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DOCTORAL
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STATEMENT

CZECH TECHNICAL UNIVERSITY IN PRAGUE

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

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The dissertation defense takes place on .... at ……… hours.

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In front of the committee for the defense of the dissertation in the field of study *Material Engineering.*
The dissertation can be viewed at the Department of Science and Research of the Faculty of Mechanical Engineering of the Czech Technical University in Prague, Technická 4, Prague 6

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1. Introduction and literature review:

Rotational molding is a molding technique used to produce hollow plastic parts with equal wall thickness and very low residual stresses in the final products. The process is used to produce a wide range of predominately hollow products of different sizes and shapes including storage tanks, shipping containers, kayaks, and barriers [1,2]. Manipulation of parameters such as the reduction of cycle time [3],[4],[5], and bubble removal [6],[7] improved the properties of rotomolded samples to a greater extent [8]. However, the main disadvantages of this process are high temperature and long production cycle time, which limit the materials that can be produced into a specific type of polymers capable of withstanding elevated temperatures for a relatively long period. These materials which are dominated by different grades of polyethylene are considered unsuitable 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.

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).However, in all 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 layer is instantaneous, and the foam does not impart any additional stiffness to the product [9],[10],[11],[12] .

There have been many attempts to incorporate different fiber types into the rotational molding process. The first attempt to produce composites via rotational molding was conducted by Torres et al. in 2003 [13] .In this study jute, wood, cabuya, pecan, sisal fibers and different types of rice shell flour were used as a filler for high-density polyethylene. Following this, many studies investigating the possibility of producing composites via rotational molding were conducted. Different natural fibers such as flax [14] ,banana and abaca [15],agave [16], [17] , coir [18] ,pine [19], maple [20], [21], wood [22] ,[23], glass fibers [24], [25], carbon fibers [25] , glass particles [26], [27], other synthetic particles [28]and nanoparticles [29], [30] as reinforcements with different grades of polyethylene [14]–[16], [18], [26],polyamide [30] ,polylactic acid [17], and polypropylene [31], as matrix were used in the studies.

However, no research has yet been reported using it successfully in industry. Contrary to other processing techniques such as injection molding and pressure molding, the rotational molding process operates at atmospheric pressure which makes reinforcing of the rotomolded product very difficult. The main problems that arise while using reinforcements in rotational molding are nonuniform distribution of the filler inside the matrix and poor adhesion between the fillers and the matrix, as no pressure is added to ensure mechanical adhesion between the two phases. This leads to the segregation and the agglomeration of the reinforcements. To overcome these problems, researchers have tried different chemical surface treatments of the fillers and/or the addition of coupling agent to the polymer matrix. Wang et al. [14], studied the effect of three different chemical treatments of flax fibers on the mechanical properties of LLDPE/flax fiber composites prepared via rotational molding. Silane, benzoylation, and peroxide were used for treatment; they reported that silane treatment was the best for improving mechanical properties and water absorption rate. Ortega et al. [15], prepared two- and three-layered banana and abaca fibers/polyethylene composites via rotational molding, and studied the effect of NaOH treatment of the fibers on the resulted composites. The results of the mechanical tests showed that the addition of banana and abaca fibers improved the tensile and flexural modulus, while the tensile and impact strength decreased, and NaOH treatment improved the properties of the composites. Lopez et al. [17], used agave, coir, and pine as reinforcements for LLDPE, with and without MAPE (maleic anhydride grafted polyethylene). The morphological tests showed that surface treatment helped to achieve better adhesion between the fibers and the polymer in all cases. In addition, mechanical properties of the composites with 20 wt% treated fibers were higher than the mechanical properties of net polyethylene and of composites prepared using untreated fibers. Hanana et al. [21], tried maple fibers as reinforcement for the LLDPE matrix and produced a composite using rotational molding. Maple fibers were treated with malleated polyethylene (MAPE) and properties of the composites were compared to composites prepared with untreated fibers. 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 exhibited higher values compared to composites with untreated fibers. The tensile strength of the untreated fibers composites decreased with increasing fiber content compared to unfilled samples, while the tensile strength of the treated-fiber composites was slightly above the unfilled samples. Impact strength decreased with increased fiber content for all composites, with slightly higher values for treated-fiber composites compared with untreated-fiber composites.

