

Kaunas University of Technology
Faculty of Mechanical Engineering and Design

The Effect of Surface Silylation of Lignocellulosic Wheat Waste on the Morphology and Properties of Polypropylene Composites

Master's Final Degree Project

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Kaunas, 2021



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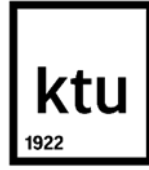
Master's Final Degree Project
Industrial Engineering and Management (6211EX018)

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The Effect of Surface Silylation of Lignocellulosic Wheat Waste on the Morphology and Properties of Polypropylene Composites

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I confirm that the final project of mine, Vinodkumar Madeswaran, on the topic “The Effect of Surface Silylation of Lignocellulosic Wheat Waste on the Morphology and Properties of Polypropylene Composites” is written completely by myself; all the provided data and research results are correct and have been obtained honestly. None of the parts of this thesis have been plagiarised from any printed, Internet-based or otherwise recorded sources. All direct and indirect quotations from external resources are indicated in the list of references. No monetary funds (unless required by Law) have been paid to anyone for any contribution to this project.

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Vinodkumar Madeswaran

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Kaunas University of Technology
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Task of the Master's final degree project

Given to the student – Vinodkumar Madeswaran

1. Title of the project –

The Effect of Surface Silylation of Lignocellulosic Wheat Waste on the Morphology and Properties of Polypropylene Composites

(In English)

Lignoceliuliozinių kviečių atliekų paviršiaus sililavimo įtaka polipropileno kompozitų struktūrai ir savybėms

(In Lithuanian)

2. Aim and tasks of the project –

Aim: To investigate the influence of surface silylation of wheat residue (by-product) particles on the propylene (PP) composition structure and properties.

Tasks:

1. To study the surface morphology of the lignocellulosic wheat by-product particles before and after treatment with hexamethyldisilazane (HMDS).
2. To determine the influence of silylated lignocellulosic filler type and amount on the mechanical properties of PP composites.
3. To analyse and investigate the interaction mechanism between lignocellulosic filler particles and PP matrix after treatment with HMDS.
4. Management part of agriculture waste filled PP composition products

3. Initial data of the project –

NA

4. Main requirements and conditions –

- 1) Standard - LST EN ISO 527-1 and LST EN ISO 527-2.
- 2) Equipment for structural and mechanical investigation of nanocomposites.

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Study field and area (study field group): Production and Manufacturing Engineering (E10), Engineering Sciences (E).

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Summary

This study analyzes polypropylene and its lignocellulosic waste composition. Two types of wheat waste such as wheat sieves and wheat husk were used. Due to the increase of compatibility with the PP matrix, the surface of waste particles was silylated with HMDS by the chemical vapor deposition method. The effect of the surface changes on the lignocellulosic waste structure and properties was investigated and analyzed by using various testing methods. The wheat waste-filled PP composite was prepared by using injection molding. It was obtained that silylation increases waste particles interaction at the interface. Therefore, the strength of the PP composition increases. The management aspect of the wheat waste-filled PP composition was analyzed and the probability for manufacturing the new wheat waste-filled PP product was carried out. This research was carried out for the implementation of the activity of project no. J05-LVPA-K-04-0045 “Development of Innovative Plastic and Other Additive Composite with Distinctive Physical and Chemical Properties” which is provided by European Regional Development Fund according to the 2014-2020 ‘Operational Program for the European Union Funds Investment’ under measure No.J05-LVPA-K “Intellect Joint Science-Business Projects” (Coordinator UAB Vilkritis, the period of implementation 28-02-2019 - 27-02-2021).

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Reikšminiai žodžiai: lignoceliuliozinės atliekos, polipropileno kompozitai, sililinimas, heksametildisilazanas

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Santrauka

Darbe tiriamos polipropileno ir lignoceliuliozės atliekų kompozitai. Naudojamos dviejų rūšių kviečių atliekos: kviečių atsijos ir kviečių lukštai, kurie suderinamumo pagerinimui buvo sililiniami HMDS cheminiu garų nusodinimo metodu. Naudojantis įvairiais tyrimo metodais, ištirta ir išanalizuota paviršiaus modifikavimo įtaka lignoceliuliozės atliekų struktūrai ir savybėms. Kviečių atliekomis užpildytas PP kompozitas buvo paruoštas injekcinio formavimo būdu. Gauta, kad sililinimas padidina atliekų dalelių sąveiką tarpfazinėje riboje, todėl padidėja PP kompozicijų stiprumas. Išanalizuotas kviečių atliekomis užpildytų PP sudėties valdymas ir atlikta naujo kviečių atliekomis užpildyto PP produkto gamybos analizė. Šie tyrimai skirti ES struktūrinių fondų projekto Nr. J05-LVPA-K-04-0045 „Inovatyvių plastiko ir kitų priedų kompozitų, pasižyminčių išskirtinėmis fizinėmis ir cheminėmis savybėmis, kūrimas“, kuris finansuojamas Europos regioninės plėtros fondo lėšomis pagal 2014–2020 m. Europos Sąjungos fondų investicijų veiksmų programos priemonę Nr. J05-LVPA-K „Intelektas. Bendri mokslo–verslo projektai“ (koordinadorius UAB „Vilkritis“, įgyvendinimo laikotarpis 2019-02-28 – 2021-02-27) vienos veiklos uždaviniams spręsti.

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List of abbreviations and terms

Abbreviations:

PP	– Polypropylene
UTM	– Universal testing machine
LDPE	– Low-density polyethylene
SEM	– Scanning electron microscope
EDS	– Energy-dispersive X-ray spectroscopy
HMDS	– Hexamethyldisilazane
TGA	– Thermogravimetric analysis
FTIR	– Fourier transform infrared spectroscopy
XRD	– X-ray diffraction
DTG	– Derivative thermogravimetry
WA	– Water absorption
WVA	– Water vapor absorption

Introduction

In the past years, various interest has been paid to “composites”. The various effort has been created on the use of waste management, to obtain a compound or product which could be used in various fields. A lignocellulosic wheat by-product is suitable for the environment and could offer the sources for obtaining polymer composites.

Polyolefin composites (polypropylene and polyethylene) are very widespread and broadly used in various functions due to their excellent properties and cost. They are often used in combination with various reinforcements. The properties of composites are based on properties of filler including the arrangement of the filler, surface chemistry, chemical composition of the filler, and properties of the matrix including nature and its functionality. The bond among the reinforcing particles and the matrix plays a major role in a composite

The work aims to investigate the influence of lignocellulosic surface silylated waste particle on its interaction with the propylene (PP) and its influence on the composite structure and properties.

The tasks of the work are:

- 1) To analyze the surface morphology of the lignocellulosic wheat by-product particles before and after silylation with hexamethyldisilazane (HMDS).
- 2) To determine the influence of silylated lignocellulosic filler and amount on the mechanical characteristics of PP composite.
- 3) To analyze and investigate the interaction mechanism between lignocellulosic filler particles and PP matrix silylation.
- 4) The management part of agriculture waste-filled PP composition products and perform an analysis of filled PP products.

1. Relevance of Research

1.1. Lignocellulosic waste

Lignocellulosic waste is byproducts of the various agriculture industry such as sugarcane, wheat, rice, and so on. It is one of the most abundant resources in the world. Mostly lignocellulosic waste is composed of three components cellulose (30-50%), lignin (10-20%), and hemicellulose (15-30%) (Fig.1) [1]. Also, these are the main three things situated in the plant cell wall. Cellulose and hemicellulose have different structure hence it has different thermal stability. In the cell wall, they are arranged in a structure known as microfibrils. This microfibrils structure gives structural stability to the cell wall [1].

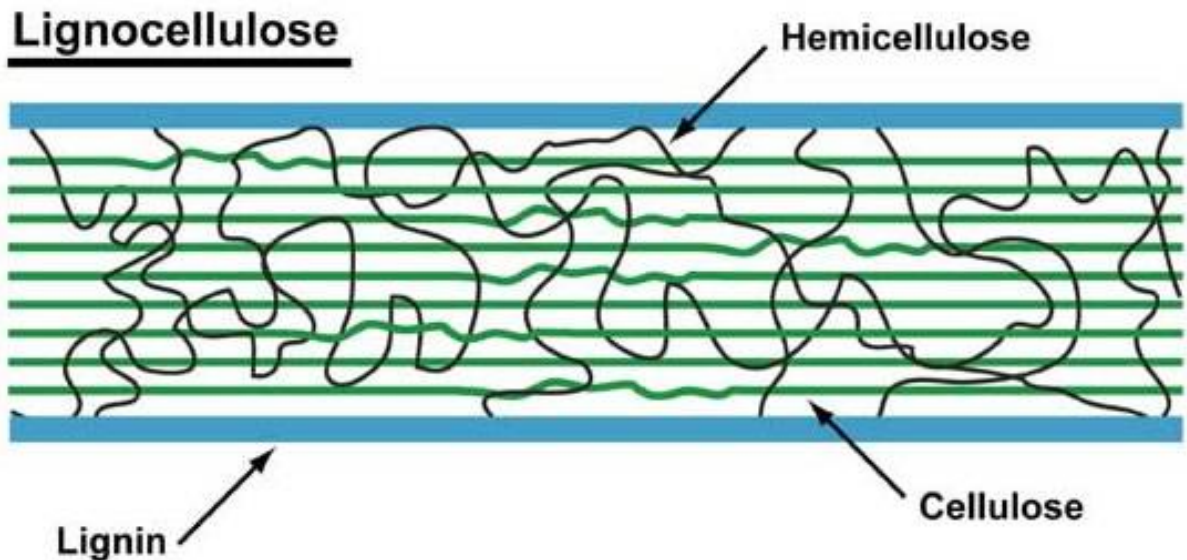


Fig. 1. Structure of lignocellulose [1]

Cellulose: It is one of the organic compounds with the formula $(C_6H_{10}O_5)_n$, complex polysaccharide matching of an uncurled series of hundred to thousand monosaccharide units (glycose units combined by a 1-4 beta glycosidic bond). It is a fatal ingredient of the cell wall also the main building material for plants on the earth. There is various kind of cellulose that are available from several sources (Fig.2) [2].

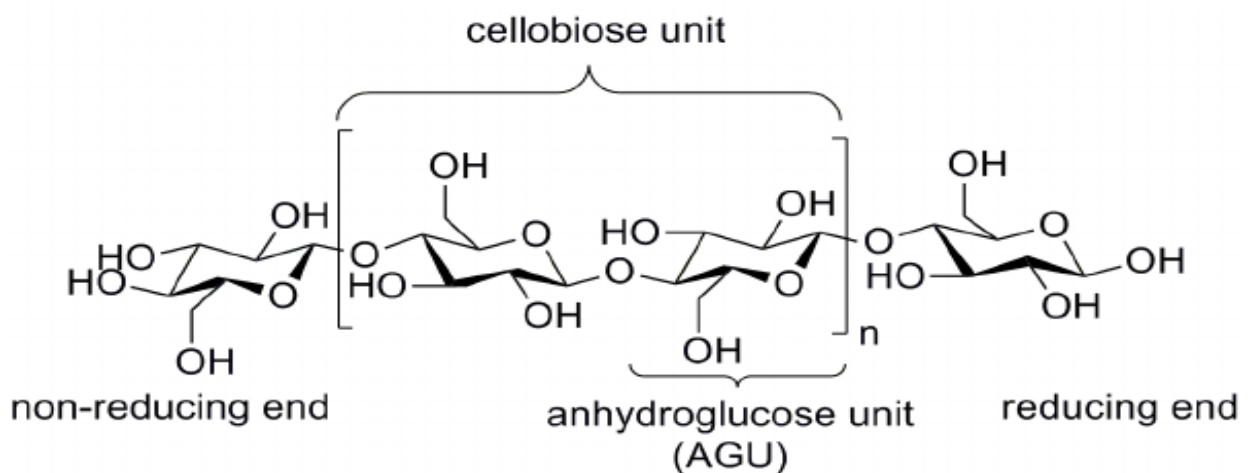


Fig. 2. Structure of Cellulose polymer chain [2]

Among the various source, one is natural fibers, made from natural sources like plants, animals, and other mineral sources. Those are segregated created on their origin.

Table. 1. Types of fibers, and their cellulose percentage [2]

Category	Description	Examples	% of cellulose
Seed fibers	Fibers extracted using seeds or seed cases	Cottonseed, Kapok	90
Leaf Fiber	Fiber produced using leaves	Sisal, Agave	33
Skin or Bast Fiber	Fiber got from skin or bast surrounding the stem	Jute, Kenaf, Hemp	33
Fruit Fiber	Fiber got from the fruit	Coconut	30-50
Stalk Fiber	Fiber is a stalk of the plant	Rice, Barley, Wheat	40-50

Table. 2. Types of lignocellulosic waste, and its percentage

Types of waste	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Almond shell	27	33	27	[1]
Bamboo	50.4	24.2	23.4	[1]
Banana waste	13.2	14.8	14	[1]
Barley husk	21.4	36.6	19.2	[1]
Barley straw	30.8	25.3	16.7	[1]
Comcob	35.4	40.6	14.8	[1]
Cotton stalk	58.5	14.4	21.5	[2]
Eucalyptus	46.7	20.7	29.2	[1]
Faba bean	28.4	20.4	14.4	[1]
Hybrid poplar	43.8	14.9	29.1	[1]
Maple	40.9	19.4	29.1	[1]
Oilseed rape	27.3	21.9	14.2	[1]
Olive stone	24	27.8	31.3	[1]
Olive tree biomass	25	18.3	16.6	[1]
Sorghum straw	35.1	24	25.4	[1]
Sugarcane bagasse	44.7	36.9	23.2	[1]
Sunflower stalk	42.1	29.7	13.4	[1]
Rice husk	36.7	37.2	24.6	[2]
Vine shoot	41.1	26	20.3	[1]
Wheat straw	37.4	36.5	19.4	[6][7]
Winter rye	40.8	26.1	16.1	[1]

Manmade fibers are synthetic fibers combined with natural ones. Synthetic fibers are made by using petrochemicals, and natural cellulose namely Rayon, Modal, and Lyocell. For example, Rayon fibers are made by the alkali cellulose with carbon disulfide. Lyocell is made by making a solvent of N-methyl morpholine-N-oxide.

Hemicellulose: It has a complex branched structure of sugars and its derivatives (100-200 sugar units, including hexoses, pentoses, and sugar acids) which provides a highly branched network. It is also another polysaccharide initiate in the cell wall of the plants. The main role of the hemicellulose is to be performed as a bonding agent between the cellulose, and lignin. It forms a covalent bond with lignin, and a non-covalent bond with cellulose makes the fiber strong, and maintains the interaction, and protects the fiber from degradation [3].

Lignin: It is quite amorphous when compared to the before described components. It is a highly polymerized molecule that has a complex cross-linked hydrophobic biopolymer. The ratio of the lignin varies on the plant. Age plays a major role here because the older plant has more lignin when compared to the young plants. Usually, lignin lies in the cell wall to give rigid support to the cell wall, and act as a barrier to the plant against microbial attack. hence it has more percentage of degradation. Hemicellulose and lignin have a covalent bond it plays a major in the mechanical strength of the plant. Softwood barks (30-60%) have more percentage of lignin when compared to hardwood barks (30-60%). whereas agriculture waste has less percentage of lignin (3-15%) (Table.2) [3].

1.2. Surface treatment of cellulose

The surface treatment is the process of modifying or changing the surface of a material by the physical, chemical, or biological characteristic that varies from the original one on the material surface. Various purpose of surface modification is:

- Enhancing the anticorrosive property
- Improving electrical conductivities, and optical properties
- Increasing bioactivities
- Improving adhesion properties
- Improves component lifetime, and increase the resistance to the environment
- Produce biocompatibility
- Increase the wettability character of the material
- Enhance the hydrophobic characters

During the surface modification of the cellulose, various types of physical, and chemical methods are plasma treatment, corona discharge, vacuum UV treatment these are physical methods, and here the chemical methods which are, treating the surface of the cellulose with the coupling agent. Here the coupling agents are silanes, and isocyanates most using a coupling agent. Grafting and alkali treatment are some other chemical methods of surface modification [5].

Plasma treatment:

Plasma is a reactive treatment process where ions of different charge and electrons are colliding if an electric potential difference exists. The main advantages are it is easy to control simply by controlling the flow of gas, pressure, and concentration. By using this method, it could be easily treating 3D materials. Price and the low rate of production are the main disadvantages of this method. It should maintain a certain environment for this experiment hence the cost is high when compared to other methods also the experimental setup is huge when compared to others.

