temperature and time, and the fibers content on the properties of glass fibers composites prepared via rotational molding , the adhesion between the fibers and the matrix was also investigated and evaluated. Finally, treated polyethylene and treated glass fibers composites were used to produce sandwiches in industrial level and the resulted sandwiches were tested and compared to the original industrial product.

5.1 Answering the thesis questions and meeting the thesis objectives:

- **To optimize the rotational molding process of plasma treated polyethylene samples.**

Investigations proved that the treatment of polyethylene powder with plasma does not affect its melting temperature, crystallinity, or the shape of its particles. The PIAT temperature range from 200 ° C to 240 ° C proved to be suitable for preparing the untreated and treated samples as no remaining bubbles were found in the samples and no sign of degradation. The treatment did not have a significant effect on the mechanical properties of the samples. However, the process significantly improved the wettability of the powder and the grafted O groups on the surface of the powder, indicating the improvement of its adhesion ability to other materials.

- **To determine the effect of using plasma treated polyethylene on the adhesion between the Polyethylene and polyurethane foam in sandwiches structures.**

The plasma treatment of polyethylene powder significantly improved the adhesion between polyethylene plates contain different percentage of treated powder and polyurethane foam in PE/PU sandwiches. The best adhesion between PE and PU of sandwiches prepared using oven PE plates was reached when plates contain 25% of 3 min were used. De-Bonding force of this sandwiches improved by 886% compared to sandwiches prepared using untreated PE plates. While the best adhesion in the sandwiches prepared using rotomolded PE plates was reached when plates contain 50% of 1 min treated powder were used. De-bonding force of this sandwiches improved by 220% comparing with sandwiches prepared using untreated PE plates.

- **To determine the effect of using plasma treated polyethylene and glass fibers on the mechanical properties of the composites prepared via rotational molding and on the adhesion between the fibers and the matrix.**

The plasma treatment of both polyethylene powder and glass fibers significantly improved the adhesion between the matrix and the fibers. The optimal composites were produced at oven temperature 220 ° C for 30 min holding time, using a mixture of 10 min treated powder and 40 min treated fibers. They showed very good adhesion between the matrix and the fibers. Tensile strength, tensile modulus, and flexural modulus of these composites were improved by 20%,82% and 98% respectively compared to pure polyethylene samples. However, impact strength was reduced by 38% compared to unfilled samples.

- **To demonstrate the possibility of the application of the developed materials in the selected industrial applications.**

Our material was applied in insulation containers produced by Olivo cold logistics, which is usually produced via rotational molding using untreated polyethylene and filled by polyurethane foam. Replacing untreated polyethylene with a 50/50 untreated/ treated polyethylene mixture successfully created adhesion between the polyethylene and polyurethane which did not exist in the original products, adding 10 wt.% of glass fiber to the mixture contribute to further improvement in the adhesion, where de-bonding force in case of the composites was improved by 40% comparing with the pure untreated/treated polyethylene mixture without fibers. Additionally, the deformation behavior of the products prepared using composites with different wall thickness under a falling weight was identical to the deformation behavior of the samples with standard wall thickness prepared without fibers. The wall thickness and the weight of the products were reduced by 20% and 30% without affecting their ability to absorb shocks.

Preparing a real kayak using glass fiber composites consists of plasma treated component helped to reduce its wait by 17% comparing with similar kayak prepared by pure polyethylene.

5.2 Summary:

Plasma treatment of polyethylene does not change the mechanical properties of pure polyethylene samples prepared via rotational molding. But it improves its ability to adhere to another materials.

Plasma treatment of polyethylene powder proved to be a successful method to improve the adhesion between the polyethylene and the polyurethane foam in sandwiches prepared via rotational molding. To reach optimum adhesion it is not necessary to use 100% treated powder, up to 50% of treated powder is enough to achieve the desired adhesion, longer treatment time is also not required to improve the adhesion, it is enough to treat the powder for 0.5 to 1 min.

Plasma treatment also proved to be successful in improving the adhesion between the polyethylene and the glass fibers, and in improving some of the mechanical properties of the composites prepared via rotational molding. Plasma treatment of both powder and fibers was needed to achieve an optimum adhesion. The treatment time of both components plays a key role in the final properties of the composites, and it is required to be mor than 5 min for the powder and 40 min and above for the glass fibers. Additionally, optimization of the rotational molding heating process is necessary as longer treated powder needs longer time to sinter properly.

Plasma treated polyethylene and its glass fibers composites with different walls thickness proved to be successful replacement of untreated polyethylene in industrial insulation containers prepared via rotational molding, without affecting their ability to absorb shocks.

5.3 Recommendation for future work

1. Working on improving the impact strength of the glass fiber composites by introducing a special coating for the glass fibers.
2. Studying another plasma treated polymers (such as Polypropylene) as a matrix for plasma treated glass fibers composites prepared via rotational molding.
3. Studying another untreated and plasma treated fibers as a filler for plasma treated polyethylene to prepare composites via rotational molding.
4. Studying the adhesion of plasma treated polyethylene to other types of polymeric foam.
5. Studying the application of plasma treated polyethylene and plasma treated glass fibers to prepare composites in 3D printing different techniques, as in these techniques similarly to rotational molding producing of the composites happened without adding any pressure, and the adhesion between the components still an open question.