W, C. Chang et al.[24], used glass fibers to prepare rotomolded composites, The results of mechanical tests showed an increase in the tensile and flexural modulus of all composites. While impact strength of all composites decreased. Similar results were achieved by Hofler et al [25] .

Cold plasma treatment for adhesion improvement has attracted the attention of researchers as an effective and environmentally friendly alternative of chemical treatment. The treatment can be used to treat both matrix and fibers to improve their wettability and draft different functional groups on their surfaces. The type of functional group depends on plasma composition, and predominately carboxyl, hydroxyl, amine, or aldehyde groups are investigated as a tool for improvement of filler–matrix interfacial properties [5]. Plasma treatment of glass fibers improved their adhesion to both polyester and epoxy resins [32], [33]. J. Trejbal et al. [34], reported that oxygen plasma treatment of glass fibers increased their wettability by 25% when compared with untreated glass fibers. Similarly, plasma-treated coir fibers/starch composites [35], and plasma-treated flax fibers/LDPE composites [36], had better mechanical properties when compared with composites prepared using untreated fibers. Another study reported that plasma treatment of carbon successfully improved their adhesion to different matrixes [37],[38],[39]. In rotational molding, Rodrguez et al. [40], used a mixture of polyethylene with untreated and plasma-treated carbon nanofibers to prepare nanocomposites with different fiber content (0.01, 0.1, and 1.0 wt%). SEM images showed that the treated carbon fiber had a better distribution inside the matrix as a result of good adhesion and fiber wetting. Mechanical testing showed that plasma-treated nanofibers increased the impact strength of composites compared to net polyethylene and composites prepared by untreated nanofibers. The tensile modulus and tensile strength also increased by 20% and 8%, respectively.

The literature review showed that only few articles that investigated preparing foam sandwiches were found, these articles studied mainly used 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. Chemical treatment methods were the most used. However, 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.

2. Thesis goal:

The main aim of thesis is to study application of plasma treated polyethylene powder and plasma treated glass fibers in the 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 by 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 tests 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 plasma treated glass fibers on the adhesion between the fibers and the matrix and on the mechanical properties of composites prepared via rotational molding. 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.

3. Materials and experiments:

3.1 Materials:

The matrix polymer used is low density linear 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 14μm were used as reinforcement by LanXESS Company (Cologne, Germany).Fisher International single-component polyurethane foam with density 25 to 35 kg/m3,form Fisher international (North Carolina, US).Release Agent Rotorelease® MKX-17-014 from Münch Chemie International GmbH (Weinheim, Germany) .

For industrial experiments Linear low-density polyethylene Clearflex 50 U, with density 0.936 g/cm3 and melt flow index 7 g/10min 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 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. 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.

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, these times was chosen depending on Hana et al. [41], and the percentage of the treated powder on the plates was varied from 0 to 100wt %. The sandwiches were made by first preparing rectangular PE plates with dimension of 83 mm x 45 mm x 4 mm either in a special mold in the oven, or by cutting them from boxes that prepared in rotational molding machine, then each 2 plates were placed in a special form prepared especially for this experiment and polyurethan foam was injected between the polyethylene plates and left to cure for 24 hours, then the excess foam was removed, and the samples were ready for testing.

Different composites were prepared to study the effect of different parameters on the properties of the final rotomolded products .To study the effect of the plasma treatment time of polyethylene powder by preparing composites from PE powder treated for different time (0,1,3,5,10 min)and mixed with 10 wt.% of untreated glass fibers. Then the effect of different oven temperatures and holding time at these temperatures was studied by preparing composite from 5 min plasma treated powder with 10 wt. % of untreated fibers at oven temperature 250 ° C or 220 ° C and held at those temperatures for different periods (15 min,30 min , 45 min and 60 min) . and then cooling started at the end of holding period. The effect of adding untreated and plasma treated polyethylene wax on the properties of composites was studied by preparing composites containing different content of the wax (3wt.% ,5 wt.%,10wt.%,15 wt.%,20 wt.%) with 5 min treated powder and 10% of untreated fibers. After that the effect of plasma treatment of the 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 to prepare the composites. Finally, the effect of different fiber 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 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 fiber in the matrix.

To study the applicability of our new materials in the industrial field, samples were prepared in Olivo cold logistic company. To test the materials. The lids of one of the original company products were first rotomolded using a mixture of untreated and plasma treated polyethylene without fibers or from the same mixture composites with different wall thickness that contains 10% of glass fibers ,filled with polyurethane and compared to the original lids which consist of untreated polyethylene with polyurethane foam.