To increase the oxygen group on the surface of the fibers, the oxygen plasma will help us. If the fibers are treated with plasma, then that could decrease the molecule mass of lignin. This reduction of lignin could impact mechanical property. [8] In this paper, the researcher proved that fiber that has been treated by plasma has some development in the tensile strength and young's modules.

In this paper [8] three different fibers are used. First, coconut fiber from the Philippines is used as a material. This coconut has 46% of cellulose, 3% of hemicellulose, 45% of lignin, and 4% of pectin.

The second fiber is produced from the leave of the plant name called *Musa textilis*. That plant is from the Philippines and that fiber is called abaca fiber. That fiber has 62.5% of cellulose, 21% of hemicellulose, and 12% of lignin. The final and third fiber is from China, this also leaves fiber made from the plant agave and that fiber name is sisal fiber. This consists of 60% cellulose, 11% hemicellulose, 8% of lignin, and 1.2% of pectin. By using the plasma generator under the diffuse coplanar surface barrier was used in this experiment. SEM was performed to analyze and determine the morphology of the surface of the fiber, shape, and other parameters. Mechanical properties were calculated by using UTM.

By comparing the treated and untreated fiber the result was calculated. The fiber is treated by plasma that has removed the surface of the waxy layer. Because this might cause some additional reaction with the other functional group. Hence this oxygen plasma treatment makes an oxygen functional group on the fiber surface that prevents the additional reaction with the other functional group [8].

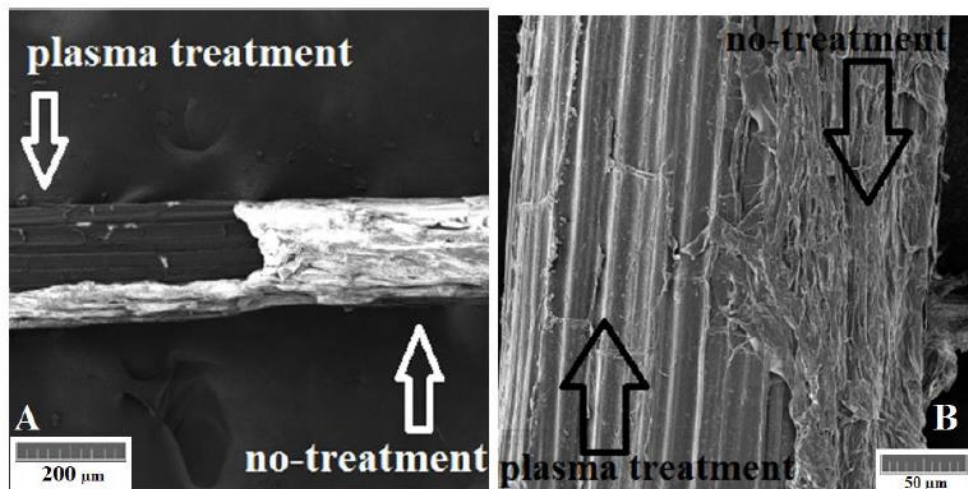


Fig. 3. Side view of abaca fiber before, and after treatment(A), and before, and after plasma treatment(B) [8]

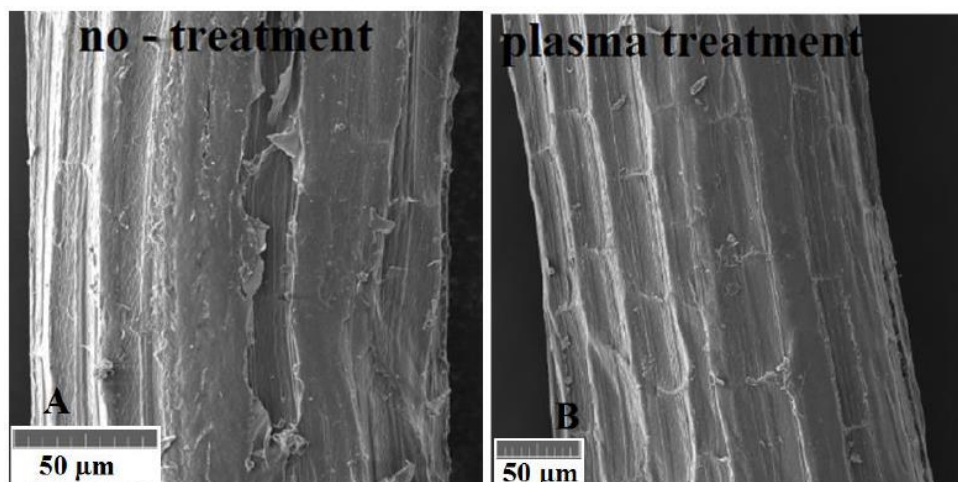


Fig. 4. Sisal fiber before treatment (A), and after treatment (B) [8]

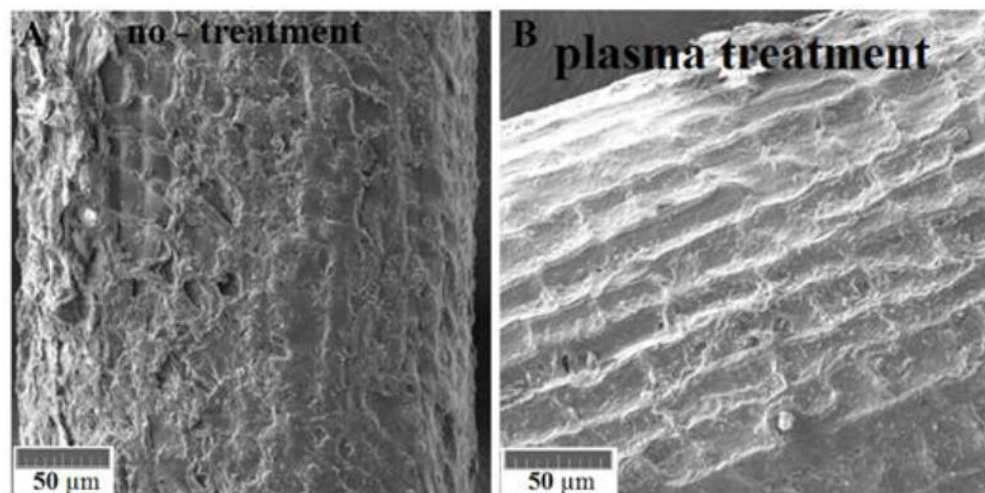


Fig. 5. Coconut fiber before treatment (A), and after treatment (B) [8]

In figures (Fig.5) it is easy to see both sides and a normal view of the fiber. The diameter of the fiber attains the dispersion state, and those dispersions are stated as variation co-efficient. Here the variation of co-efficient of coconut fiber is 37%, for sisal, it is 29% and abaca has 34% of variation co-efficient. After all the measurements it is easy to see the increase in the roughness of the fiber after treating with plasma this was clearly shown in the microscope. Due to oxygen plasma discharge, new oxygen functional was added to the surface of the fiber, which could help the fiber to maintain the interfacial interaction with the resin. The comparison between the treated, and untreated fiber shows the variation in the strength of the fibers.

Corona discharge:

Corona discharge is rather can say a modified version of plasma treatment. Corona discharge is also called plasma at standard atmospheric pressure. This plasma is formed by high voltage and the proximity of two metal plates (electrodes) in the atmosphere. This method modifies the property of the surface of the material to provide a good lifetime, and improve the bonding character of the surface, and enhance the corrosion resistance. The advantages of this method are very easy to use, the price is low when compared to plasma treatment, and the system is robust and easy to maintain. Here the drawbacks are limitations because by using this method It can only modify a very limited number of polymers. Treatment is two-dimensional, and most of this system is designed to work in open-air conditions [13].

Isotactic polypropylene (iPP), LDPE were used in this experiment. The contact angle of the material was measured to find the characterization of the sample. With the help of UTM, the strength of the adhesive joints was calculated for both material, this could help to find the mechanical properties. Hydroperoxide of the modified sample was calculated Spectro photochemically.

For treated iPP, the surface energy was calculated. After treatment shows the increase of surface energy of the polar component. Hydroperoxide concentration also increased gradually with density. After corona discharge, for a long time, the polarity of the additive added LDPE to the non-added one. Also, the hydrophobic property increases gradually with the course of the experiment period [13].

Silylation process:

By introducing the silanol group on the surface of the molecule with the help of the coupling agent increase the hydrophobic nature. Dimethylchlorosilane, isocyanatepropyltriethoxysilane, and hexamethyldisilazane (HMDS) are some of the reactive silylation agents [5][11]. HMDS is quite

inexpensive, stable, and easy to handle hence, it is a widely used one. During the silylation process, ammonia is the only by-product which is one of the main advantages. Easy handling is another advantage. But high reacting time and low silylation are some disadvantages [15]. To overcome this, the catalyst could be added. The surface modification by the silylation process helps to increase the hydrophobic nature, also thermal degradation, and reinforcement characteristics. there are two common methods of surface modification in the most common method is the liquid phase. In which the cellulose is immersed in the solution containing a silylating agent. Another method is called the vapor phase in which the surface is modified by using the vapor of the silylating agent at a particular temperature which gives a more stable, and smoother layer [16][17][18].

1.3. Review of literature analysis

Preparation of cellulose by using fluorine bearing silane coupling agent

The researcher used two types of fluorine-bearing alkoxy silanes as a silane agent. The names of the silane agents are 3,3,3-tri fluoro propyl trimethoxysilane (TFPS) and 1H,1H,2H,2H, perfluorooctyl trimethoxysilane (PFOS). In this research [19] they used microcrystalline cellulose, Avicell (AV), and Whatman Paper (WP) as cellulose, and Bi-distilled water, and high purity commercial n-dodecane, α - bromonaphthalene, diiodomethane, and formamide to measure contact angle water was used.

Grafting was done by mixing the silane solution with the cellulose. The material was undergone heat treatment under the vacuum for two hours then it kept for drying for 48 hours. After that contact angle was measured to analyze the surface modification. SEM and EDS were calculated to find the morphology of the material. After the analysis researcher found that the contact angle was increased after treatment that reduces incoming water hence the polar and dispersive character of the material also changed. This shows that the hydrophobicity of the cellulose increased [19].

Preparation of natural fiber/polymer composite using silane

Researcher [20] tried so many types of silanes (mainly Trialkoxysilanes) in the Natural fiber-reinforced composite (NFPC) to better the nature of the composites. Natural fibers have a lot of perks when compared to inorganic filler such as glass, carbon fibers. But the polar fibers have fundamentally low compatibility when compared to the non-polar fibers, this low compatibility is a major disadvantage for the natural composites. Because the hydrogen bond might form in between the two fibers, and that leads to form a bundle, and that cause irregularly distribution with non-polar matrix during the compounding process. This causes a reduction in stress transfer efficiency. Hence all the natural fibers should treat to improve their resistance regarding water, and enhance their wettability property, and promote adhesion. Silanes are considered an effective coupling agent, and they are mostly used to boost the nature of the composites. In the past years, many types of silanes are undergone tested as the coupling agent, and only very few got good results, most of the trialkoxysilanes got good results as a coupling agent [2]. In the research [20] amino silanes mainly gamma – aminopropyltriethoxysilane (APS) are said to mostly used stated as the coupling agent.

Hydrolysis process of silane: Alkoxy silanes can react with the silica group, and reduce their hydroxyl group, but silanes don't do the same when they are reacting with the hydroxyl group of cellulose because of the lower acidity of hydroxyl cellulose group when related with silanes. Also, the cellulose is mostly unreacted to chemicals, and their hydroxyl group has low accessibility. Hence the researchers used a different strategy [20] here in their research, to trigger the alkoxy silane they

hydrolyze the alkoxy group then they formed the silanol group more reactive. To hydrolyze the alkoxy group water is needed though under room temperature the fibers have some water molecules that are not enough to make perfect hydrolysis of silanes.

Here the researcher [20] mentioned the effect of hydrolysis in the silane structure, all the alkoxy groups are mainly ethoxy, methoxy. If hydrolyzing the alkoxy group under the same state, the methoxy group of the trimethoxy silane hydrolyzes first when compared to triethoxysilane. The number of the alkoxy group will help to find the volume of water to hydrolyze also, which affect the adhesion nature. Usually, Di and Tri alkoxy silane is more adhesive in nature than monoalkoxysilane. To hydrolyze one molecule of tri alkoxy silane at least a minimum of three molecules of water.

Interaction mechanism: In this research paper [20], they mentioned various methods to combine silanes and natural fiber. The main methods are fiber surface treatment, and modification of the cell wall is to treat silane solution with the fiber surface is by spraying. In this method, silanes are formed in solution, and directly sprayed on the surface of fibers, if the solution that made is without water then sprayed silane could undergo partial hydrolyzation. But there is a problem with spraying because spraying only result in the surface, and the inside of the fibers remain the same. In another method, the silane solution is directly entering into the extruder during the extrusion process. This process is easy and simple, but the main disadvantage is it will take some time to hydrolyze.

Here, the matrices (thermoplastic) are grafted with silanes, and this is used as a new coupling agent that will straight blend with the fibers and matrices. This method doesn't need any hydrolysis process. Interaction between the coupling agent and the fibers may proceed through the following process: [20]

- *Hydrolysis:* monomers of the silane are hydrolyzed with the water, catalyst, and redeeming the OH group that will enhance the reactivity of the silanol group.
- *Self-condensation:* condensation is important during the hydrolysis process because condensation should be less to make the silane free without absorbing the hydroxyl group. During the bulking process also, the concentration should be controlled to make the molecular size in the perfect state to diffuse into the walls of the cell. It can be controlling the condensation by controlling the pH of the hydrolysis arrangement.
- *Adsorption:* After the hydrolysis, the reactivity of the silanol group will enhance hence, the responsive silanol monomers are adsorbed to the OH group. Which also, based on the atomic size of the monomer. This silanol also adsorbs each other and form a polysiloxane structure.
- *Grafting:* the hydrogen bond between the fiber and the silanol group could be converted into the covalent bond, and during this process, it will eliminate some water molecules. The remaining silanol group in the fiber will again react with each other. The covalent bond that formed is not stable to hydrolysis.

The consequence of silane treatment on the property of fiber: It can be converting the hydrophilic fiber into hydrophobic by treating properly the surface of the fibers with silanes. The surface treatment only reduces the water absorption property, and, does not completely reduce because the silane did not fill the in the walls of the cell. But with the help of bulking treatment, it may decrease the size of the cell wall, and it can deactivate the hydroxyl functionality. The treatment to convert the hydrophilic fiber to hydrophobic fiber that could decline the hydrogen bond in the filler. The treatment of filler with a silane solution could cause a significant rise in the contact angle, the increase in contact angle increases hydrophobic nature.

Silane treatment also affects thermal steadiness. Throughout the preparation of the composites, the fillers are undergone heating in the extruder or the compounding machine. From this study [20] they are saying that there are only a few positive effects in the thermal property. In this study, the thermal stability of the fibers is analyzed using TGA. During the treatment, if the system contains an acidic catalyst or increase in temperature that significantly reduces the fiber strength. In some cases, the silane with an acidic catalyst is used as moderator at that time the pH was equal to the natural fiber in that time the fiber strength might affect.

Interaction with polymer matrices: Mechanical property is mainly based on the interaction among the silane treated fiber, and the matrix. Physical compounding of the fiber and the matrix increases the adherence this is due to inter-molecular entanglement. Between the jute fiber and polypropylene, the interfacial shear strength is determined by the microdroplet micromechanical test.

Also, physical blending only offers a limited development in mechanical properties. To get significant improvement in mechanical property covalent bond is needed. A strong covalent bond among the fibers and matrix leads to brittle composite. Hence, having only one option to make an effective covalent bond among the fiber, and matrix by plasma discharge. From this study [2020] it can identify that the most widely used silanes for natural fibers composites are trialkoxysilanes. Silanes are formed into reactive silanol by hydrolysis, and then it is condensed, adsorbed on the surface of the fibers at the specific temperature, and the pH. To increase the adhesion property, the hydrogen bond between the fiber and the matrix is changed into a covalent bond by heating the fiber at a certain temperature even though that bond is prone to hydrolysis. To improve sustainable adhesion, it needs to have chemical bonding than physical. Free radical is one of the effective ways to couple the matrix, and the fiber. By treating properly, the fiber, and the silane can increase the adhesion property also, it can expand the mechanical nature of the composite.