References

[1] R. J. Crwaford and J. L. Throne, Rotational Moulding Technology, First edit, William Andrew, New York, pp.1-13,2002.

[2] K. O. Ogila, M. Shao, W. Yang, and J. Tan, “Rotational molding: A review of the models and materials,” *Express Polym. Lett.* BME-PT and GTE (Hungary), vol. 11, pp. 778–798, 2017, doi: 10.3144/expresspolymlett.2017.75.

[3] C. Arpagaus, G. Oberbossel, and P. Rudolf von Rohr, “Plasma treatment of polymer powders – from laboratory research to industrial application,” *Plasma Process. Polym.* Wiley-VCH Verlag (Germany), vol. 15, PP. 133 -193, 2018, doi: 10.1002/ppap.201800133.

[4] J. R. Roth, “Industrial Plasma Engineering: Volume 2: Applications to Nonthermal Plasma Processing,” First edit, CRC Press (United States),pp 30-45, 2001, doi: 10.1201/9781420034127.

[5] M. Pavlatová, M. Horáková, J. Hladík, and P. Špatenka, “Plasma surface treatment of powder materials - Process and application,” *Acta Polytech.*Czech Technical Univercity (Prague), vol. 52, pp. 83–88, 2012, doi: 10.14311/1562.

[6] N. M. Faleh and F. M. Hani, “The Influence of Rotational Speed on the Wall Thickness and Mechanical Characteristic of Rotomouldable Plastics,” *Asian J. Appl. Sci.* Science Alert (Pakistan), vol. 6,pp. 135-143, 2018, doi: 10.24203/ajas.v6i3.5353.

[7] T. Jachowicz and V. Krasinskyi, “Influence of Rotational Moulding Process Parameters on Accuracy of Polymer Casts,” *Acta Mech. Slovaca*, Technical University of Košice (Slovakia), vol. 21, pp. 40–46, 2017, doi: 10.21496/ams.2017.006.

[8] P. L. Ramkumar, S. D. Waigaonkar, and D. M. Kulkarni, “Effect of oven residence time on mechanical properties in rotomoulding of LLDPE,” *Sadhana - Acad. Proc. Eng. Sci.* Indian Academy of Sciences (India), vol. 41, pp. 571–582, 2016, doi: 10.1007/s12046-016-0489-4.

[9] D. -W Sun and R. J. Crawford, “Analysis of the effects of internal heating and cooling during the rotational molding of plastics,” *Polym. Eng. Sci.* John Wiley & Sons Inc (United states), vol. 33, pp. 132–139, 1993, doi: 10.1002/pen.760330303.

[10] S. J. Liu and K. H. Fu, “Effect of enhancing fins on the heating/cooling efficiency of rotational molding and the molded product qualities,” *Polym. Test.* Elsevier (Netherlands), vol. 27, pp. 209–220, 2008, doi: 10.1016/j.polymertesting.2007.10.004.

[11] M. P. McCourt, M. P. Kearns, and P. J. Martin, “The effect of internal mould water spray cooling on rotationally moulded polyethylene parts,” *AIP Conf. Proc.*American Institute of Physics (United States), vol. 1960, PP 1-6, 2018, doi: 10.1063/1.5034984.

[12] A. G. Spence and R. J. Crawford, “The effect of processing variables on the formation and removal of bubbles in rotationally molded products,” *Polym. Eng. Sci.* John Wiley & Sons Inc (United states), vol. 36, pp. 993–1009, 1996, doi: 10.1002/pen.10487.

[13] E. H.-J. M.Z. Abdullah,S. Bickerton,D. Bhattacharyya,R.J. Crawford, “Rotational Molding Cycle Time Reduction Using a Combination of Physical Techniques,” *Polym. Eng. Sci.* John Wiley & Sons Inc (United States), vol. 49, pp. 1846–1854, 2009.

[14] G. GOGOS, “Bubble Removal in Rotational Molding,” *Polym. Eng. Sci.* John Wiley & Sons Inc (United States), vol. 44, pp. 388–394, 2004.

[15] E. Oterkus, C. Diyaroglu, D. De Meo, and G. Allegri, *Fracture modes, damage tolerance and failure mitigation in marine composites*. Elsevier (Netherlands), pp.79-102, 2016.

[16] J. Xiong, Y. Du, D. Mousanezhad, M. Eydani Asl, J. Norato, and A. Vaziri, “Sandwich Structures with Prismatic and Foam Cores: A Review,” *Adv. Eng. Mater.* John Wiley & Sons, Inc (United State), vol. 21, pp. 1–19, 2019, doi: 10.1002/adem.201800036.

[17] G. Belingardi, M. P. Cavatorta, and R. Duella, “Material characterization of a composite-foam sandwich for the front structure of a high speed train,” *Compos. Struct.* Elsevier (Netherlands), vol. 61, pp. 13–25, 2003, doi: 10.1016/S0263-8223(03)00028-X.