3.3 Testing methods:

Tensile strength and modulus were measured according to ASTMD638 using the TINUS OLSEN H50KT universal testing machine The three-point bending test was performed according to ASTM D790 using MTS Exceed E42 bending machine. Charpy impact tests were performed using CEAST 7.5 J, according to ASTM D6110. The samples were notched with a 2 mm offset. The tests were performed at room temperature. De-bonding test for PE/PU sandwiches was performed using a customized testing machine, prepared especially to perform the test. Falling weight test of the industrial composites were performed using Gravity falling hammer with hammer weight is 11.6 kg and with a line height of 3500 mm (hammer is completely at the top).

4. Results and discussion:

4.1 Characterization of Plasma treated polyethylene powder:

The results showed that the plasma treatment did not affect the shape of the polyethylene powder, as the treatment is surface modification techniques, using the correct processing conditions should not affect the shape or the structure of the power particles [42]. Plasma treatment does not affect the thermal behavior of polyethylene and both untreated and treated polyethylene can be prepared using the same regime [43]. 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[41].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.

4.2 PE/PU sandwiches :

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 1. 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.

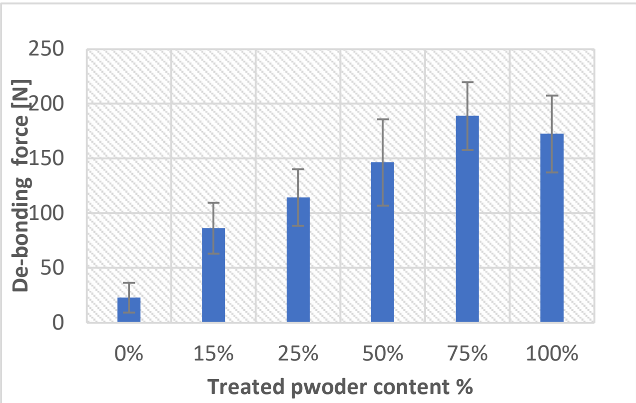

Figure 1: Effect of 1 min treated powder content in polyethylene plates on the force needed to de-pond PE/PU sandwiches.

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. In all sandwiches prepared using untreated PE plates the samples were ripped off without any foam left on the bonding surface Figure (2,a) , and this was also the case in most of the sandwiches prepared using PE plates that contain 15% treated powder Figure (2,b) while a PU appeared on the surface of PE plates that contain 50% of treated powder Figure (2,c) and maximum amount of the residue was noticed at the plates that contain 100% treated powder Figure (2,d).

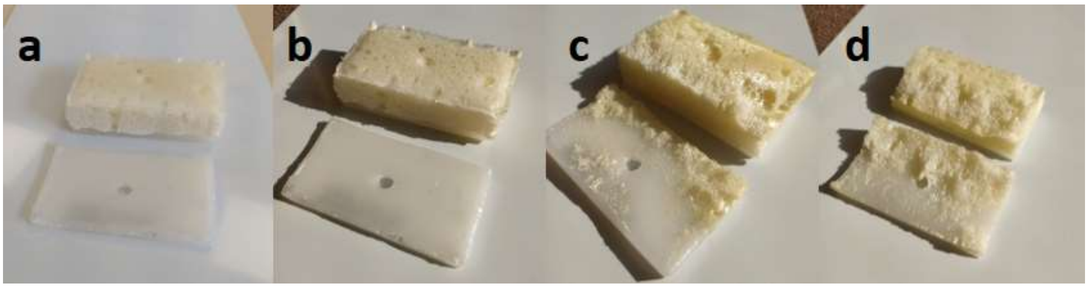

Figure 2:PU residue on the upper plate bonding surface after testing: a) sample prepared with untreated powder, b) samples contain 15% of 1 min treated powder, c) samples contain 50% of 1 min treated powder, d) samples contain 100 % of 1 min treated po

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 3 and 4, respectivaley.