Surface tretament of cotton fibre with silane agent

The aim of this research [21] to reduce the hydrophilic property of the cotton fiber using a silane especially isocyanatepropyltriethoxysilane (IPTS), why because this is reactive to the hydroxyl group, and also, even very reactive to the low quantity that presents in the cellulose nanocrystal surface. In this research [21] cellulose nanocrystal is attained from the cotton fiber by hydrochloric acid hydrolysis. The nanocrystal is presented in the geometry like needle structure, which attained by hydrolytic break of the glycosidic linkage endorsed by hydronium ions that could enter the amorphous region of cellulose. Alkaline treatment is done before the acid hydrolysis to eliminate the non-cellulose fibers [22].

The cotton fiber was treated in the alkaline solution for two. The treated fiber is added to 35mL of HCL for three hours at 80°C, and this solution undergoes stirring for 45 mins. The chemicals used throughout the surface treatment were dimethylformamide (DMF), tetrahydrofuran (THF), 3-isocyanatepropyltriethoxysilane (IPTS), and the catalyst dibutyltindilaureate (DBTDL). After hydrolysis [21], the cellulose nanocrystal powder is obtained.

After the surface modification [21] the morphology shows the cotton fiber surface became more uniform and smoother. This is due to the elimination of non-cellulose fibers. Even the removal is in low concentration that makes changes in the cellulose surface. Surface treatment of the nanocrystal with IPTS was done on the surface of the fibers can delay their spreading in hydrophobic polymer matrices. The main reason for the selection of IPTS because this has a more reactive nature with less

hydroxyl group. During the process the condensation step is comparatively slow hence, the catalyst is added to initiate the reaction. The condensation step is important as well because of the oligomeric structure of polysilsesquioxane close to the exterior of the nanocrystal. This formation was very important in the surface treatment of the fiber. Despite the small quantity of the OH group located in the surface of the nanocrystal surface. This oligomeric formation could endorse an effective surface covering. SEM helped to analyze the morphology of the material (Fig 8).

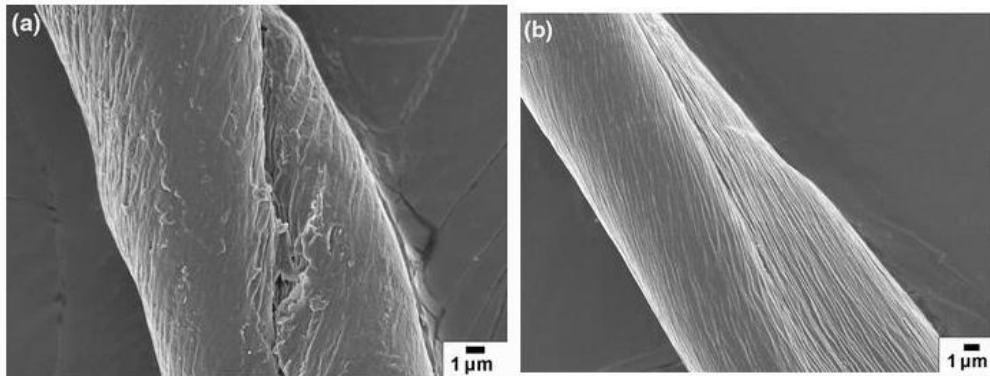


Fig. 6. SEM result before modification (a), and after modification (b) [21]

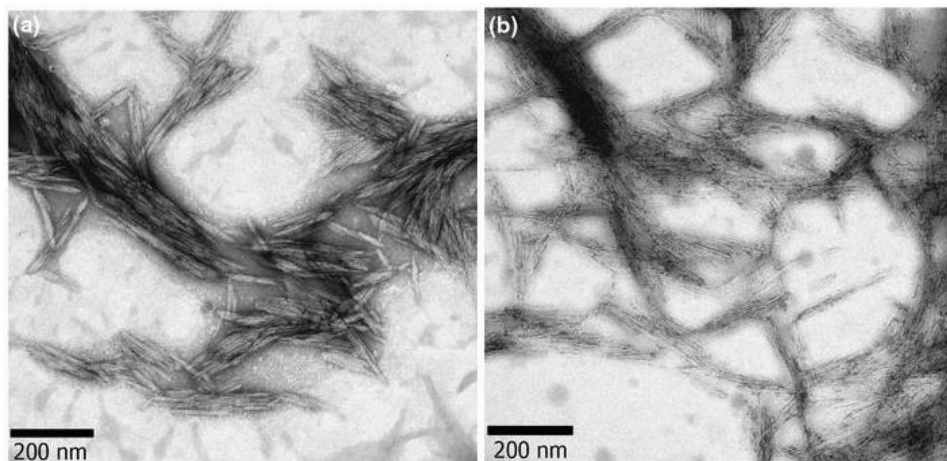


Fig. 7. TEM image before modification (a), and after modification (b) [21]

The chemical modification on the surface of nanocrystal was attained. The treatment of nanocrystals with IPTS was done to reduce the hydrophilic surface character of the crystal which, could boost the compatibility of the crystals with hydrophobic matrices.

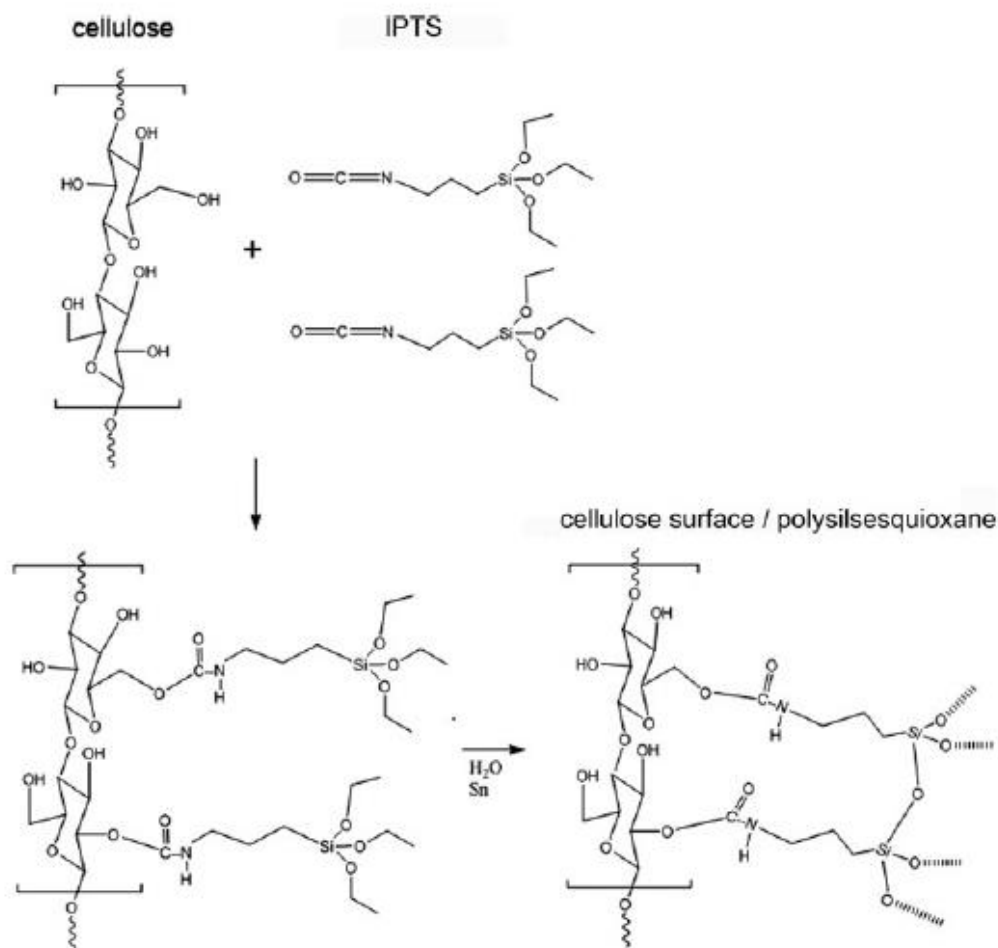


Fig. 8. Cellulose surface formation [21]

Treatment of cellulose fibers by using silanes with functionalized property

Surface modification[25] of the cellulose was done by organofunctional silane in the medium of ethanol or water. Silane was hydrolyzed into a substrate of cellulose hence it attained the adsorption equilibrium after that heat was practiced. To decrease the hydrophilic nature of the fiber, and, to enhance the adhesion property, the chemical alteration of the surface of the cellulose is necessary. This study [25] involves the grafting of the functionalized silane coupling agent. To expand the adhesion nature among the surfaces the tri-alkoxy silane is used. Gamma-Methacryloxypropyltrimethoxysilane (MPS), γ -Aminopropyltriethoxysilane (APS), Hexadecyltrimethoxysilane (HDS), γ -Mercaptopropyltrimethoxysilane (MRPS) are the silane coupling agent used in this research [24][25].

The fiber used in this research was the form of commercial microcrystalline particles. In this research paper [25], adsorption isotherms are studied, and the pre-hydrolyzed silanes were used as adsorption on the cellulose surface. This process is followed by layer by layer based on the ratio among the silane. Thermal treatment of the fiber is confirmed by the ESCA spectroscopy in the temperature of 120°C that tempted the chemical bonding of the silane. Due to the complexity of silane chemistry, they end up calling FTIR spectroscopy this will help to find the chemical group in the surface. The analysis was made between treated and untreated samples. The contact angle of the modified cellulose was analyzed before and after heat treatment. After analyzing the contact angle, and IGC, it can be found that the hydrophilic nature of the treated cellulose decreases. After treated with HDS or MPS-TEA some hydrophobic surfaces could be obtained. During the polymerization test, that showed due

to the presence of enough amount of functional group on the silane make them take part in the growth of polymer and gives the growth to chemical implanting of the fibers.

1.4. Conclusion of the literature survey:

From the above review of various research and reports, it was proven that the surface modification of cellulose would increase the hydrophobic nature. The above review shows the perks of various techniques of surface modification and various types of coupling agents. But from that HMDS seems pretty good because it has a lot of advantages when compared to another silane coupling agent. So, to rise the hydrophobic nature treating fiber surface is one of the methods.

2. Experimental

2.1. Materials

Polymer: polypropylene PPH-HV-50-46- (Plastimex-Sp z.o.o., Poland) with a melting point of $T_m = 160^\circ\text{C}$.

Fillers: agricultural by-products were applied for polypropylene properties modification.

- Wheat Husk
- Wheat Sieves

Compatibilizer: maleic anhydride grafted polypropylene Orevac CA 100 (Palmer Holland, USA). Orevac CA 100 is a type of polypropylene that is chemically functionalized with a high content of maleic anhydride such with properties:

- melt index – 10g/10 min
- melting point - 167°C
- density – 0.91g/cm^3 ,

The grafted maleic anhydride encourages polarity to PP and so, it shows adhesion properties on glass and natural fibers and mineral fillers. Therefore, it was used as a coupling agent to expand the reliable bonding strength among PP resin and natural fibers.

Modifier: liquid hexamethyldisilazane, HMDS with the molecular formula $(\text{CH}_3)_3\text{SiNH}\text{Si}(\text{CH}_3)_3$. It has the sum of the atomic weight of 161.4 g/mol and purity with 99% was used for filler particles surface silylation.

Antioxidant: in PP composition was added SONGNOXTM21B (mix of phosphite antioxidant: antioxidant = 2:1) (Songwon, Korea) to prevent plastic degradation when exposed to heat during processing.

The fillers – wheat husk and sieves used in this experiment are lignocellulosic residues from UAB Malsena – one of the biggest, and modern grain processing companies in Lithuania.

Procedure for obtaining wheat husk: when the impurities from the wheat husk removed, they underwent a cleaning process. In that scrubbing, grinding, and brushing of husk from grain would happen. After cleaning of the surface, the grains go into the airflow that sucks away removed husk, dust, and unwanted impurities. Such a mix was used in the project for PP modification (Fig.9.)

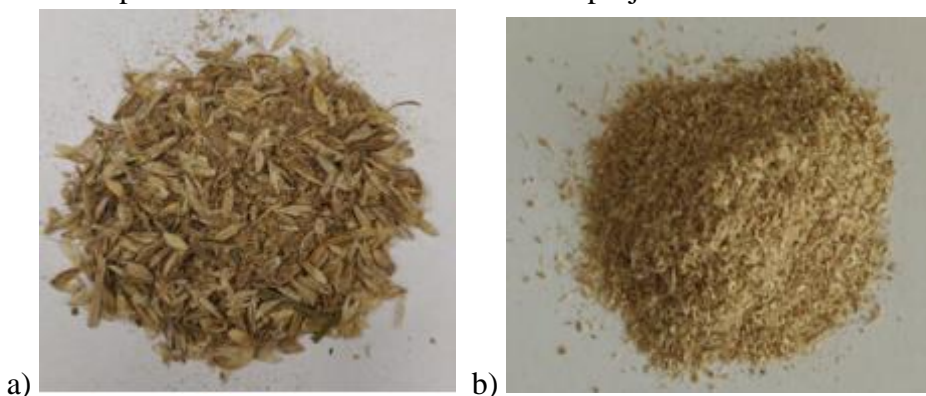


Fig. 9. Sample of wheat husk with dust and other impurities before milling (a), and after milling (b)

Procedure for obtaining wheat sieves: wheat grains inside have some living organisms like insects inside of them, which would live the whole time inside the grain. Such grain looks like a normal grain, but they have lower mechanical properties. Those infected grains are eliminated from the good grains by passing through an impact machine. The infected grains are destroyed during the impact and removed by a pneumatic machine. These grain residues were milled and used for the PP modification (Fig. 10.)

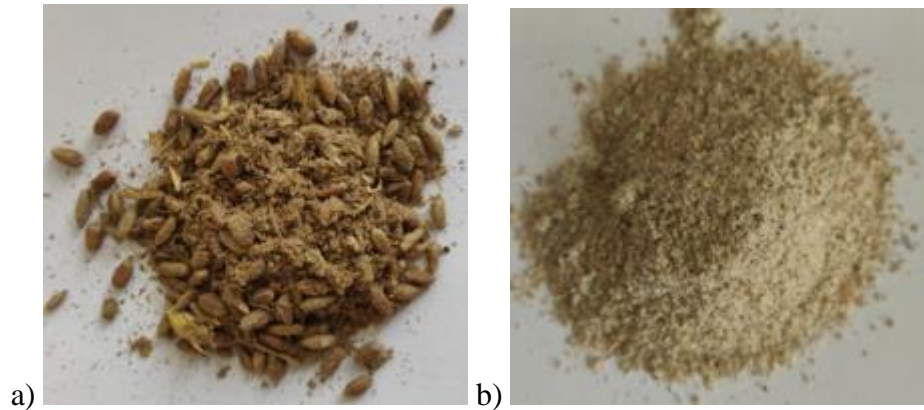


Fig. 10. Sample of wheat sieves before milling (a), and after milling (b)

2.2. Particles modification procedure

Silylation procedure – chemical vapor deposition method (CVD) was performed to modify the surface of wheat sieves and the husks particle. CVD is a process where the solid material is deposited from a vapor of a coupling agent by a chemical reaction. 1200 g of particles were placed in the desiccator filled with 55ml of hexamethyldisilane (HMDS) with molecular formula $[(CH_3)_3Si]_2NH$ (Fig.11.). The desiccator was kept in the oven for six hours at a temperature of $120^\circ C$ and periodically checked.



Fig. 11. Filler particles silylation procedure

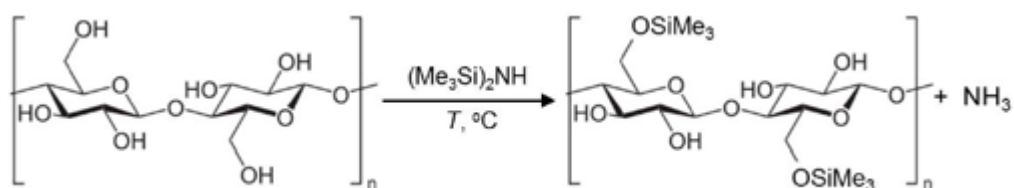


Fig. 12. The scheme of HMDS silylation of cellulose-containing materials

2.3. Methods of structure characterization

FTIR: the investigation of the filler particles was executed by Spectrum GX Perkin-Elmer FT-IR spectrometer (Perkin-Elmer, Waltham, MA, USA) which has the range from 4000 to 400 cm^{-1} . The particles were mixed with analytical grade KBr at a weight ratio of 1/100. All the spectrum was documented with a resolution of 4 cm^{-1} with a total of 10 scans.