[18] A. Siriruk, Y. Jack Weitsman, and D. Penumadu, “Polymeric foams and sandwich composites: Material properties, environmental effects, and shear-lag modeling,” *Compos. Sci. Technol.* Elsevier (Netherlands), vol. 69, pp. 814–820, 2009, doi: 10.1016/j.compscitech.2008.02.034.

[19] N. Z. M. Zaid;R,Rejab,N.A.N Mohamed, “Sandwich Structure Based On Corrugated-Core: A Review,” 3rd Int. Conf. Mech. Eng. Malaysia, 2015.

[20] T. Khan, V. Acar, M. R. Aydin, B. Hülagü, H. Akbulut, and M. Ö. Seydibeyoğlu, “A review on recent advances in sandwich structures based on polyurethane foam cores,” *Polym. Compos.* John Wiley & Sons, Inc (United State), vol. 41, pp. 2355–2400, 2020, doi: 10.1002/pc.25543.

[21] D. W. McCullough, B. R. Pakulsky, and J. W. Liddle, “Polyurethane foam for automotive knee bolsters,” *SAE Tech. Pap.* International(United states),vol.203,pp. 1-13, 1992, doi: 10.4271/920336.

[22] F. V. Billotto, M. M. Mirdamadi, and B. A. Pearson, “Design, application development, and launch of polyurethane foam systems in vehicle structures,” *SAE Tech. Pap.*SAE International(United states), vol. 724, pp 1-9, 2003, doi: 10.4271/2003-01-0333.

[23] L. Mkrtchyan, M. Maier, and U. Huber, “Structural polyurethane foam: Testing and modelling for automotive applications,” *Int. J. Crashworthiness*.Taylor & Francis (United Kingdom), vol. 13, pp. 523–532, 2008, doi: 10.1080/13588260802221310.

[24] J. Moon, S. B. Kwak, J. Y. Lee, D. Kim, J. U. Ha, and J. S. Oh, “Synthesis of polyurethane foam from ultrasonically decrosslinked automotive seat cushions,” *Waste Manag.* Elsevier (Netherlands), vol. 85, pp. 557–562, 2019, doi: 10.1016/j.wasman.2019.01.018.

[25] A. Demharter, “Polyurethane rigid foam, a proven thermal insulating material for applications between +130°C and -196°C,” *Cryogenics (Guildf).* Elsevier (Netherlands), vol. 38, pp. 113–117, 1998, doi: 10.1016/S0011-2275(97)00120-3.

[26] N. Sarier and E. Onder, “Thermal characteristics of polyurethane foams incorporated with phase change materials,” *Thermochim. Acta.* Elsevier (Netherlands), vol. 454, pp. 90–98, 2007, doi: 10.1016/j.tca.2006.12.024.

[27] N. V. Gama *et al.*, “Bio-based polyurethane foams toward applications beyond thermal

insulation," *Mater. Des.* Elsevier (Netherlands), vol. 76, pp. 77–85, 2015, doi: 10.1016/j.matdes.2015.03.032.

[28] K. Kolat, G. Neşer, and Ç. Özes, "The effect of sea water exposure on the interfacial fracture of some sandwich systems in marine use," *Compos. Struct.* Elsevier (Netherlands), vol. 78, pp. 11–17, 2007, doi: 10.1016/j.compstruct.2006.01.009.

[29] A. Das and P. Mahanwar, "A brief discussion on advances in polyurethane applications," *Adv. Ind. Eng. Polym. Res.* Elsevier (Netherlands), vol. 3, pp. 93–101, 2020, doi: 10.1016/j.aiepr.2020.07.002.

[30] S. J. Liu and C. H. Yang, "Rotational molding of two-layered polyethylene foams," *Adv. Polym. Technol.* John Wiley & Sons Inc (United states), vol. 20, pp. 108–115, 2001, doi: 10.1002/adv.1008.

[31] Y. Dou and D. Rodrigue, "Morphological, thermal and mechanical properties of polypropylene foams via rotational molding," *Cell. Polym.* SAGE Publications (United Kingdom) vol. 40 , pp. 198–211, 2021, doi: 10.1177/02624893211018825.

[32] C. Casavola, V. Moramarco, and C. Pappalettere, "Impact response of polyethylene sandwich panel obtained by rotational moulding," *Fatigue Fract. Eng. Mater. Struct.* John Wiley & Sons Inc (United states), vol. 37, pp. 1377–1385, 2014, doi: 10.1111/ffe.12182.

[33] R. C. V. Fletes, P. O. Gudiño, F. J. M. Sánchez, O. V. L. Milton, E. Mendizabal, and R. González-Núñez, "A three-layer foamed composite prepared by rotational molding," *Annu. Tech. Conf. - ANTEC, Conf. Proc.* Society of Plastics Engineers (United states), pp. 1709–1713, 2016.

[34] K. K. Chawla, *Composite Materials: Science and Engineering*, Third edit, Springer (Germany), pp 105-195, 2012.