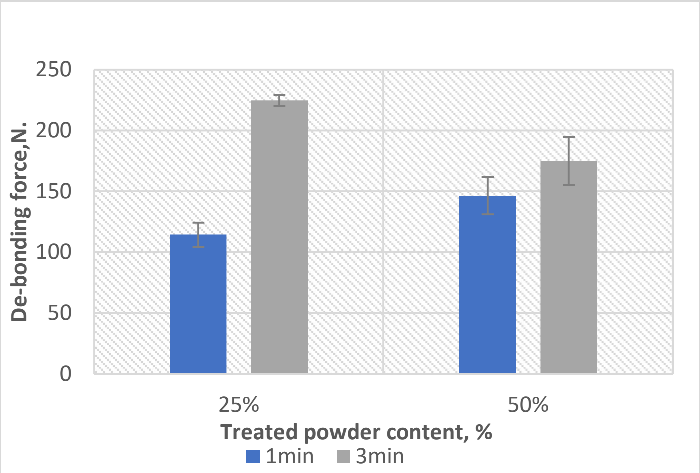

Figure 3:Effect of powder treatment time on de-boding force needed to tear the sandwiches.

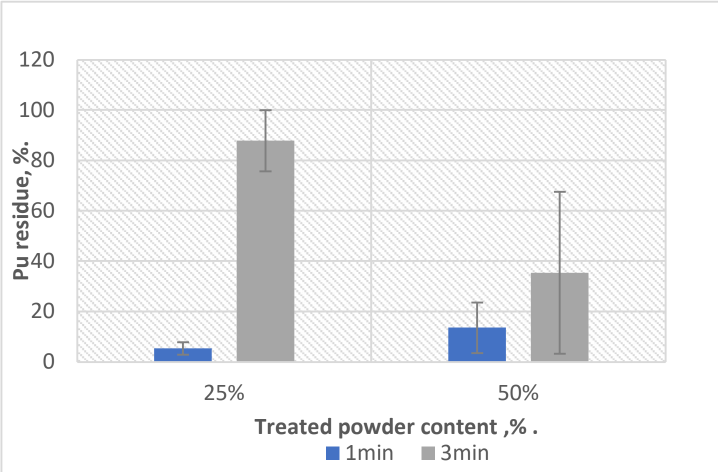

Figure 4: Effect of powder treatment time on PU residue on the bonding surface.

De-bonding force inceased with increasing treatement time, and this is because increasing powder treatement time increases the wettability and concentration of the O groubs as it was demonstreted by Hana et al. [41]. 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.

Using PE plates that were cut from rotomolded boxes instead of plates molded in the oven to prepare the sandwiches gave similar results, where De-bonding force increased by increasing the treated powder content in the plates, but the maximum force was reached at 50% of treated powder in the plates, while 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.

4.3 Glass fiber composites:

Preliminary results showed that incorporation of glass fibers to the polyethylene in composites prepared using rotational molding decrease both tensile strength and impact strength as the fibers content increased form 0 to 20wt,%, while tensile modulus increased with increasing fibers content [44].

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 only slightly increased the tensile strength Figure 5 . The reason for these results could be either insufficient treatment time for composites prepared with powder treated for 1 and min, or increased number of bubbles on the outer surface and uneven inner surface for composites prepared with powder treated for 5 and 10 min [45].

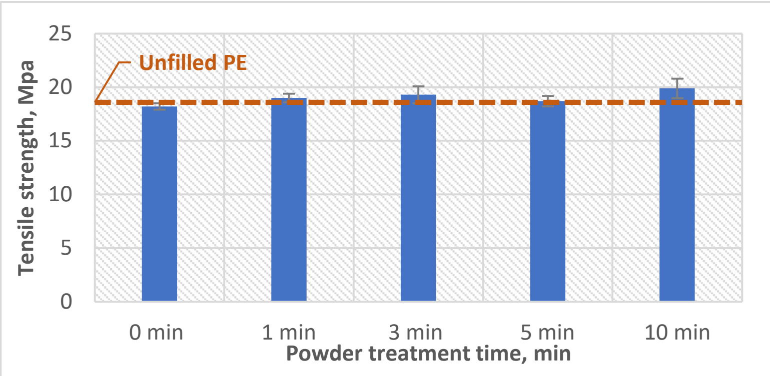

Figure 5: The effect of PE powder treatment time on the tensile strength of the composites produced using treated powder and 10 wt.% untreated glass fibers.

All composites showed higher modulus than pure polyethylene as it can be seen in Figure 6 , 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 flexural modulus presented in Figure 7, 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. A slight decline in the modulus can be noticed in the modulus when using longer time treated powder (5 min and 10 min) [45].