TGA: was done to find the thermal stability of the particle by measuring the weight change corresponding to the temperature change. TGA 4000 Perkin-Elmer equipment was used. The parameters of testing environment nitrogen gas (N_2), flow rate – 20 ml/min, heating rate – 10°C/min.

SEM: S-3400N (Hitachi, Japan) was used to describe the shape, and surface morphology of the filler particles.

SEM-EDX: Instrument used to analyze the elemental composition of the sample and the energy-dispersive X-ray spectrometer (EDX, Bruker, Berlin, Germany) with a Bruker XFlash 4030 detector was used.

XRD: diffraction was executed using a DRON-6 diffractometer (Bourestnik, St. Petersburg, Russia). Diffraction patterns were documented at 35KV and 20MA. The measurements were noted in the 2 θ range of 2.5°-50 ° at the step size of 0.02 °(2 θ).

2.4. Methods of physical properties determination

Bulk density – was estimated according to the equation (Eq.1):

$$\rho = V/M \quad (\text{Eq.1})$$

In this case, a plastic container with a volume of 50ml was filled with the lignocellulosic sample and weighted under the resolution of 0.001g (Fig. 13). The average value of three measurements was used.



Fig. 13. Determination of bulk density of filler particles

Contact angle measurement – measurement was achieved with a pocket goniometer PG2 (Rycobel NV, Deerlijk, Belgium) at ordinary temperature with the help of the sessile drop method. Deionized water (~5 μL) was placed on the sample surface, and the image of the surface was captured. CA of the samples was measured by using software Motic Images Advanced 3.2. For this study, the tablet was performed by compressing husk, and sieves powder at 3 MPa for three minutes. The mean of three measurements at various places on the various sample was used.

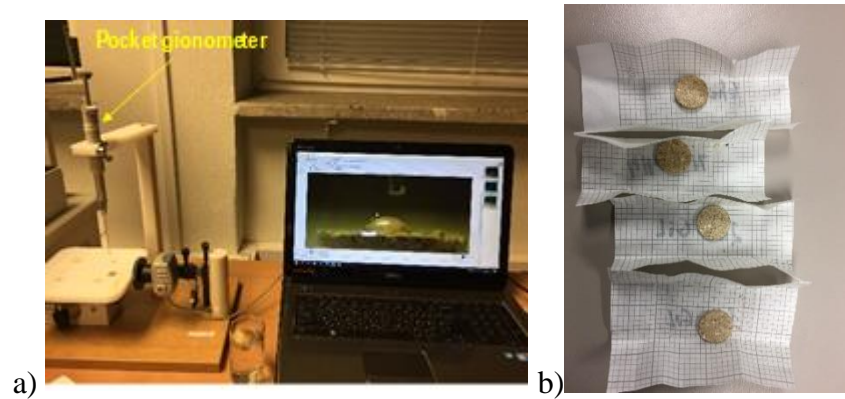


Fig. 14. The testing set for determination of the contact angle (a), and tablets of pressed filler particles (b)

Water vapor absorption test – the sample was poured into a plastic container and weighted (W_0). Then it was placed in the desiccator filled with water to obtain relative humidity $RH=100\%$ (Fig.15). It was placed in the oven at 50°C for a long time. After definite time samples are weighted and the mass of the sample at a specific period W_t was measured. WVA is calculated according to Eq.2.

$$WVA = [(W_t - W_0)/W_0] * 100 \quad (\text{Eq.2})$$



Fig. 15. Specimens in the desiccator filled with water

2.5. Mechanical properties at tension determination method

The specimen was made by using injection molding. The working temperature of the injection molding is 200°C . Six different specimens of type 1A with different composition [Table.3] was made for mechanical testing. The specimen was based on the requirement of standard LST EN ISO 527 used for tensile measurement (Fig16). The dimension of the specimen was 10mm in width.



Fig. 16. The specimen used to measure tensile strength

Six different PP compositions were used those are PPH, Orevac C100, wheat sieves, wheat husk, and Songnox 21B (Table.3)

Table. 3. Polypropylene compositions used for investigation

Components	Composition, wt%					
	I	II	III	IV	V	VI
PPH	100	70	74.8	49.8	74.8	49.8
PP-g-MA (Orevac C100)	-	30	15	30	15	30
Wheat sieves	-	-	10	20	-	-
Wheat husk	-	-	-	-	10	20
Songnox 21B	-	-	0.2	0.2	0.2	0.2
Content, wt%	100	100	100	100	100	100

UTM was used to calculate tensile strength (Tinius Olsen, Rehill, England). Vernier caliper was used to measure the thickness, it was measured at five dissimilar places, and the average was calculated. By using the average thickness of five different specimens the tensile strength was calculated.



Fig. 17. The specimen in the UTM

The tension was applied to the specimen from both the end. With the help of UTM the stress, strain, and young's modulus were calculated. Here, stress is a dividend of the amount of force applied to the specimen, and the cross-section area of the specimen. Stress equation is (Eq.3):

$$\sigma = F/A_0 \quad \text{Eq. 3}$$

σ	Stress (N/m ² , Pa)
F	Force (N)
A ₀	The cross-section area of the specimen (m ²)

Also, the strain was calculated. Here, the strain refers deformation of the specimen after the force is applied. The strain equation is (Eq.4)

$$\varepsilon = (L - L_0) / L_0 \quad \text{Eq.4}$$

ε	Strain
L	Length after the force applied
L ₀	Length at initial

Finally, Young's modulus was calculated. The Young's modulus is stress divided by strain (Eq.5).

$$E = \sigma / \varepsilon \quad \text{Eq.5}$$

3. Result and discussion

3.1. Lignocellulosic wheat waste particles characterization

Wheat sieves have more percentage of hemicellulose than cellulose because the cell wall of the endosperm of wheat is rich in hemicellulose (Table 4) (Fig.18). Besides, as can be seen from Fig.10 there are many grains in the composition of wheat sieves sample, resulting in a high amount of starch and proteins. The wheat husk has cellulose that is thrice larger than the content in wheat sieves. The hydrophilic nature of the husk is significantly lower than the sieves due to the wax layer.

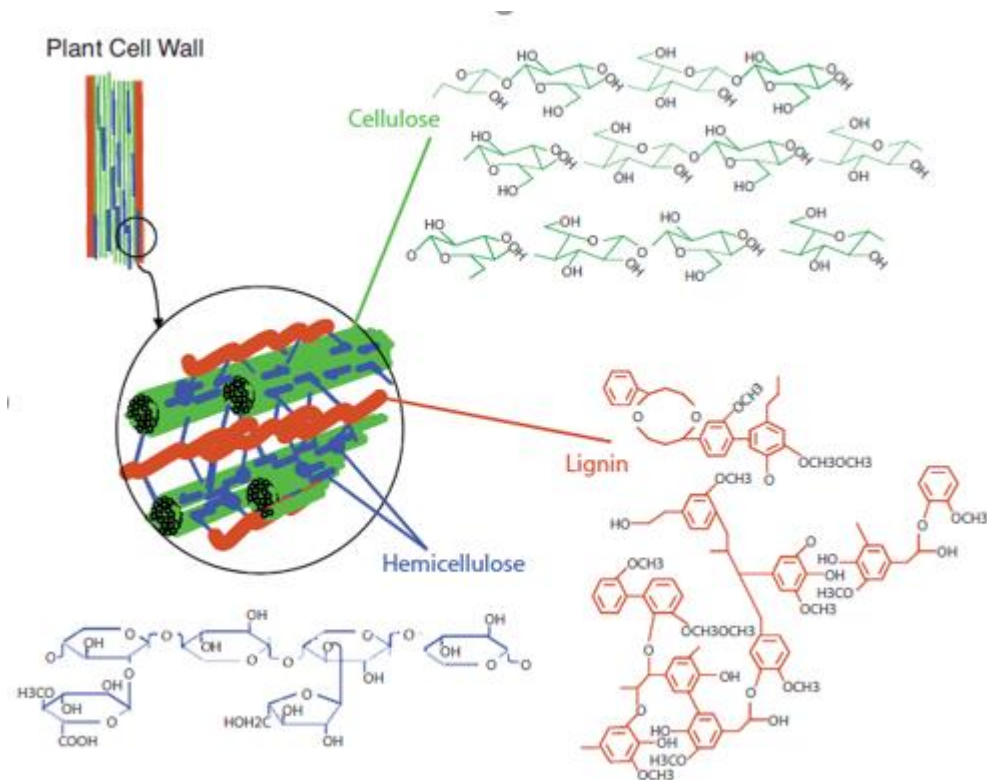


Fig. 18. Broken view of lignin, hemicellulose, and cellulose from the plant cell wall

Table 4. Composition % of lignocellulosic particles in wheat sieves, and wheat husk

Sample	Composition %				
	Cellulose	Hemicellulose	Lignin	Others	Reference
Wheat sieves	9.60 – 10.5	31.5 - 33	44.9 – 46.2	12 - 14	[6]
Wheat husk	36	18	16	30	[7]

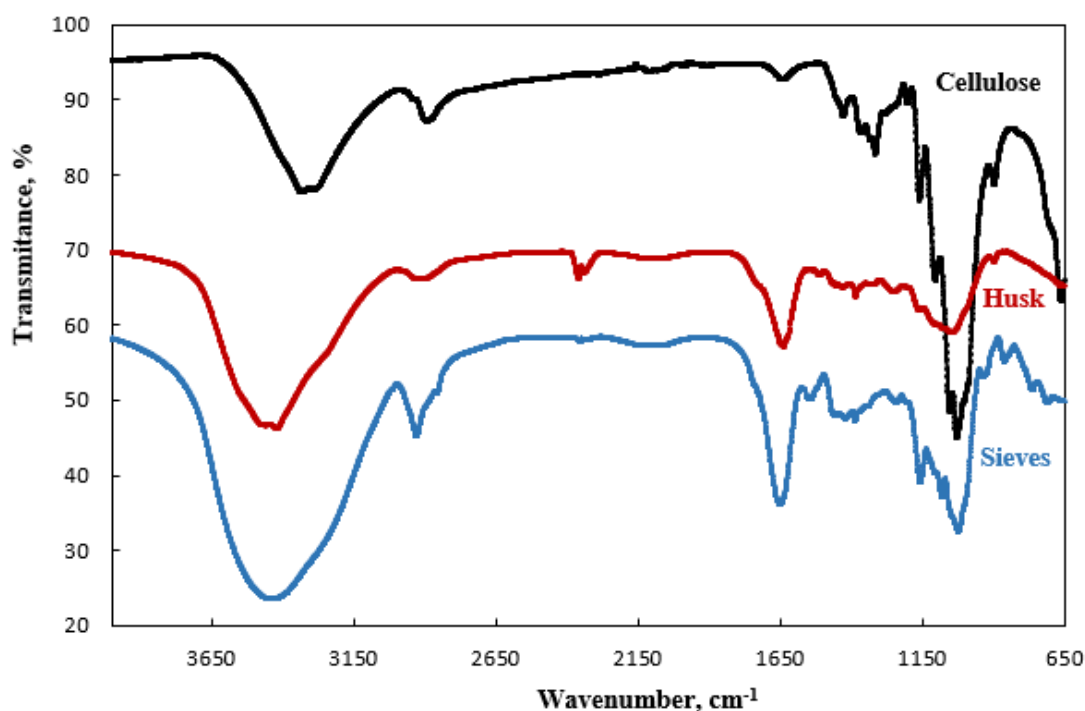
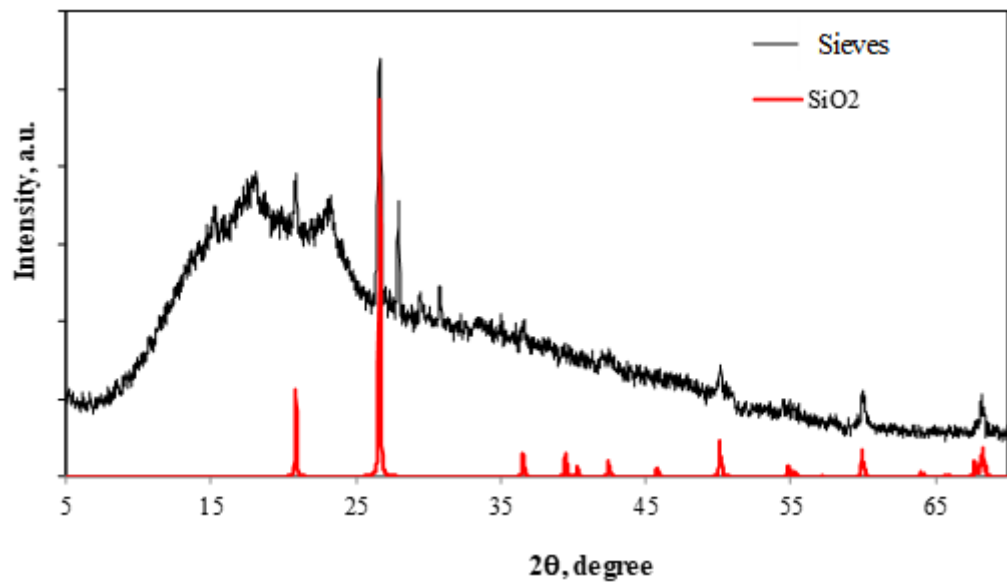


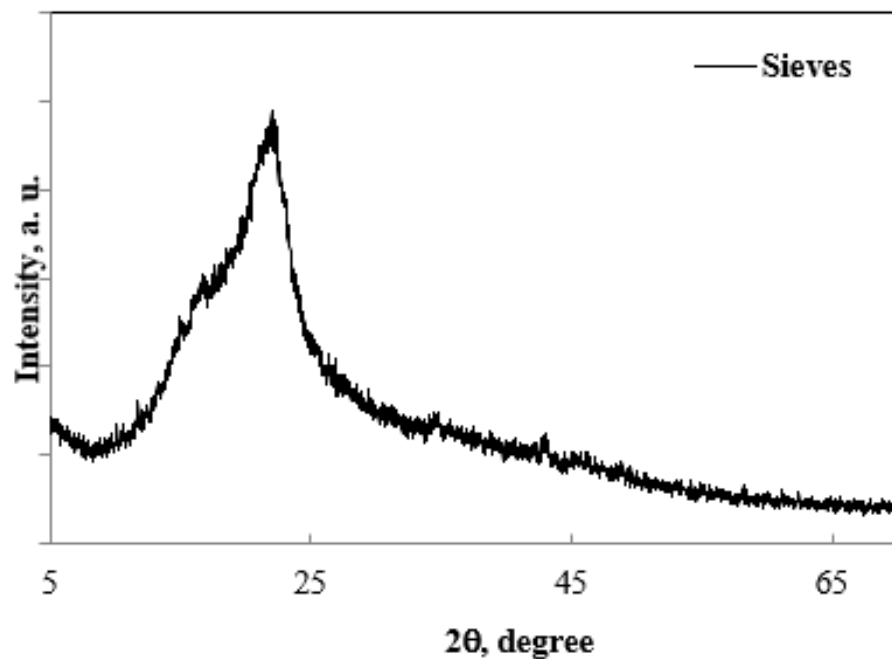
Fig. 19. FTIR spectra of wheat sieves, husk, and the cellulose

In Fig.19 FTIR spectra of wheat sieves, and the husk is represented and compared with the spectra of cellulose. All three spectra appeared to be similar and associated with cellulose and hemicellulose. Cellulose has an intensive peak at 1100 cm^{-1} , which represents the strong occurrence of C-O stretching. The non-intensive peak at the band around 1600 cm^{-1} showings a small amount of C=O group. Around the region, $1300 - 1200\text{ cm}^{-1}$ cellulose peaks could refer to the vibration of C-O stretching. In the regions around $1620-1600\text{ cm}^{-1}$, the cellulose has low peaks related to C=C stretching. In the regions from $2830\text{ to }2700\text{ cm}^{-1}$ cellulose peaks represents C-H. The spike at 3300 cm^{-1} shows the presence of O-H stretching. There is only an absorption band at 2356 cm^{-1} , which indicates SiO_2 impurities, especially in the case of husk.