[35] D. D. L Chung, *Composite Materials: Science and Applications,* 2nd Edition, Springer (Germany),pp 110-140, 2010.

[36] P. N. Khanam and M. A. A. AlMaadeed, "Processing and characterization of polyethylene-based composites," *Adv. Manuf. Polym. Compos. Sci.* Taylor and Francis (United kingdom) , vol. 1, pp. 63–79, 2015, doi: 10.1179/2055035915Y.0000000002.

[37] H. M. Hai Nguyen,Wael Zatar, "Mechanical properties of hybrid polymer composite," in *Hybrid Polymer Composite Materials Properties and Characterisation*. 1st Edition. Elsevier (Netherands) 2017, pp. 83–113.

[38] Y. Zhou, M. Fan, and L. Chen, "Interface and bonding mechanisms of plant fibre composites: An overview," *Compos. Part B Eng.* Elsevier (Netherands), vol. 101, pp. 31–45, 2016, doi: 10.1016/j.compositesb.2016.06.055.

[39] R. D. A. Maya Jacob John, "Recent developments in chemical modification and characterization of natural fiber-reinforced composites," *Polym. Compos.* John Wiley & Sons, Inc (United State), vol. 29, pp. 187–207, 2008.

[40] F. W. Fabris, N. S. M. Cardozo, and R. S. Mauler, "Improving the Properties of LDPE / Glass Fiber Composites With Silanized-LDPE," *Polym. Compos.* John Wiley & Sons, Inc (United State),Vol 30,pp 872-879, 2009, doi: 10.1002/pc.

[41] U. Q. Trois-rivipres, "Influence of Maleic Anhydride as a Coupling Agent on the

Performance of Wood Fiber- Polystyrene Composites," *Polym. Eng. Sci.* John Wiley & Sons Inc (United states),vol. 31, pp. 1351–1357, 1991.

[42] A. Nourbakhsh, A. Karegarfard, A. Ashori, and A. Nourbakhsh, "Effects of Particle Size and Coupling Agent Concentration on Mechanical Properties of Particulate-filled Polymer Composites," *J. Thermoplast. Compos. Mater.* SAGE Publications (United Kingdom), vol. 23,pp 169-174, 2010, doi: 10.1177/0892705709340962.

[43] D. Ray, B. K. Sarkar, A. K. Rana, and N. R. Bose, "Effect of alkali treated jute fibres on composite properties," *Bull. Mater. Sci.*Springer (Germany), vol. 24, pp. 129–135, 2001, doi: 10.1007/BF02710089.

[44] W. Liu, A. K. Mohanty, L. T. Drzal, P. Askel, and M. Misra, "Effects of alkali treatment on the structure, morphology and thermal properties of native grass fibers as reinforcements for polymer matrix composites," *J. Mater. Sci.* pringer (Germany), vol. 39, pp. 1051–1054, 2004, doi: 10.1023/B:JMSC.0000012942.83614.75.

[45] A. Gomes, T. Matsuo, K. Goda, and J. Ohgi, "Development and effect of alkali treatment on tensile properties of curaua fiber green composites," *Compos. Part A Appl. Sci. Manuf.* Elsevier (Netherands), vol. 38, pp. 1811–1820, 2007, doi: 10.1016/j.compositesa.2007.04.010.

[46] Z. Kouadri. A. Benyahia, A. Merrouche, M. Rokbi, "Study the effect of alkali treatment of natural fibers on the mechanical behavior of the composite unsaturated Polyester-fiber Alfa," *Mechanics & Industry* . EDP Sciences (France),vol. 15 pp. 69–73, 2014.

[47] J. I. P. Singh, S. Singh, and V. Dhawan, "Effect of alkali treatment on mechanical properties of jute fiber-reinforced partially biodegradable green composites using epoxy resin matrix," *Polym. Polym. Compos.* SAGE Publications (United Kingdom), vol. 28, pp. 388–397, 2020, doi: 10.1177/0967391119880046.

[48] A. K. Bledzki, A. A. Mamun, M. Lucka-Gabor, and V. S. Gutowski, "The effects of acetylation on properties of flax fibre and its polypropylene composites," *Express Polym. Lett.* BME-PT and GTE (Hungary), vol. 2, pp. 413–422, 2008, doi: 10.3144/expresspolymlett.2008.50.

[49] Y. Seki, "Innovative multifunctional siloxane treatment of jute fiber surface and its effect on the mechanical properties of jute/thermoset composites," *Mater. Sci. Eng. A*. Elsevier (Netherands), vol. 508, pp. 247–252, 2009, doi: 10.1016/j.msea.2009.01.043.

[50] P. V. Joseph *et al.*, "The thermal and crystallisation studies of short sisal fibre reinforced polypropylene composites," *Compos. Part A Appl. Sci. Manuf.* Elsevier (Netherands), vol. 34, pp. 253–266, 2003, doi: 10.1016/S1359-835X(02)00185-9.