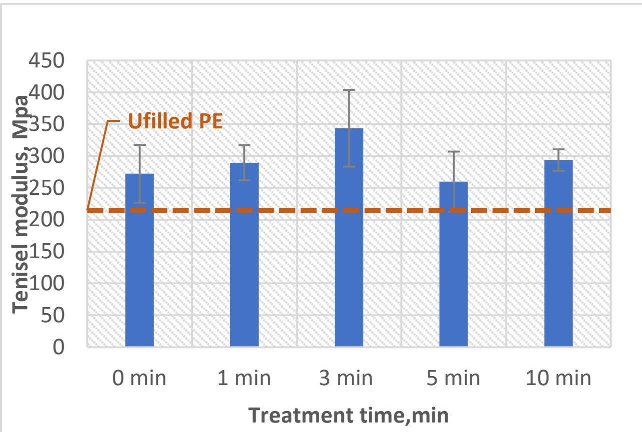

Figure 6:The effect of PE powder treatment time on the tensile modulus of the composites produced using treated powder and 10 wt.% untreated glass fibers.

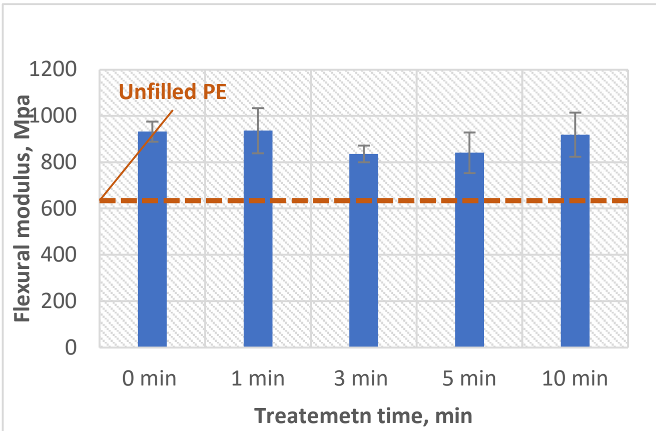

Figure 7: The effect of the PE powder treatment time on the flexural modulus of the composites produced using treated powder and 10 wt.% untreated glass fibers.

The impact strength of the composites is presented in Figure 8, 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 [45].

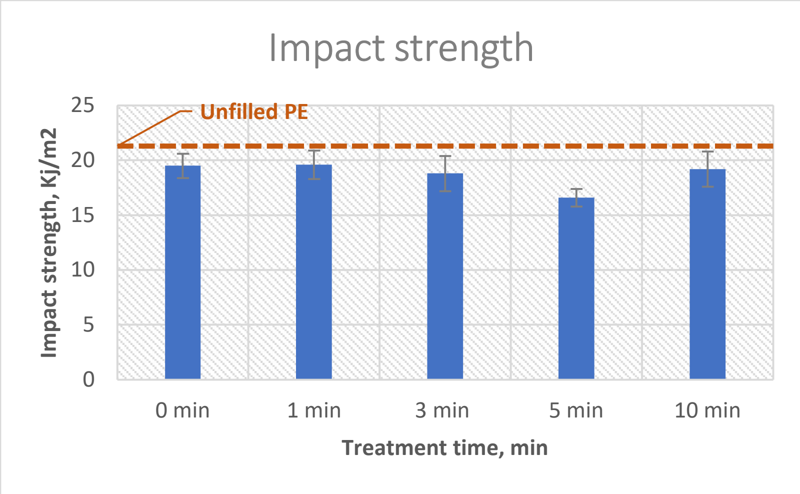

Figure 8: The effect of the PE powder treatment time on the impact strength of the composites produced using treated powder and 10 wt.% untreated glass fibers.

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 highest values of tensile modulus and flexural modulus were obtained for the composite prepared at oven temperature 220 ° C for 30 min. 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 [45].

Incorporation of untreated and treated wax with different percentage in the composites decreased all mechanical properties of the composites that containing wax comparing with composites did not contain wax. However, both tensile and flexural modulus were still higher than the modulus of the pure polyethylene.

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 Figure 9. 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 components. 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 fibers. The reason for this increase could be that the treatment of glass fibers added oxygen groups to the fiber surfaces and increases in 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 [45].