XDR diffractograms show the chemical nature and the degree of crystallinity of material (Fig.20). It is visible both the wheat waste has low peaks intensities. The peaks are low which means the arrangement is not in order also there is a disorder in the arrangement. The atomic position of the crystal structure also represents the peak intensity. The diffraction patterns of wheat sieves mainly have four characteristics peaks at $2\theta = 15, 17, 18,$ and 23° . These peaks are typical of the A-type starch formed by short chain amylose [28]. Besides, the peaks are higher in the region where the SiO_2 atom presents. Hence this shows the sieves have Impurities (Fig.20.a). The diffraction pattern of the husk has four peaks characteristics of nature cellulose (Cellulose I). Which are approximately located at $2\theta = 15, 17, 22,$ and 34.7 respectively. Corresponding to the (110), (110), (002), and (004) planes of crystal respectively [27]. The intensity of peaks is low showing that the degree of crystallinity of samples is very low.



a)



b)

Fig. 20. XRD diffractograms of wheat waste particles

3.2. The effect of surface treatment of the morphology on lignocellulosic wheat waste particles

The previous investigation shows that the addition of wheat waste decreases the mechanical properties of the PP composition due to the low adhesion interaction of filler with the polymer matrix. Hence, the surface of the samples was modified by silylation to increase the compatibility of blend components. From the FTIR spectra present in Fig.21, it is visible that the new absorption spike is noticed at 839 cm^{-1} in the spectra of wheat husk. It can be assigned to vibration of Si-C stretching shows the various chemical elements with trimethylsilyl ($-\text{O}-\text{Si}-(\text{CH}_3)_3$) appear on the surface of the husk. However, no changes were detected in the spectrum of sieves. It may be supposed that sieves surface silylation influences the intensity of bands associated with OH groups. It should be mentioned that moieties are present in a very fine layer on the fiber surface. Hence, their amount is low and detection by FTIR is difficult [6].

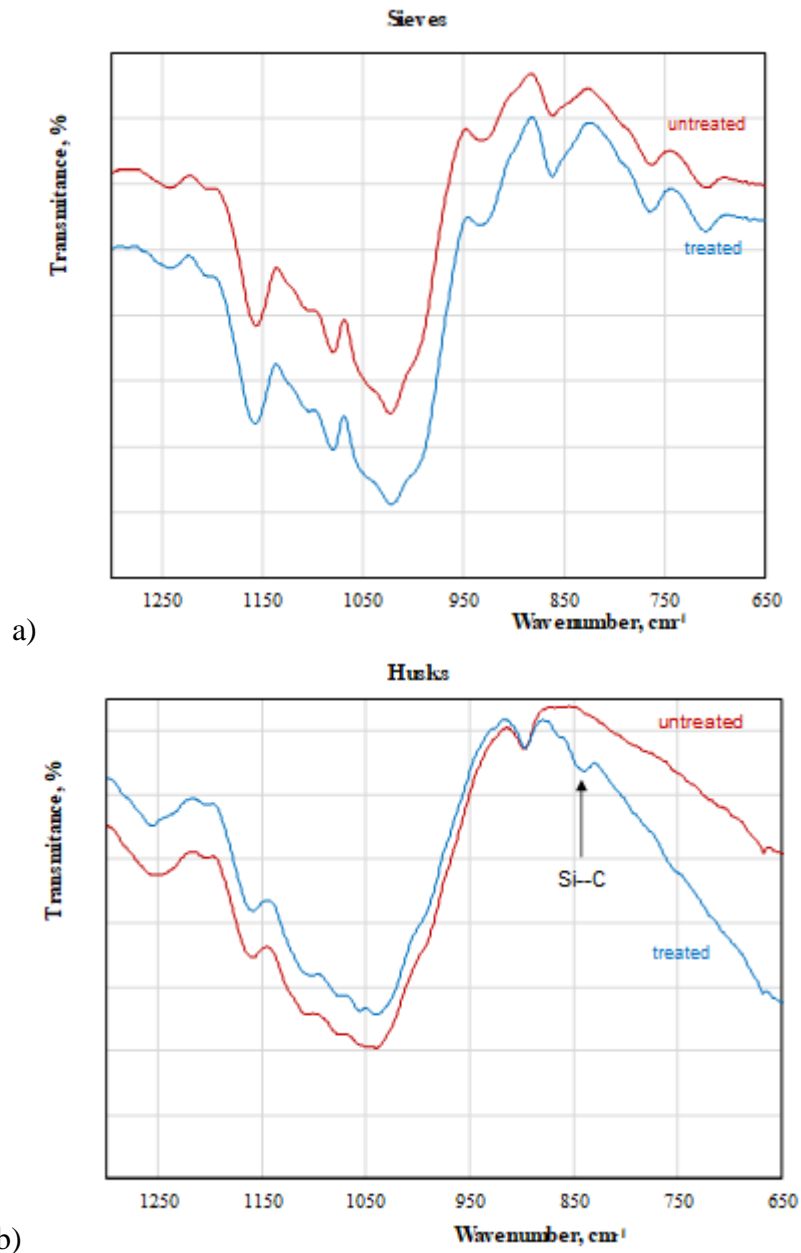


Fig. 21. FTIR spectra of wheat sieves (a), and wheat husk (b)

SEM was executed to observe the morphology, particle size, and shape of the lignocellulosic wheat waste. Fig.22 a) shows a clear view of the shapes of the untreated wheat sieves show different shape. Some look like irregular circles, while some others look like a rectangle in shape. Besides, starch granules are visible. They are mostly spherical or oval with various sizes. The shapes of particles of treated wheat sieves seem the same when compared to the untreated sieves. But at the higher magnification of treated sieves seems smoother than the untreated one.

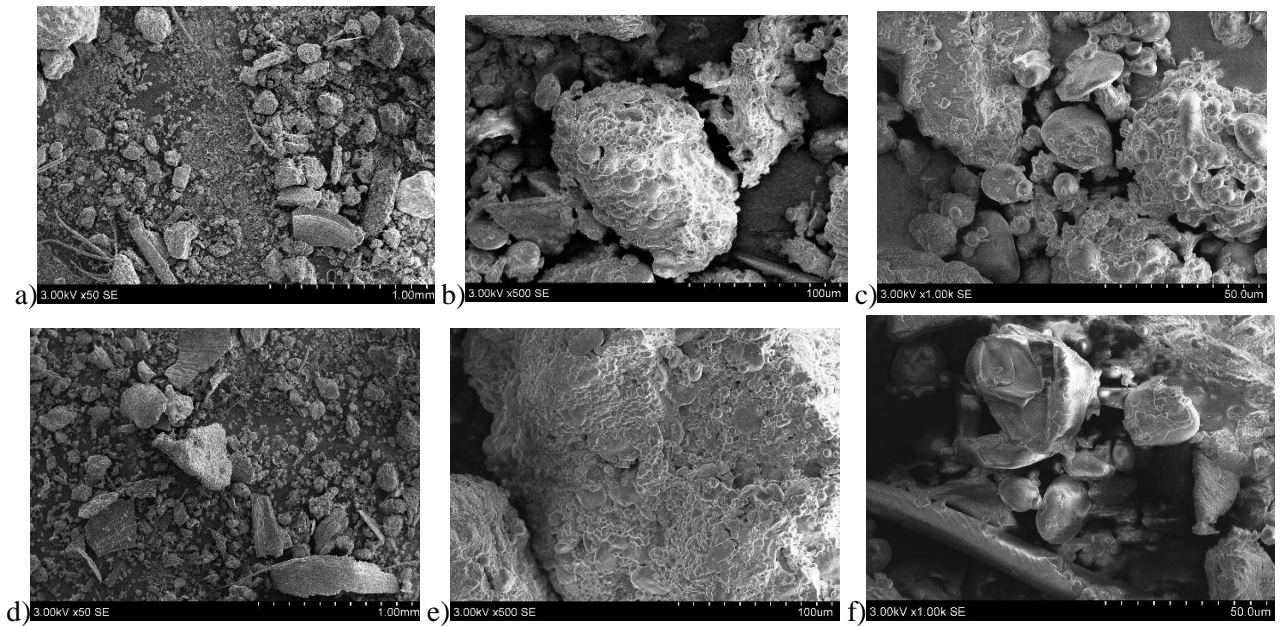


Fig. 22. SEM micrograph of wheat sieves before treatment (a-c), and after treatment (d-f) at different magnification: a, d – 50; b, e – 500, and c, f – 1000

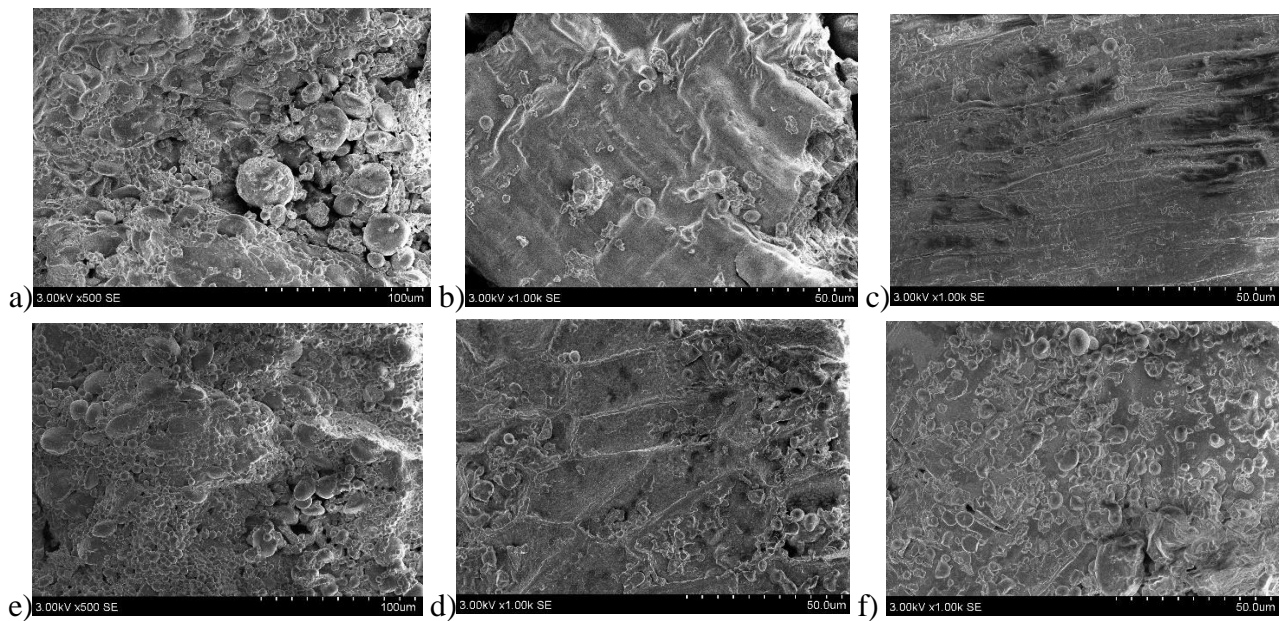


Fig. 23. Surface morphology of wheat sieves before treatment (a-c), and after treatment (d-f) at different magnification

Fig.24 shows the histogram of the untreated and treated wheat sieves. In untreated sieves, the length fluctuated from 0.1 to 0.5mm, and the average value is 0.2mm, while in untreated sieves, the length fluctuated from 0.1 to 0.9mm, and the average length is 0.4mm. The area also remains the same with no marked changes.

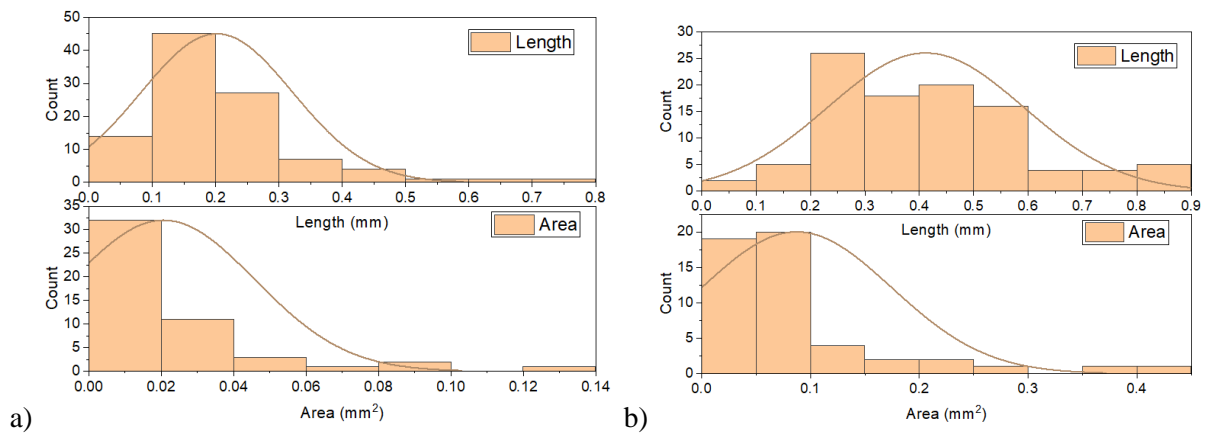


Fig. 24. Histogram of wheat sieves particle size dissemination before (a), and after treatment (b)

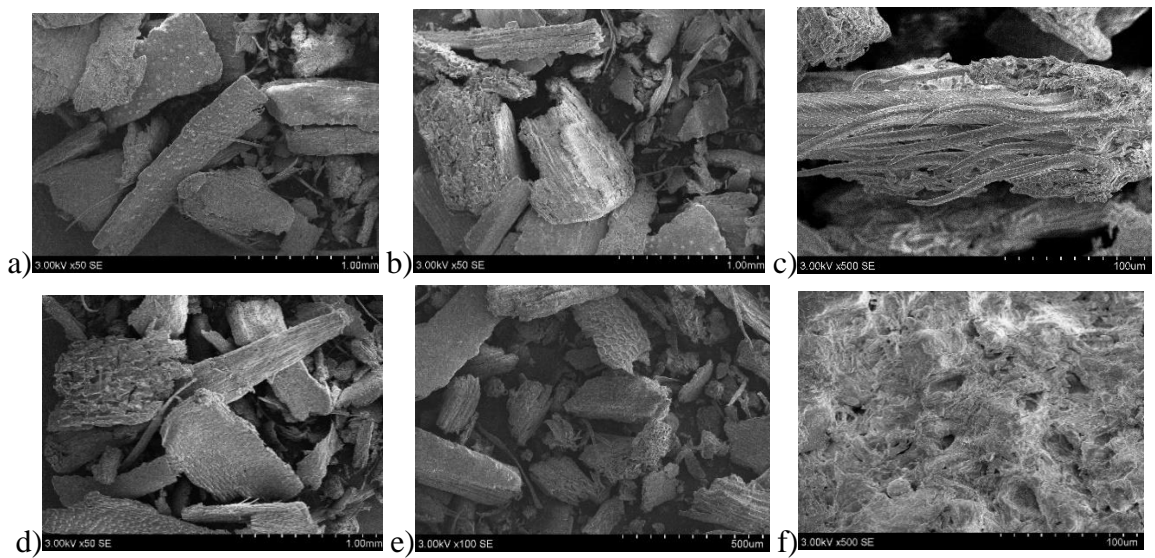


Fig. 25. SEM micrograph of wheat husk before treatment (a-c), and after treatment (d-e) at different magnification

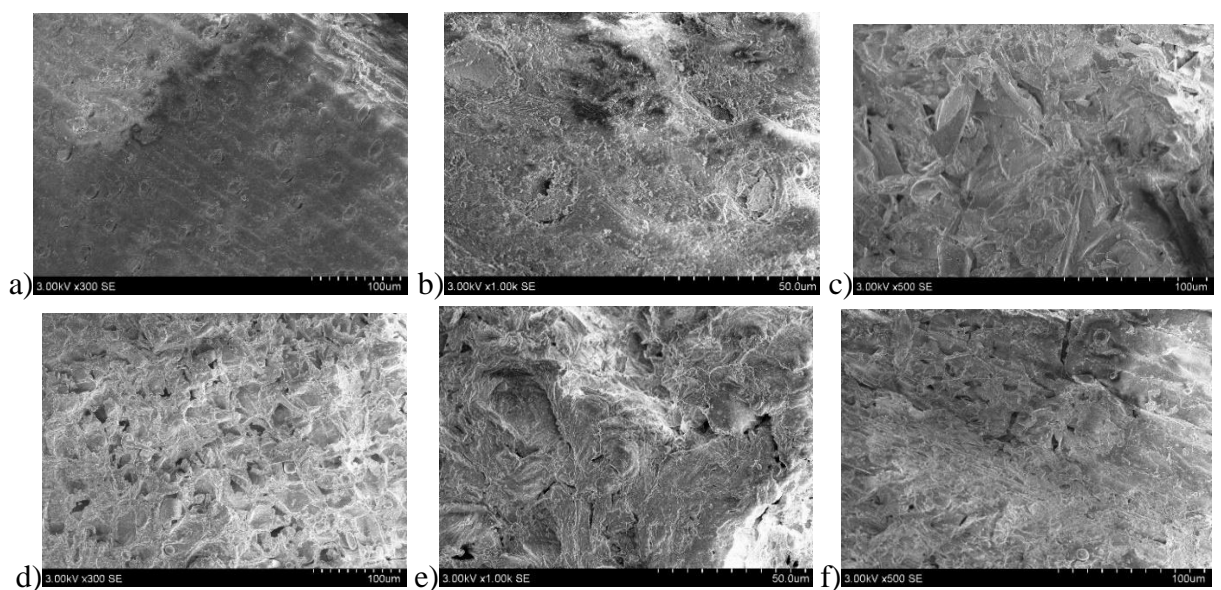


Fig. 26. Surface morphology of wheat husk before (a-c), and after treatment (d-f) at different magnification