[51] G. Kalaprasad *et al.*, "Effect of fibre length and chemical modifications on the tensile properties of intimately mixed short sisal/glass hybrid fibre reinforced low density polyethylene composites," *Polym. Int.* John Wiley & Sons Inc (United states), vol. 53, pp. 1624–1638, 2004, doi: 10.1002/pi.1453.

[52] D. Bikiaris, P. Matzinos, J. Prinos, V. Flaris, A. Larena, and C. Panayiotou, "Use of Silanes and Copolymers as Adhesion Promoters in Glass Fiber / Polyethylene Composites," *J. Appl. Polym. Sci.* John Wiley & Sons Inc (United states),Vol 80,pp. 2877–2888, 2001.

[53] V. Feuillade and A. Bergeret, “Relationships between the glass fibre sizing composition and the surface quality of sheet moulding compounds (SMC) body panels,” *Compos. Sci. Technol.* Elsevier (Netherands),vol. 66, pp. 115–127, 2006, doi: 10.1016/j.compscitech.2005.05.009.

[54] S. Park, J. Jin, and J. Lee, “Influence of silane coupling agents on the surface energetics of glass fibers and mechanical interfacial properties of glass fiber- reinforced composites,” *J. Adhes. Sci.* Taylor and Francis (United kingdom) ,vol 14,pp. 1677–1689, 2012, doi: 10.1163/156856100742483.

[55] A. C. Cadore-rodrigues, L. F. Guilardi, V. F. Wandscher, G. K. R. Pereira, L. F. Valandro, and M. P. Rippe, “Surface treatments of a glass- fi ber reinforced composite : Effect on the adhesion to a composite resin,” *J. Prosthodont. Res.* Elsevier (Netherands), vol. 64,pp. 301-306, 2019, doi: 10.1016/j.jpor.2019.09.001.

[56] M. Hamdi, M. N. Saleh, and J. A. Poulis, “Improving the adhesion strength of polymers: effect of surface treatments,” *J. Adhes. Sci. Technol.* Taylor and Francis (United kingdom) ,vol. 34, pp. 1853–1870, 2020, doi: 10.1080/01694243.2020.1732750.

[57] J. Trejbal, V. Šmilauer, A. Kromka, Š. Potocký, and L. Kopecký, “Wettability enhancement of polymeric and glass micro fiber reinforcement by plasma treatment,” *NANOCON 2015 - 7th Int. Conf. Nanomater. - Res. Appl. Conf. Proc.Czech Technical University (Prague)*, pp. 315–320, 2015.

[58] V. Cech, R. Prikryl, R. Balkova, A. Grycova, and J. Vanek, “Plasma surface treatment and modification of glass fibers,” *Compos. Part A Appl. Sci. Manuf.* Elsevier (Netherands),vol. 33, pp. 1367–1372, 2002.

[59] A. Haji, “Effect of Plasma Treatment on Glass Fiber / Epoxy Resin Composite,” *2nd International Congress of Innovative Textiles* ,Turky, 2019.

[60] X. Yuan, K. Jayaraman, and D. Bhattacharyya, “Effects of plasma treatment in enhancing the performance of woodfibre-polypropylene composites,” *Compos. Part A Appl. Sci. Manuf.* Elsevier (Netherands),vol. 35, pp. 1363–1374, 2004, doi: 10.1016/j.compositesa.2004.06.023.

[61] J. Gabriel *et al.*, “Surface lignin removal on coir fibers by plasma treatment for improved adhesion in thermoplastic starch composites,” *Carbohydr. Polym.* Elsevier (Netherands), vol. 165, pp. 429–436, 2017, doi: 10.1016/j.carbpol.2017.02.042.

[62] B. Enciso and J. Abenojar, “Influence of plasma treatment on the adhesion between a polymeric matrix and natural fibres,” *Cellulose.* Elsevier (Netherands), vol. 24, pp. 1791–1801, 2017, doi: 10.1007/s10570-017-1209-x.

[63] J. Jang and H. Yang, “The effect of surface treatment on the performance improvement of carbon fiber / polybenzoxazine composites,” *J. Mater. Sci.* Springer(Germany) , vol. 5, pp. 2297–2303, 2000.

[64] P. Taylor *et al.*, “The Influence of Plasma Surface Treatment of Carbon Fibers on the Interfacial Adhesion Properties of UHMWPE Composite The Influence of Plasma Surface Treatment of Carbon Fibers on the Interfacial Adhesion Properties of UHMWPE Composite,” *Polym. Plast. Technol. Eng.*Taylor&Francis (United Kingdom), vol. 51, pp. 273–276, doi: 10.1080/03602559.2011.617406.

[65] J. Xie *et al.*, “Improving carbon fi ber adhesion to polyimide with atmospheric pressure plasma treatment,” *Surf. Coat. Technol.* Elsevier (Netherands), vol. 206, pp. 191–201, 2011, doi: 10.1016/j.surfcoat.2011.04.016.

[66] F. Rezaei, M. D. Dickey, M. Bourham, and P. J. Hauser, “Surface modification of PET film via a large area atmospheric pressure plasma: An optical analysis of the plasma and surface characterization of the polymer film,” *Surf. Coatings Technol.* Elsevier (Netherands), vol. 309, pp. 371–381, 2017, doi: 10.1016/j.surfcoat.2016.11.072.