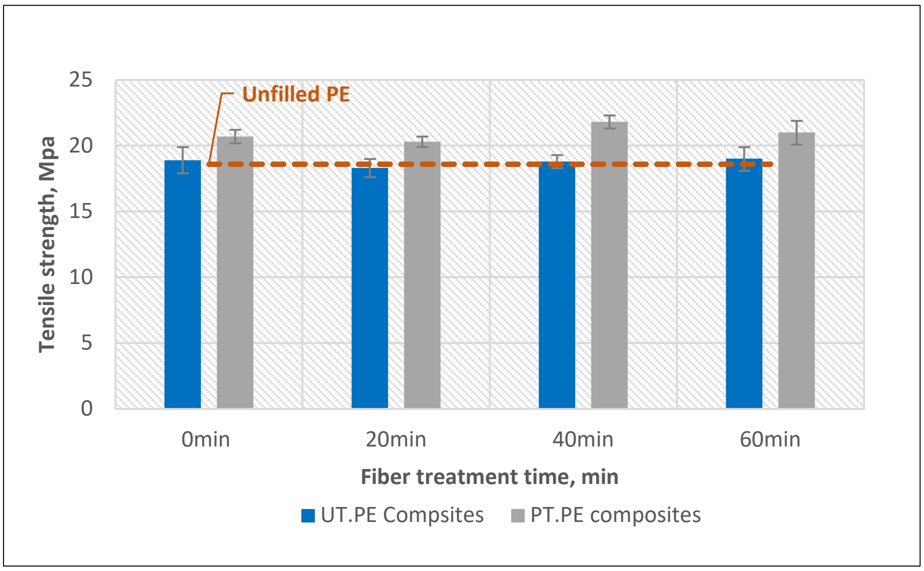

Figure 9: The effect of glass fiber treatment time on the tensile strength of the composites prepared using untreated and 40-min treated PE with 10 wt.% untreated and plasma-treated glass fibers.

Plasma treatment of the fibers did not significantly affect the rest of the mechanical properties.

The effect of fiber content on the tensile strength of the composite is presented in Figure 10 .The composites were prepared using 10-min treated powder and 40-min treated glass fibers [45]. 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.

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 11 and 12 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% of the same composites compared to unfilled PE samples.

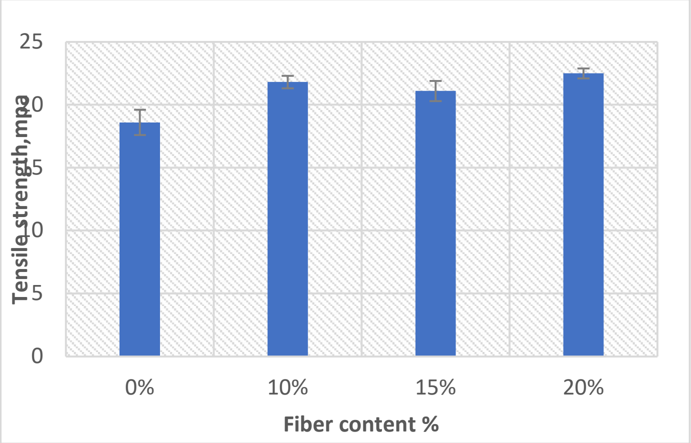

Figure 10: The effect of fiber content on the tensile strength of the composites prepared using 10-min treated powder and 40-min treated fibers.

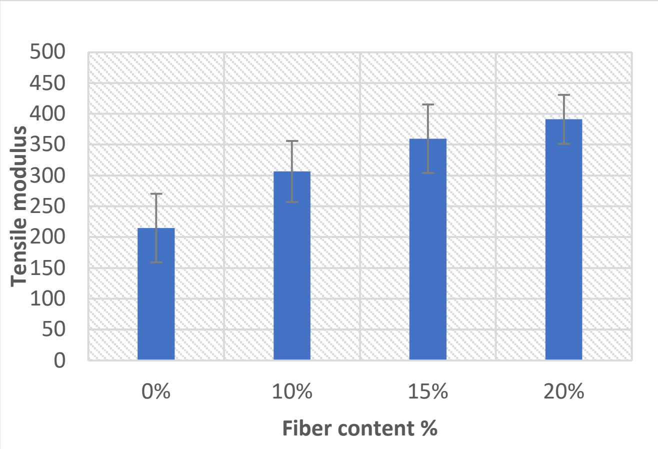

Figure 11: The effect of fiber content on the tensile modulus of the composites prepared using 10-min treated powder and 40-min treated fibers.