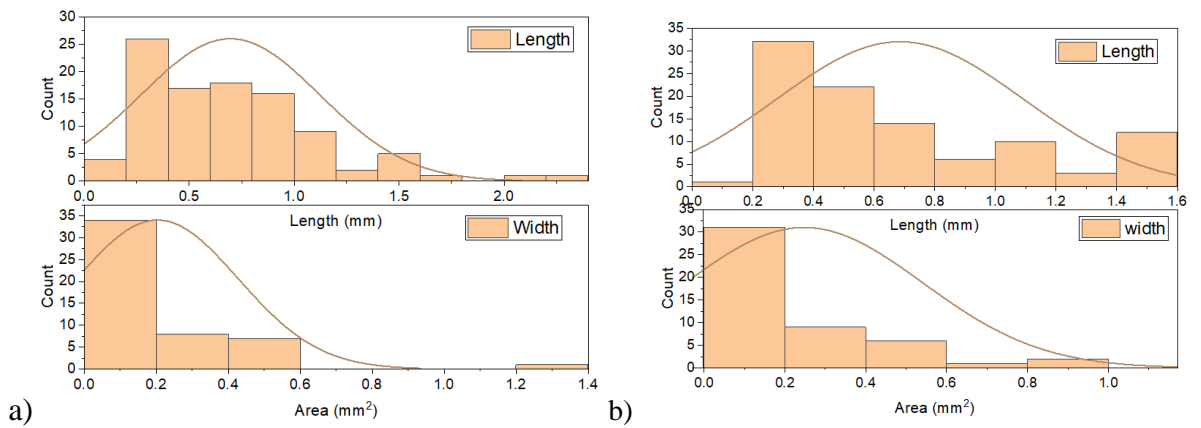


Fig. 27. Histogram of wheat husk particle size dissemination before treatment (a), and after treatment (b)

The particle shape of wheat husk is close to a rectangular shape (Fig.25). Comparison of the shape of untreated and treated husk show no difference in particle shape

The histogram shows the particle distribution of wheat husk before and after treatment (Fig.27). Here, the length of the husk fluctuated from 0.5 to 2.0 mm, and the average is near 1 mm and in the treated husk the length distributed from 0.2 to 1.5 mm here, the average is 0.8mm. That shows there are no changes in the length of husk after treatment. That is the same for width also because both treated and untreated husk has the same average width.

Fig.28 and Fig. 29 illustrate the inspection spectra of the particles acquired for wheat sieves and the husk correspondingly. All the waste samples contain carbon, oxygen, and a minute amount of silicon, potassium, phosphorous, sulfur, sodium, calcium, aluminum, magnesium. The elemental composition and oxygen/carbon ratio of untreated and treated samples are in Table.5.

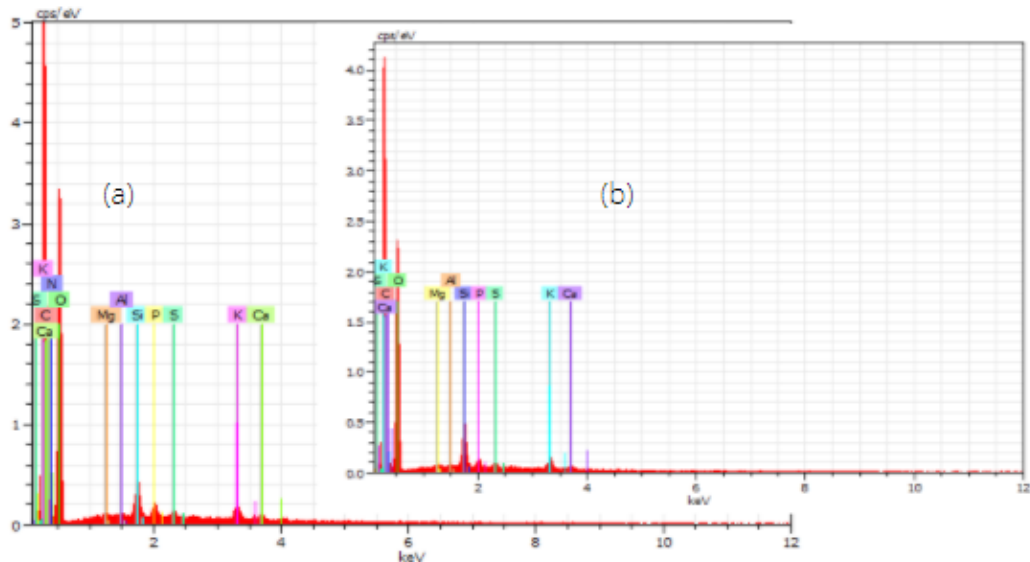


Fig. 28. SEM-EDS data of wheat sieves before (a), and after treatment (b)

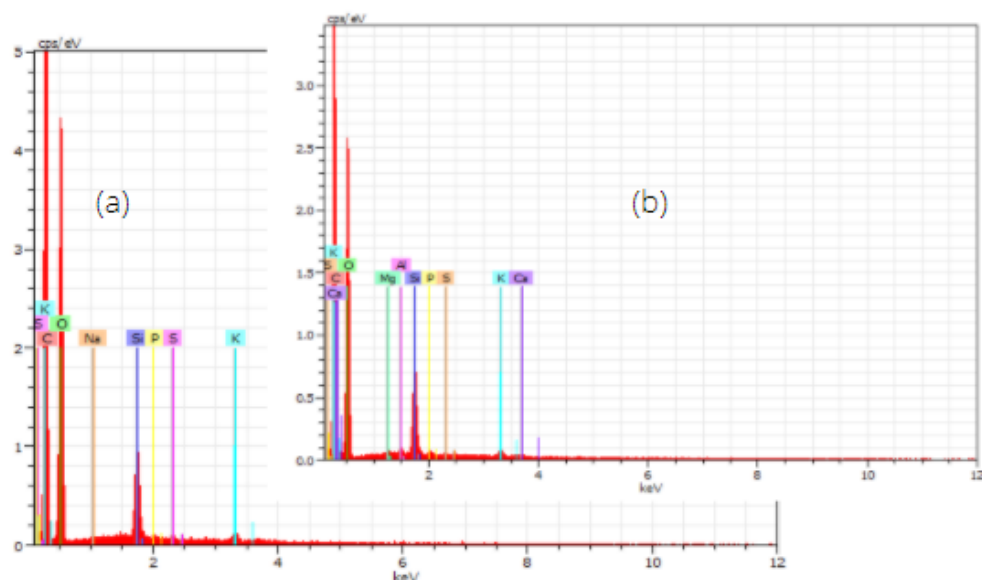


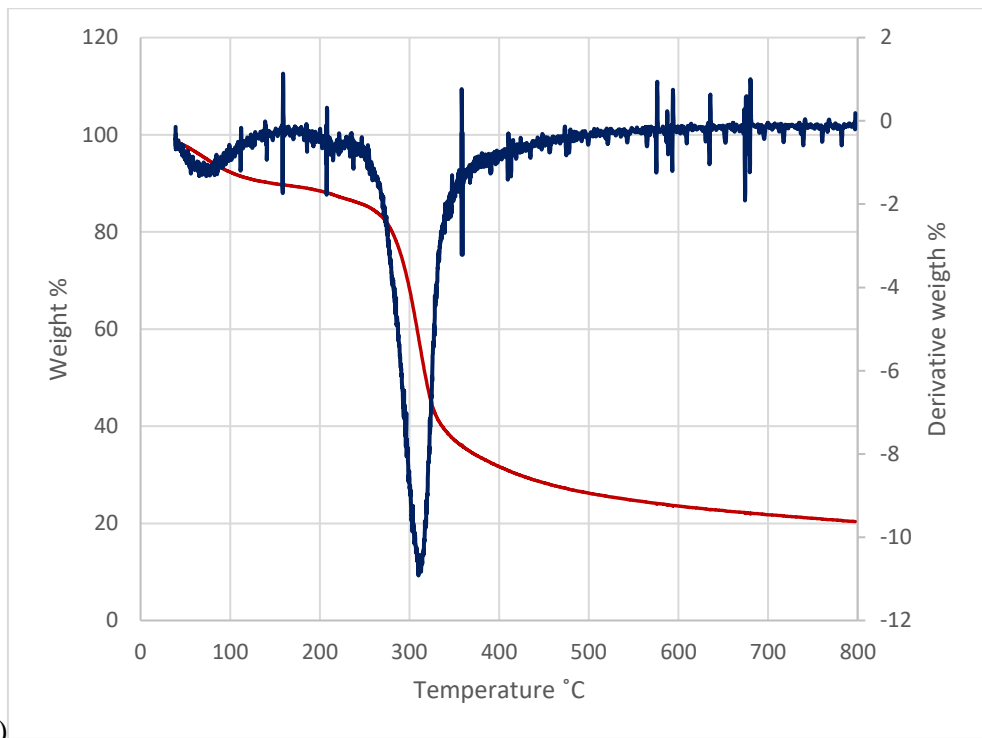
Fig. 29. SEM-EDS data of wheat husk before (a), and after treatment (b)

Table. 5. Elementary analysis of untreated and treated wheat waste particles

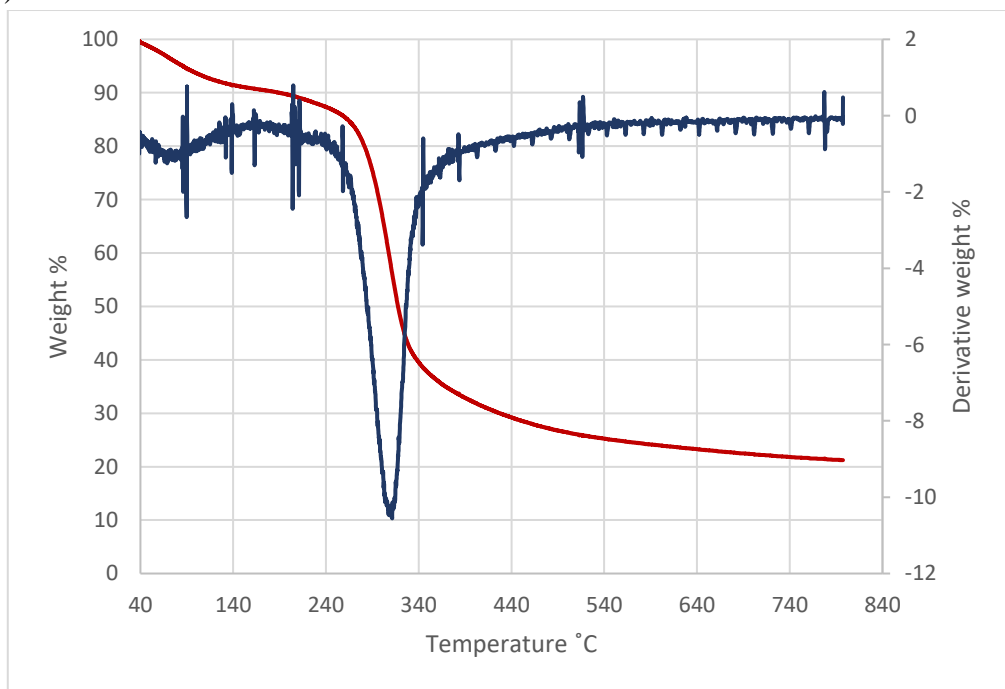
Elements	Wheat sieves untreated			Wheat sieves treated		
	wt%	at%	O/C	wt%	at%	O/C
Carbon	49.97	57.55	0.70	50.85	58.69	0.68
Oxygen	46.6	40.3		46.1	39.94	
Silicon	0.77	0.38		1.44	0.71	
Elements	Wheat husk untreated			Wheat husk treated		
	wt%	at%	O/C	wt%	at%	O/C
Carbon	49.97	57.63	0.72	49.31	57.17	0.72
Oxygen	47.63	41.23		47.38	41.24	
Silicon	1.93	0.95		2.47	1.22	

All the wheat samples show a high amount of oxygen. It is close to the value characteristic of cellulose. However, from Table.6 it is evident that the O/C ratio practically does not depend on the sample type and surface nature. Meanwhile, the amount of silicon on the sieves and husk surface after treatment with HMDS increases approximately 90 and 30%.

TGA and DTG curves were used to estimate the weight loss and to find the decomposition of wheat samples at various temperatures. From Fig.30 it is visible that different lignocellulosic waste to be investigated has similar TG and DTG curves due to their similar composition. As we can be seen from TGA curves, initially the weight of samples drops slowly, then the weight drops sharply and finally turns back to the normal slope



a)



b)

Fig. 30. TGA and DTG curves of wheat sieves before (a), and after treatment (b).

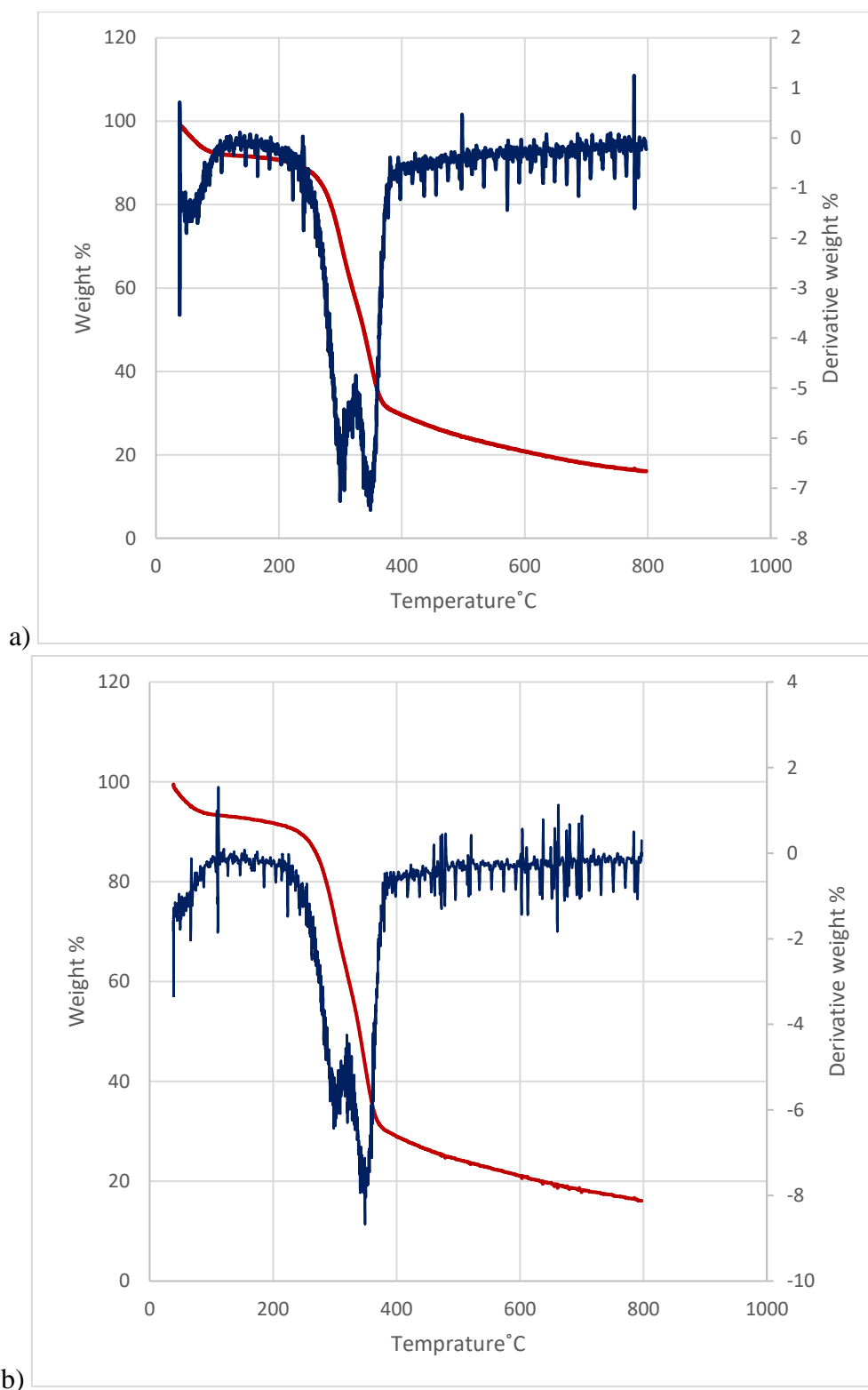


Fig. 31. TGA and DTG curves of wheat husk before (a), and after treatment (b)

The initial loss of weight is detected at 50°C because of the evaporation of absorbed water in the wheat waste particles. After that, the wheat sieves got their single decomposition step at a temperature of 312°C. For the husk, two decomposition steps are characteristic at temperatures 307°C, and 350°C. The spike around 300°C matches the hemicellulose and its thermal decomposition and the glycosidic linkage of cellulose, while the spike at 350°C is because of the decomposition of α -cellulose. The lignin decomposition proceeds near 420°C. The treatment of samples surface with HMDS shows no

influence on the decomposition temperature of wheat waste. However, a more detailed inspection shows that up to 50% of weight loss the decomposition of treated samples proceeds slower due to the origin of a chemical fraction with trimethylsilyl ($-O-Si-(CH_3)_3$) on the surface of lignocellulosic particles [Table.6]. Residue amount in the case of sieves is higher (21mg) compare to the husk (16mg).