[67] and S. G. S. B. A. D. J. M. Berg, “Studies on Surface Wettability of Poly (Dimethyl) Siloxane (PDMS) and Glass Under Oxygen-Plasma,” *J.MicroElec.MechSys*.Elsevier (Netherands),vol. 14, pp. 590–597, 2005.

[68] P. Sundriyal, M. Pandey, and S. Bhattacharya, “Plasma-assisted surface alteration of industrial polymers for improved adhesive bonding,” *Int. J. Adhes. Adhes.*Elesiever (Netherland), vol. 101,pp 101-119, 2020, doi: 10.1016/j.ijadhadh.2020.102626.

[69] R. M. Thurston, J. D. Clay, and M. D. Schulte, “Effect of atmospheric plasma treatment on polymer surface energy and adhesion,” *J. Plast. Film Sheeting.* SAGE Publications (United Kingdom), vol. 23, pp. 63–78, 2007, doi: 10.1177/8756087907078698.

[70] D. Hegemann, H. Brunner, and C. Oehr, “Plasma treatment of polymers for surface and adhesion improvement,” *Nucl. Instruments Methods Phys. Res. Sect. B Beam Interact. with Mater. Atoms*. Elsevier (Netherands),vol. 208, pp. 281–286, 2003, doi: 10.1016/S0168-583X(03)00644-X.

[71] M. Ouitzau, M. Wolter, and H. Kersten, “Plasma treatment of polyethylene powder particles in a hollow cathode glow discharge,” *Plasma Process. Polym.* Taylor&Francis (United Kingdom), vol. 6, pp. 392–396, 2009, doi: 10.1002/ppap.200930909.

[72] H. Šourková and P. Špatenka, “Plasma activation of polyethylene powder,” *Polymers.* MDPI (Switzerland), vol. 12, pp 2090-2110, 2020, doi: 10.3390/POLYM12092099.

[73] S. H. Park and S. D. Kim, “Oxygen plasma surface treatment of polymer powder in a fluidized bed reactor,” *Colloids Surfaces A Physicochem. Eng. Asp.* Elsevier (Netherands), vol. 133, pp. 33–39, 1998, doi: 10.1016/S0927-7757(97)00109-X.

[74] Z. Weberová, H. Šourková, J. Antoň, T. Vacková, and P. Špatenka, “New method for optimization of polymer powder plasma treatment for composite materials,” *Polymers.* MDPI (Switzerland), vol. 13, pp 965-980,2021, doi: 10.3390/polym13060965.

[75] J. Sezemský and P. Špatenka, “Adhesion improvement between pe and pa in multilayer rotational molding,” *Polymers.* MDPI (Switzerland)., vol. 13, pp 331-344, 2021, doi: 10.3390/polym13030331.

[76] V. A. E. Lumirca Del Valle Espinoza Leon and J. C. J. J. and E. B. A. V. P. Leila Lea Yuan Visconte, “Rotomolding and polyethylene composites with rotomolded lignocellulosic materials : A review,” *J. Reinf. Plast. Compos.* SAGE Publications (United Kingdom), vol. 39, pp. 459–472, 2020, doi: 10.1177/0731684420916529.

[77] F. G. Torres and M. Aguirre, “Rotational Moulding and Powder Processing of Natural Fibre Reinforced Thermoplastics,” *Int. Polym. Process.* Walter de Gruyter GmbH (Germany), vol. 18, pp. 204–210, 2003.

[78] F. G. Ã. Torres and C. L. Aragon, “Final product testing of rotational moulded natural

fibre-reinforced polyethylene," *Polym. Test.* Elsevier (Netherands), vol. 25, pp. 568–577, 2006, doi: 10.1016/j.polymertesting.2006.03.010.

[79] L. T. A. W. C. B. WANG, S. PANIGRAHI, "Pre-treatment of Flax Fibers for use in Rotationally Molded Biocomposites," *J. Reinf. Plast. Compos.* SAGE Publications (United Kingdom), vol. 26, pp. 447–463, 2007, doi: 10.1177/0731684406072526.

[80] Z. Ortega, M. D. Monzón, A. N. Benítez, M. Kearns, M. Mccourt, and P. R. Hornsby, "Banana and Abaca Fiber-Reinforced Plastic Composites Obtained by Rotational Molding Process Banana and Abaca Fiber-Reinforced Plastic Composites Obtained by Rotational Molding Process," *Mater. Manuf. Process.* Taylor&Francis (United Kingdom), vol. 28, pp. 37–41, 2013, doi: 10.1080/10426914.2013.792431.

[81] E. O. Cisneros-lópez *et al.*, "Effect of fiber content and surface treatment on the mechanical properties of natural fiber composites produced by rotomolding," *Compos. Interfaces.* Taylor&Francis (United Kingdom), vol. 6440, pp. 35–53, 2016, doi: 10.1080/09276440.2016.1184556.