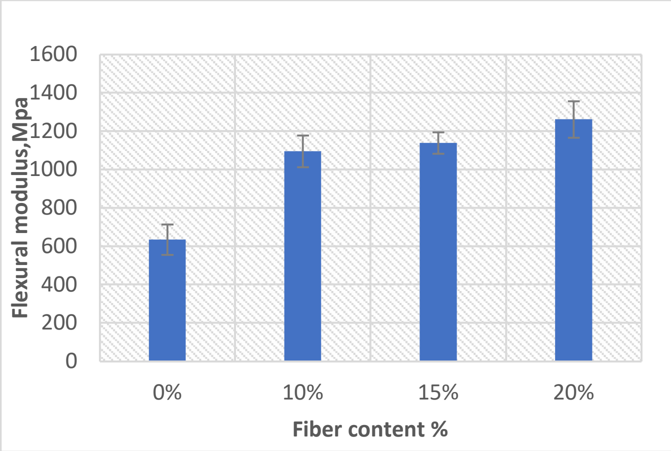

Figure 12: The effect of fiber content on the flexural modulus of the composites prepared using 10-min treated powder and 40-min treated fibers.

The results of higher content of glass fiber on the impact strength is presented in Figure 13. As shown, the impact strength kept decreasing with increasing fiber content to reach 38% at 20 wt.% glass fiber content comparing 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.

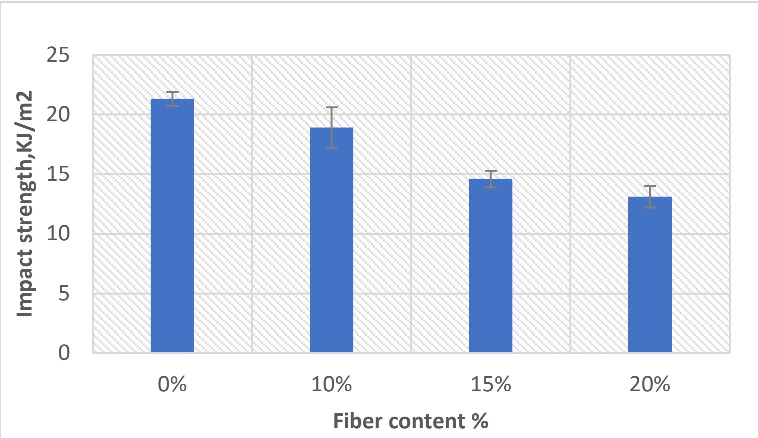

Figure 13: The effect of fiber content on the impact strength of the composites prepared using 10-min treated powder and 40-min treated fibers.

4.4 Morphology analysis:

SEM images of fractured surfaces of composites prepared using powder treated for different time with untreated fibers are presented in Figure 14. The surface of composites prepared using the untreated power Figure (14,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 (14,b), the gap between the matrix and the fibers can still be seen and no trace of polyethylene is shown on the fiber surface. With increasing treatment time to 3 min Figure (14,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 (14 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 an increase amount of polyethylene residue is left on the fiber surface after breaking; this indicates good adhesion between the fibers and the matrix. These images are consistent with Zuzana et al. [46] on the adhesion between treated powder and a glass rod.

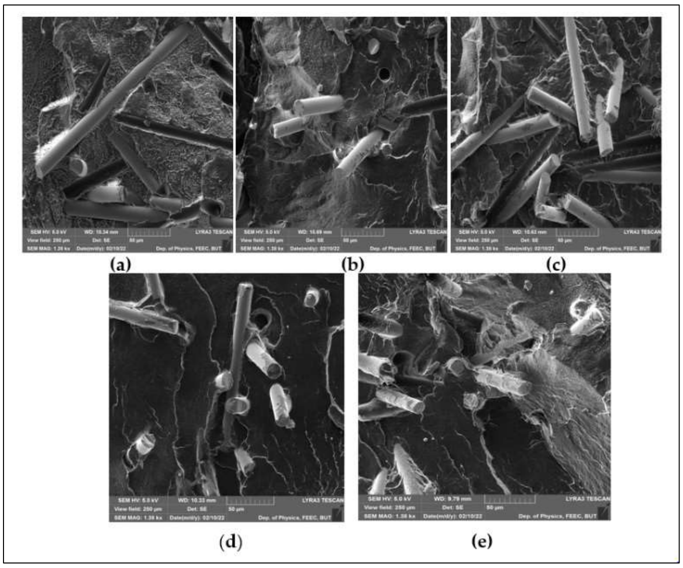

Figure 14: SEM images of fracture surface of composites prepared using untreated and plasma treated polyethylene with untreated fibers: a) composites with untreated PE, b)composites with 1 min plasma treated PE, c) composites with 3 min plasma treated PE, d) composites with 5 min plasma treated PE, e) composites with 10 min plasma treated PE.