Table. 6. Kinetics of temperature changes in wheat sample

$\Delta\mu$, %	Temperature (°C) of weight changes of samples:			
	wheat sieves		wheat husk	
	untreated	treated	untreated	treated
5	73	90	66	69
10	150	190	222	241
50	319	324	339	340
75	538	540	489	489
Residue at (800 °C), mg	21	21	16	16



Fig. 32. Bulk density of wheat sieves, and husk

From Fig.32 it is evident that the bulk density of the untreated sieve decreases after treatment. The change in density after treatment is 9% and for husk, density decreased (14%). After treatment, the interaction between the particles decreased due to increasing repulsion between particles. Therefore, the ability of the particles to form aggregates also decreased.

The contact angle changes of wheat sieves and husk during the surface treatment are shown in Fig.34, and 35. The contact angle of water on wheat sieve surface after treatment with HMDS started to increase gradually and reached 81°. In the husk, it was 72° and after treatment it increased to 108°. At initially, the contact angle was low, which shows the hydrophilic nature, and after treatment with HMDS, the contact angle increased and got more hydrophobic nature this is due to surface treatment of the wheat sample with HMDS.

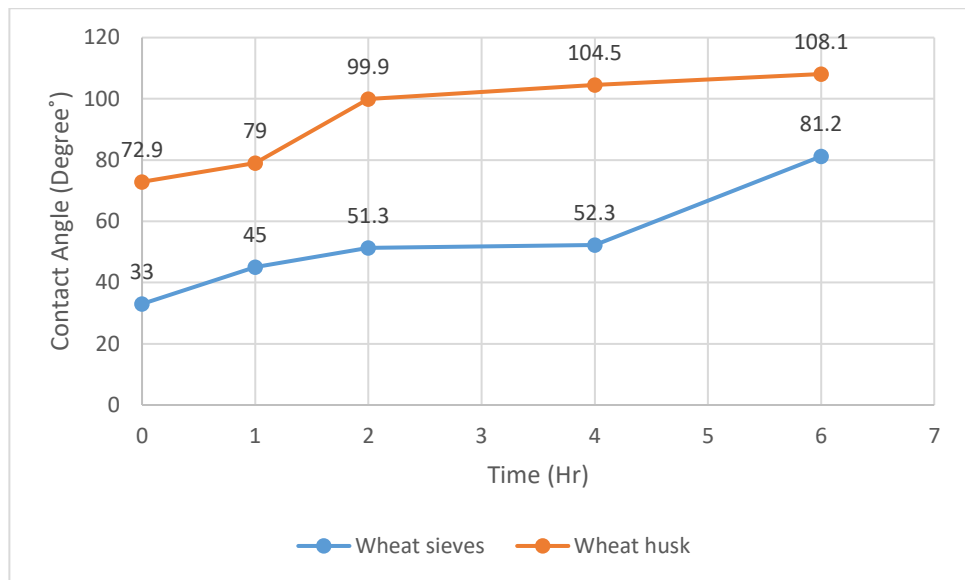


Fig. 33. The contact angle of water sieves, and husk

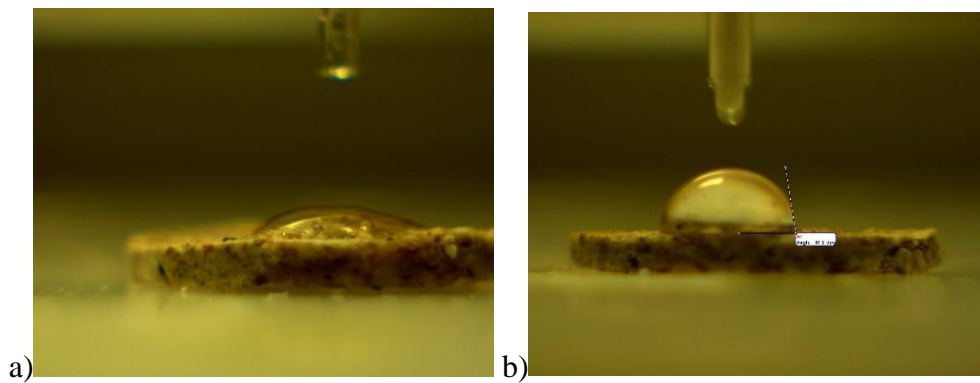


Fig. 34. The contact angle between wheat sieves untreated (a), and treated (b)

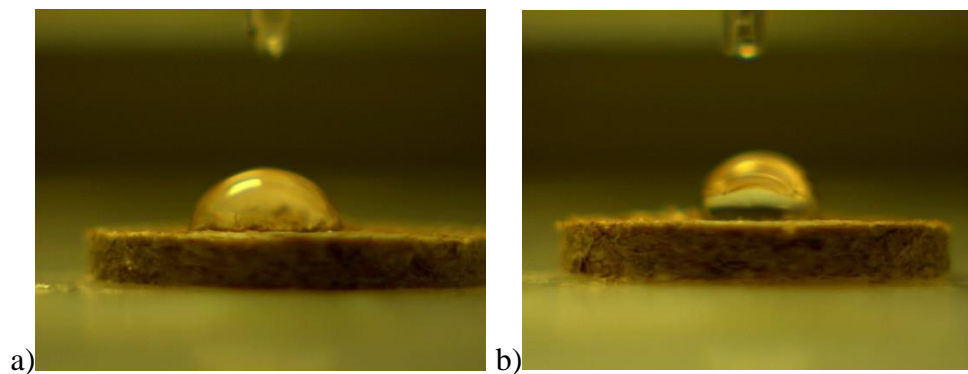


Fig. 35 Contact angle between wheat husk untreated (a), and treated (b)

Water vapor absorption test was determined for wheat waste at temperature 50°C at relative humidity $\text{RH} = 100\%$ for 15 days. Fig.36 shows the WVA the water-absorbing nature of the wheat waste. In the beginning, both the samples absorb the same amount of water but after 144 h untreated sieves started to absorb more water than treated sieves here, in the husk, after 72 hours itself the untreated husk started to absorb more water than the treated one. In the end, untreated sieves absorb 36% of water more than the treated sieves here, in the husk, it absorbed 11% than the treated one. After treatment, the untreated sample absorbs a lot of water this might due to surface modification.

Absorption mainly takes place due to hemicellulose, cellulose, and lignin, and the surface of cellulose contents [6]. From the correlation coefficient result of all the samples, it was clear strength of the relationship is high but for treated sieves, the strength is low when related to untreated sieves this might due to the surface treatment of samples.

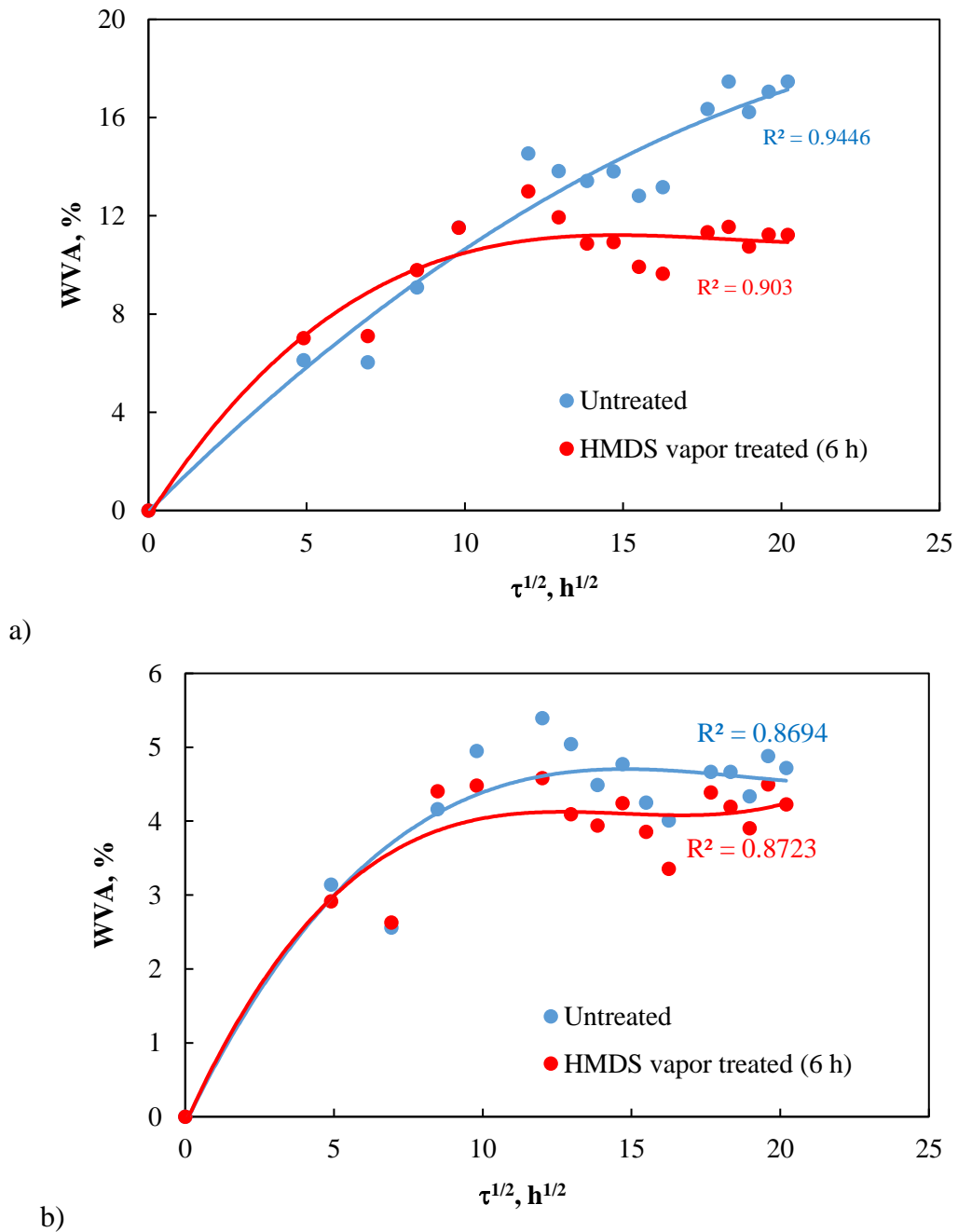


Fig. 36. WVA as a function of the square root of time of PP composite (a) with wheat sieves, and (b) with wheat husk

3.3. The effect of surface treatment on the polypropylene and lignocellulosic wheat waste composite structure and mechanical properties

The stress-strain curve of the material helps to understand the deformation behavior of the material. From Fig.37 it is evident that the deformation character of all compositions is similar. However, wheat waste fillers decrease the deformation ability of PP, although slightly increases the tensile strength.

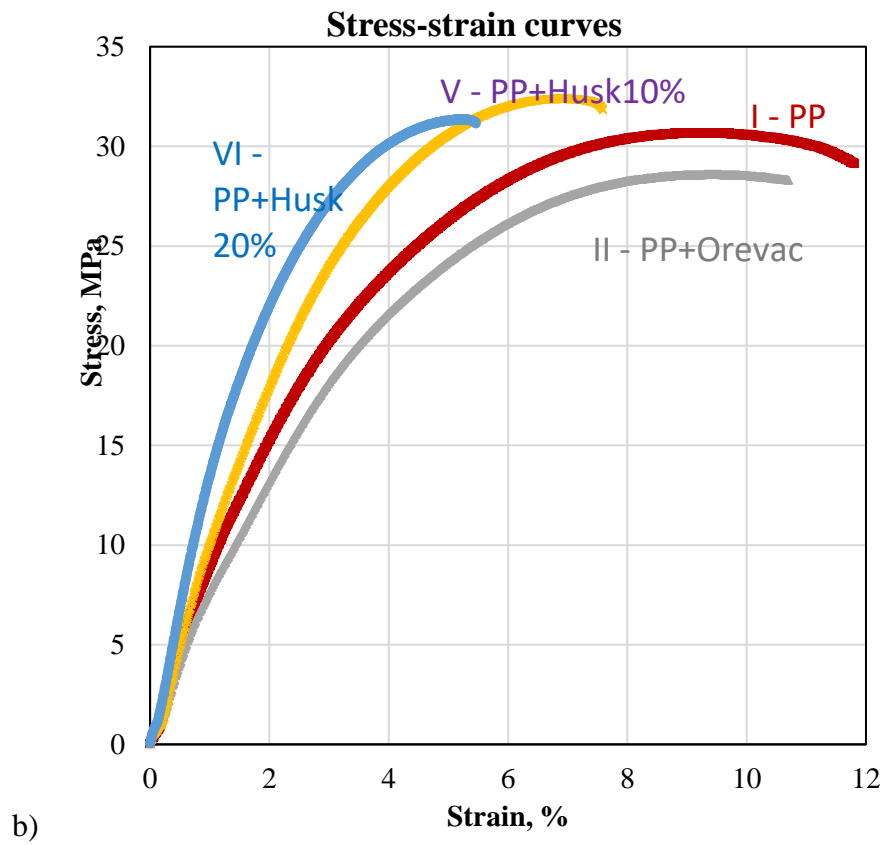
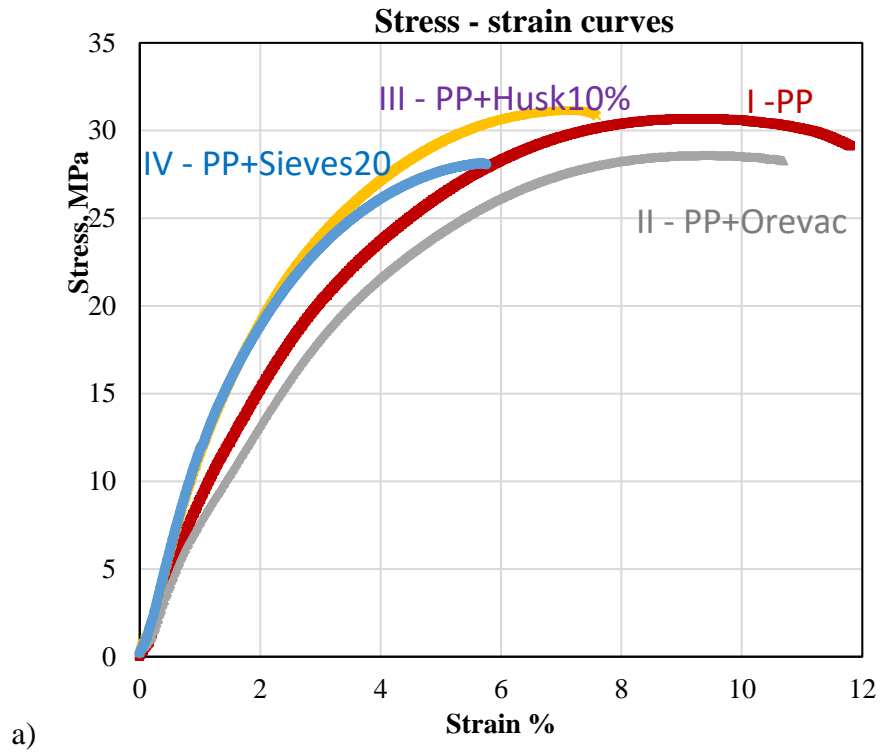