[82] D. R. Erick Omar Cisneros-López, Aida Alejandra Pérez-Fonseca, Yolanda González-García, Daniel Edén Ramírez-Arreola, Rubén González-Núñez, Denis Rodrigue, "Polylactic acid–agave fiber biocomposites produced by rotational molding: A comparative study with compression molding," *Adv. Polym. Technol.* John Wiley & Sons, Inc (United State), vol. 37, pp. 2528–2540, 2018.

[83] F. E. Hanana and D. Rodrigue, "Rotational Molding of Self-Hybrid Composites Based on Linear Low-Density Polyethylene and Maple Fibers," *Polym. Compos.* John Wiley & Sons, Inc (United states), vol. 39, pp. 4094–4103, 2017, doi: 10.1002/pc.

[84] F. E. Hanana, D. Y. Chimeni, and D. Rodrigue, "Morphology and mechanical properties of maple reinforced LLDPE produced by rotational moulding : Effect of fibre content and surface treatment," *Polym. Polym. Compos.* SAGE Publications (United Kingdom), vol. 26, pp. 299–308, 2018, doi: 10.1177/096739111802600404.

[85] M. Barczewski, M. Szostak, D. Nowak, and A. Piasecki, "Effect of wood flour addition and modification of its surface on the properties of rotationally molded polypropylene composites," *Polimery.* Łukasiewicz Research Network – Industrial Chemistry Institute (Poland), vol 63, pp 772-777, 2018, doi: 10.14314/polimery. 2018.

[86] J. Andrzejewski, A. Krawczak, K. Weso, and M. Szostak, "Rotational molding of biocomposites with addition of buckwheat husk filler . Structure-property correlation assessment for materials based on polyethylene (PE) and poly (lactic acid) PLA," *Compos. Part B Eng.* Elsevier (Netherlands), vol. 202, pp 5-18,2020, doi: 10.1016/j.compositesb.2020.108410.

[87] J. R. R. Martín and E. G. D. Rodrigue, "Improving the Compatibility and Mechanical Properties of Natural Fibers / Green Polyethylene Biocomposites Produced by Rotational Author ' s personal copy," *J. Polym. Environ.*Springer (Germany), vol. 28, pp. 1040–1049, 2020.

[88] A. Arribasplata-seguin, R. Quispe-dominguez, W. Tupia-anticona, and J. Acosta-sullcahuam, "Rotational molding parameters of wood-plastic composite materials made of recycled high density polyethylene and wood particles," *Compos. Part B Eng.* Elsevier (Netherlands), vol. 217, pp. 876-894, 2021.

[89] N. Gupta, "Effect of coir content on mechanical and thermal properties of LLDPE /

coir blend processed by rotational molding," *Sadhana - Acad. Proc. Eng. Sci.* Indian Academy of Sciences (India), vol. 40,pp 46-86, 2021, doi: 10.1007/s12046-021-01566-8.

[90] W. C. Chang, E. Harkin-Jones, M. Kearns, and M. McCourt, "Multilayered glass fibre-reinforced composites in rotational moulding," *AIP Conf. Proc.* American Institute of Physics (United States),vol. 1353, pp. 708–713, 2011, doi: 10.1063/1.3589598.

[91] G. Höfler, K. Jayaraman, and R. Lin, "Rotational moulding and mechanical characterisation of micron-sized and nano-sized reinforced high density polyethylene," *Key Eng. Mater.* Trans Tech Publications (Switzerland), vol. 809 , pp. 65–70, 2019, doi: 10.4028/www.scientific.net/KEM.809.65.

[92] M. C. Tanzi, S. Farè, and G. Candiani, Organization, Structure, and Properties of Materials. Foundations of Biomaterials Engineering. *Foundations of Biomaterials Engineering* .Elsevier (Netherlands) , pp. 3-103, 2019.

[93] W. Yan, R. J. T. Lin, and D. Bhattacharyya, "Particulate reinforced rotationally moulded polyethylene composites - Mixing methods and mechanical properties," *Compos. Sci. Technol.* Elsevier (Netherlands), vol. 66, no. 13, pp. 2080–2088, 2006, doi: 10.1016/j.compscitech.2005.12.022.

[94] W. Yan, R. J. T. Lin, S. Bickerton, and D. Bhattacharyya, "Rotational Moulding of Particulate Reinforced Polymeric Shell Structures," *Mater. Sci. Forum.* Trans Tech Publications (Switzerland), vol. 437–438, pp. 235–238, 2003, doi: 10.4028/www.scientific.net/msf.437-438.235.

[95] M. I. Baumer, J. L. Leite, and D. Becker, "Influence of calcium carbonate and slip agent addition on linear medium density polyethylene processed by rotational molding," *Mater. Res.*Springer (Germany), vol. 17, pp. 130–137, 2014, doi: 10.1590/S1516-14392013005000159.

[96] S. D. W. V. Girish Chandran, "Mechanical Properties and Creep Behavior of Rotationally Moldable Linear Low Density Polyethylene-Fumed Silica Nanocomposites," *Polym. Compos.* John Wiley & Sons, Inc (United states), vol. 38, pp. 421–430, 2017.