Figure 15. shows the interface between the matrix and the fiber in composites prepared using untreated powder and fibers (Figure 15,a) comparing to composites prepared using 10 min treated powder and 40 min treated fibers. It is clearly observed that the adhesion between the treated powder and treated fibers is significantly improved, fiber surface is totally covered by polymer matrix, which indicates that treatment of both powder and glass fibers was necessary to achieve sufficient adhesion between the fibers and the matrix. A similar good adhesion was not achieved in the literature where short glass fibers were used as reinforcements for composites prepared by rotational molding [24], [25].

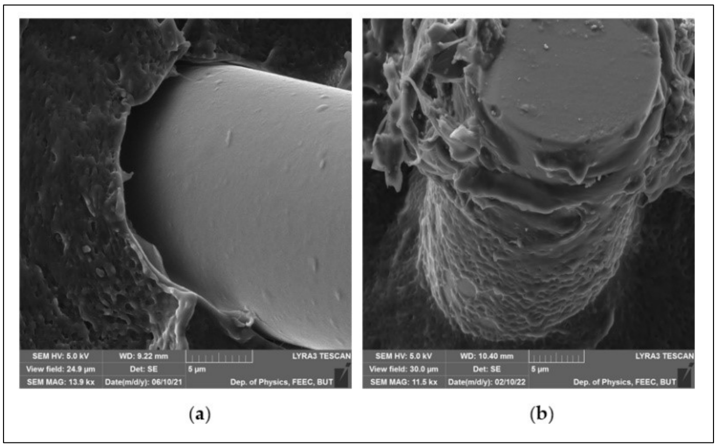

Figure 15: SEM images show the adhesion between PE and glass fibers :a) untreated PE and untreated fiber, b) 10 min plasma treated PE and 40 min plasma treated glass fibers.

4.5 Industrial results:

Images of specimen after falling weight test are presented in Figure 16 . Each specimen was hit by the hammer falling from different heights. Figure (16,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 (16,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 16.

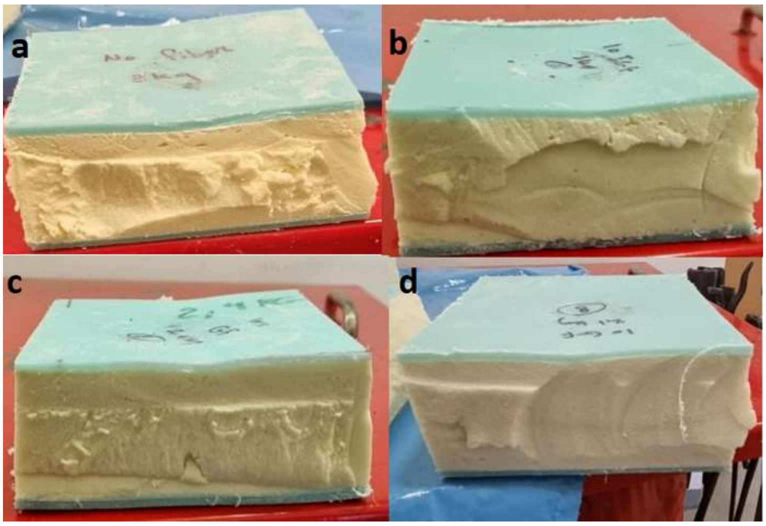

Figure 16: The deformation of the samples after falling weight: a) Samples prepared using treated powder with wall thickness 5 mm, b) samples contain 10% of glass fibers with wall thickness 5 mm, c) Samples contain 10 of glass fibers with wall thickness 4 mm, d) Samples contain 10% of glass fibers with 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.

5. Conclusions:

5.1 Conclusion 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 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 reduced weight and 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.

5.1 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.

List of publication related to this work:

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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.

Summary

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 fiber 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.