[97] E. Calò *et al.*, "Rotational molding of polyamide-6 nano composites with improved flame retardancy," *Int. Polym. Process.* Walter de Gruyter GmbH (Germany), vol. 27, pp. 370–377, 2012, doi: 10.3139/217.2552.

[98] W. Mhike, W. W. Focke, and J. K. O. Asante, "Rotomolded antistatic and flame-retarded graphite nanocomposites," *J. Thermoplast. Compos. Mater.* SAGE Publications (United Kingdom), vol. 31, pp. 535–552, 2018, doi: 10.1177/0892705717712634.

[99] G. Höfler, R. J. T. Lin, and K. Jayaraman, "Rotational moulding and mechanical characterisation of halloysite reinforced polyethylenes," *J. Polym. Res.*Springer (Germany), vol. 25, pp 132-142,2018, doi: 10.1007/s10965-018-1525-3.

[100] Z. Zepeda-Rodríguez *et al.*, "Mechanical and thermal properties of polyethylene/carbon nanofiber composites produced by rotational molding," *Polym. Compos.* John Wiley & Sons, Inc (United states), vol. 41, pp. 1224–1233, 2020, doi: 10.1002/pc.25448.

[101] Nováček Vojtěch and Spaenak Petr, “Aplikace plasmové úpravy pro vláknové kompozity s termoplastovou matricí,” Czech Technical University in Prague, 2018.

[102] S. K. and B. V. Vojtěch Nováček, Petr Špatenka, Tatana Vacková, Zdeňka Jeníková, “Enhanced interfacial strength of plasma treated polyethylene and glass Vojtěch,” *Instant J. Mech. Eng.* RAFT Publications(United states), vol. 2, pp. 01–08, 2019.

[103] Z. Ghanem, S. P. Sasidharan, Z. Jenikova, and P. Špatenka, “Rotational molding of plasma treated polyethylene/short glass fiber composites,” *Int. J. Eng. Manag. Sci.* University of Debrecen University (Hungary), vol. 4, pp. 103–108, 2019, doi: 10.21791/ijems.2019.4.11.

[104] P. S. Sari, S. Thomas, P. Spatenka, Z. Ghanem, and Z. Jenikova, “Effect of plasma modification of polyethylene on natural fibre composites prepared via rotational moulding,” *Compos. Part B Eng.* Elsevier (Netherlands), vol. 177, pp. 117-127,2019, doi: 10.1016/j.compositesb.2019.107344.

[105] Z. Ghanem, H. J. Šourkova, J. Sezemsky, and P. Špatenka, “The Effect of Plasma Treatment of Polyethylene Powder and Glass Fibers on Selected Properties of Their Composites Prepared via Rotational Molding,” *Polymers.* MDPI (Switzerland), vol 14, pp 2592-2612, 2022.

[106] Sumesh. K .R;Z. Ghanem;P.Spatenka., “Investigating the Influence of Plasma Treated Polyethylene powder and Carbon Fibers in Enhancing the Mechanical properties of Polymer Composites using Rotomoulding Method,” *Int. J. Adv. Manuf. Technol.*Springer (Germany), (Submited, under review) 2022.

List of Author publications

- [103] Z. Ghanem, S. P. Sasidharan, Z. Jenikova, and P. Špatenka, “Rotational molding of plasma treated polyethylene/short glass fiber composites,” *Int. J. Eng. Manag. Sci.* University of Debrecen University (Hungary), vol. 4, pp. 103–108, 2019, doi: 10.21791/ijems.2019.4.11.
- [104] P. S. Sari, S. Thomas, P. Spatenka, Z. Ghanem, and Z. Jenikova, “Effect of plasma modification of polyethylene on natural fibre composites prepared via rotational moulding,” *Compos. Part B Eng.* Elsevier (Netherlands), vol. 177, pp 117 - 127,2019, doi: 10.1016/j.compositesb.2019.107344.
- [105] Z. Ghanem, H. J. Šourkova, J. Sezemsky, and P. Špatenka, “The Effect of Plasma Treatment of Polyethylene Powder and Glass Fibers on Selected Properties of Their Composites Prepared via Rotational Molding,” *Polymers.* MDPI (Switzerland), vol 14, pp 2592-2612, 2022.
- [106] Sumesh. K .R;Z. Ghanem;P.Spatenka., “Investigating the Influence of Plasma Treated Polyethylene powder and Carbon Fibers in Enhancing the Mechanical properties of Polymer Composites using Rotomoulding Method,” Submitted to *Int. J. Adv. Manuf. Technol.*Springer (Germany), 2022 (Under review).

Conferences

- Presented a presentation “The effect of plasma treatment of polyethylene powder on the mechanical properties of composites prepared by rotational molding” in 2nd Advanced Materials Science World Congress conference , Berlin 14–15 June 2021.
- Presented a presentation “Plasma treatment of polyolefin powder – process and application” in Polymer Connect conference, Barcelona 5-7 July 2021.