Fig. 37. Stress-strain curve of various PP compositions

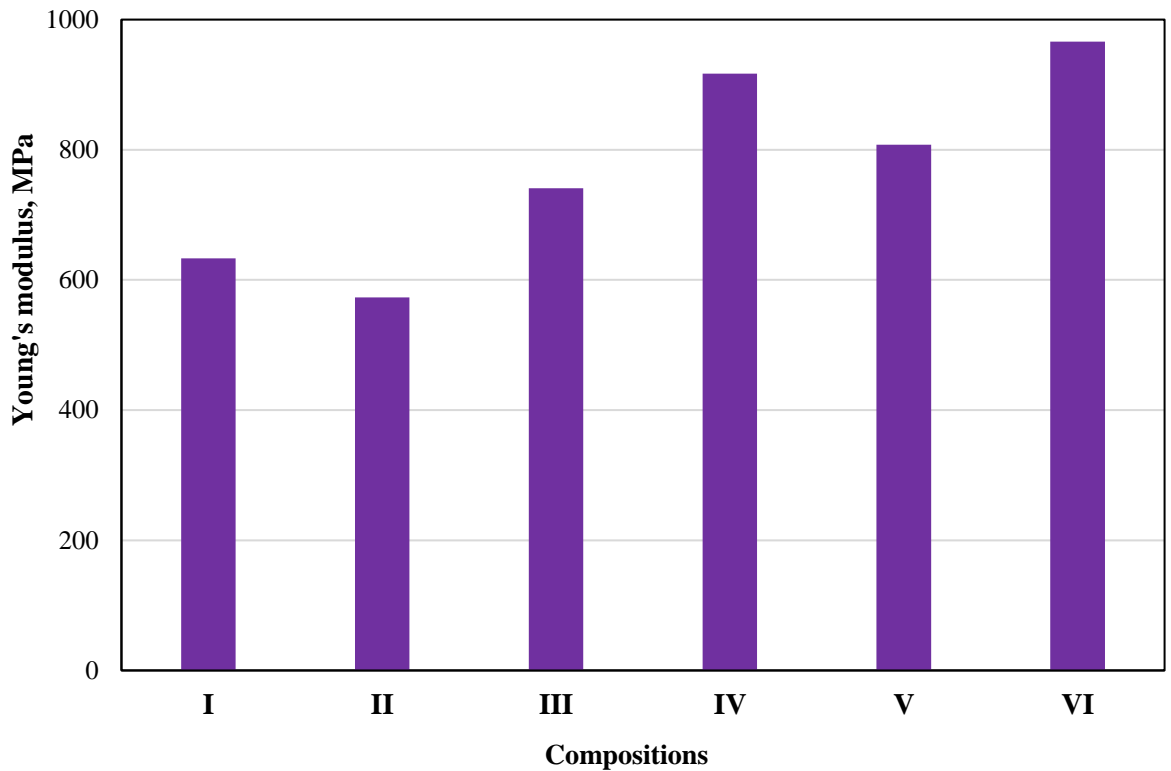
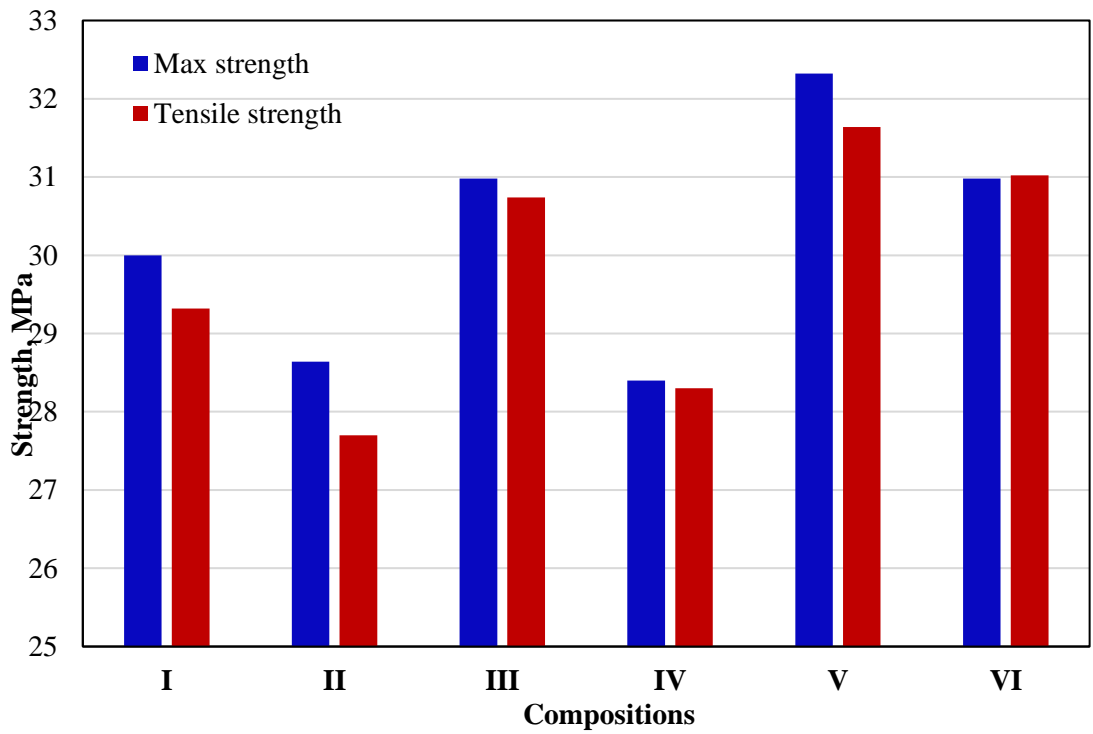


Fig. 38. Dependence of Young's modulus from PP compositions

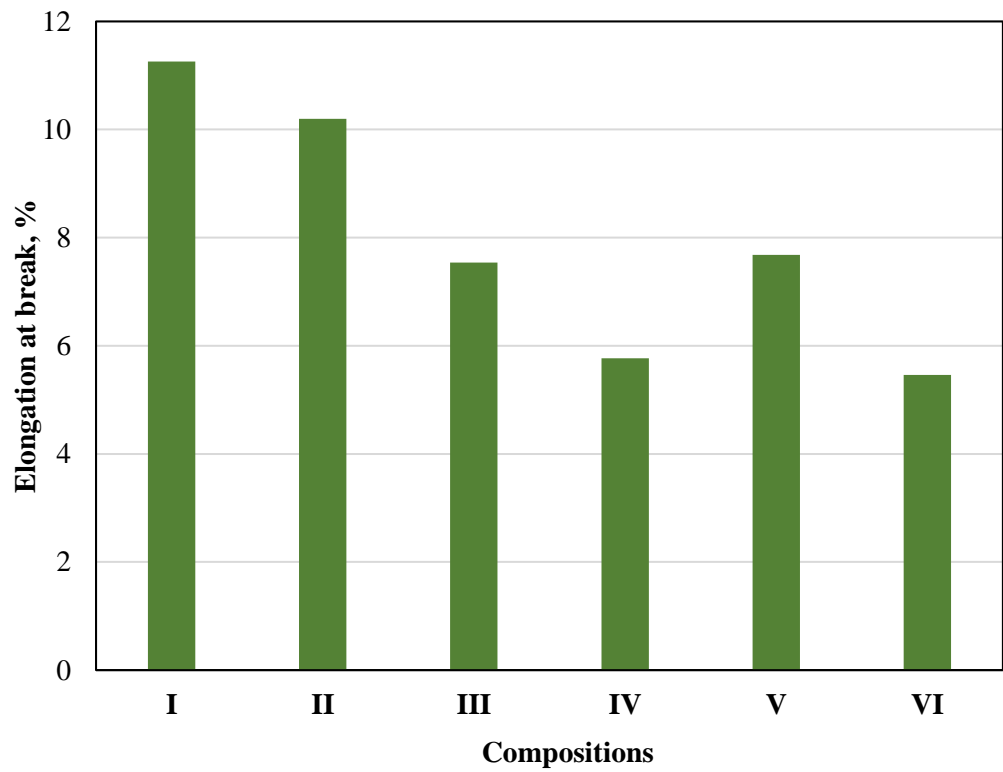
From Fig.38 it is visible that filler increases Young's modulus. Higher filler content higher PP stiffness.

The mechanical properties of the composition of PP and lignocellulosic wheat waste are represented in Fig.39 Addition of compatibilizer decreases the strength of PP. The maximum strength of PP was 30MPa which is 3.3% less than the maximum strength of the wheat sieve composition (10%) and 7.6% less than the wheat husk composition(10%). Whereas the maximum strength of wheat husk composition is 4% higher than the wheat sieve composition. The strength of the composite is based on various factors including the toughness of the filler, nature of the interfacial region. The strength of the composition is increased when compared to PP due to the addition of fillers. Tensile strength of the composition also increased like maximum strength. The tensile of the wheat sieve composition is 5% higher than the tensile of PP whereas, the wheat husk composition is 7% higher than the tensile of PP this might due to the addition of fillers.

Elongation at break refers to the ratio of elongated length to the original length of the specimen after the force is applied. High elongation at break% represents the high ductility property of the sample whereas the lower mean low ductile nature. Elongation at break of PP is 11% which is 4% higher than the wheat sieve and the husk composition. This clearly shows the addition of fillers reduced the deformation property of the PP.



a)



b)

Fig. 39. Dependence of mechanical properties at the tension of PP upon composition (a) strength, and (b) elongation at break

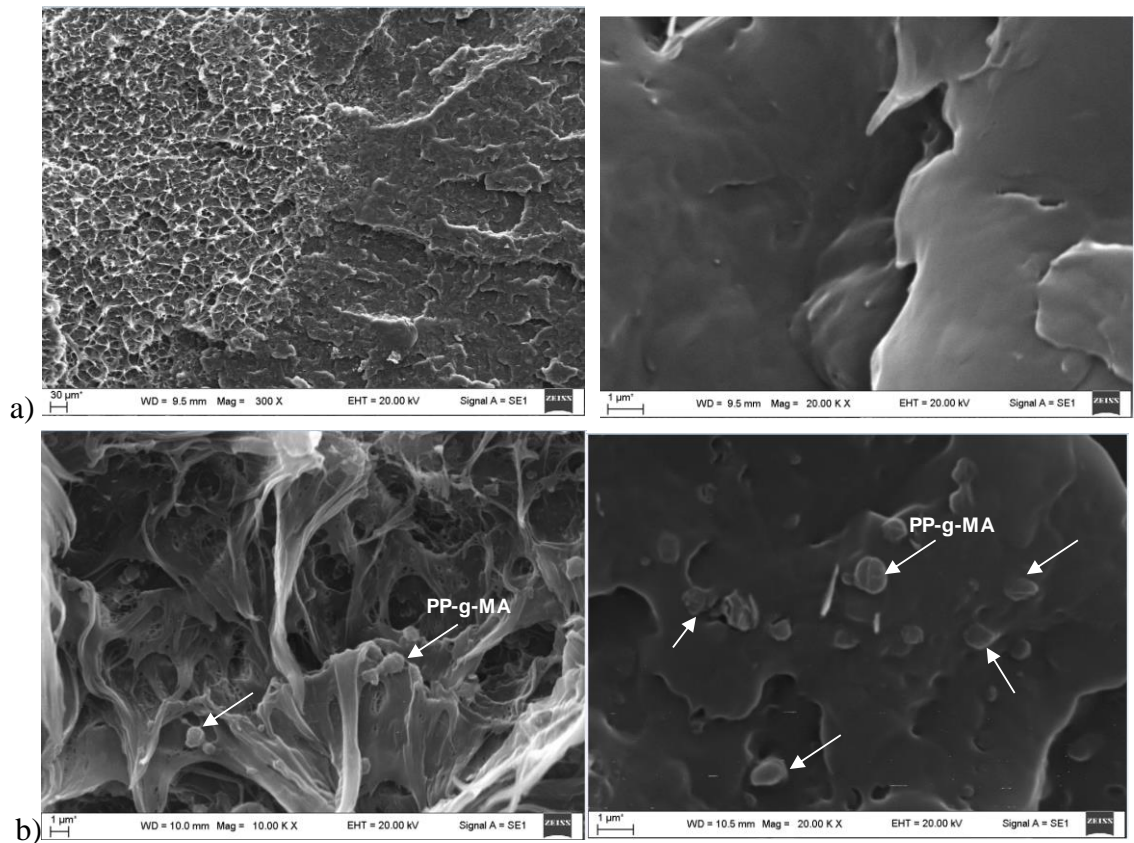


Fig. 40. SEM micrograph of a broken part of PP (a) and PP: PP-g-MA=70:30 % (b)

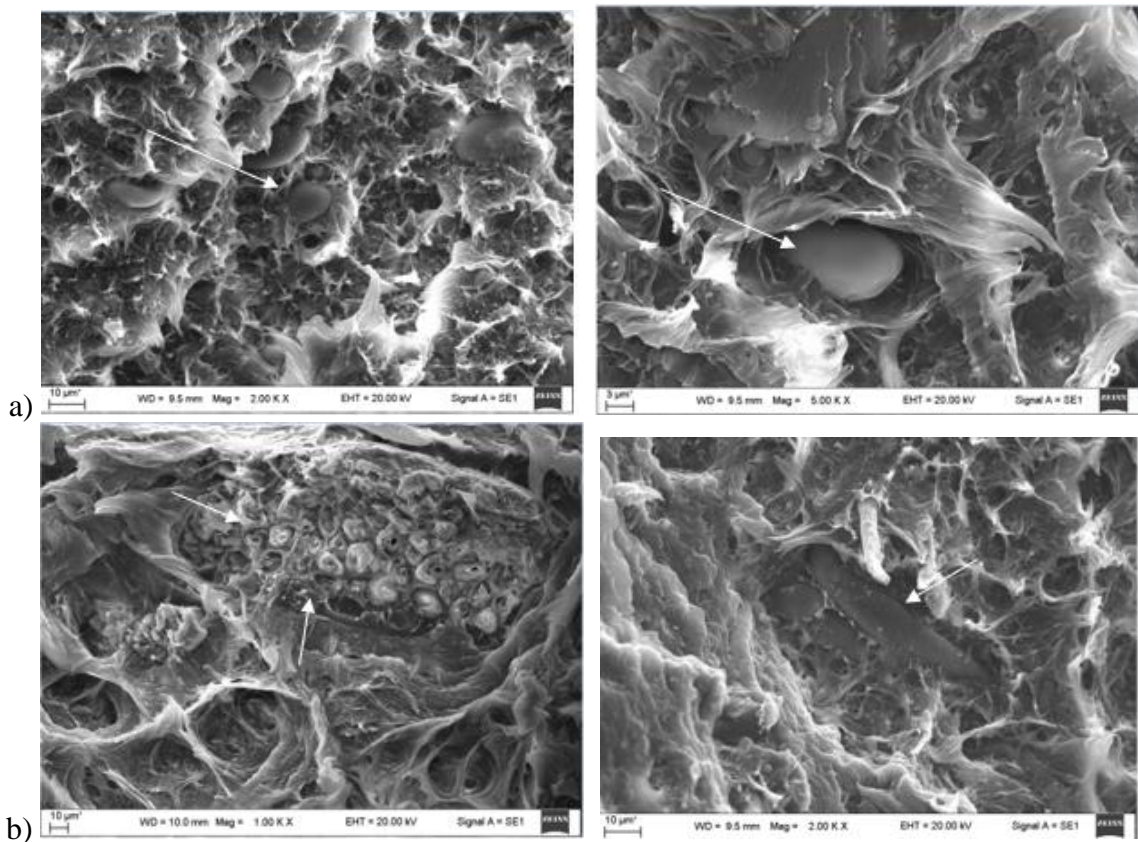


Fig. 41. SEM micrograph of broken part of PP and wheat waste: a – IV composition (PPH 49.8 % + sieve 20% + PP-g-MA 30%); b – VI composition (PPH 49.8% + husk 20% + PP-g-MA 30%)

The morphology of PP compositions was investigated by SEM. The images of tensile fractured surfaces of PP compositions without and with compatibilizer are illustrated in Fig. 40. The homogenous morphology is characteristic for pure PP (Fig. 40, a), while small PP-g-MA spherical domains surrounded by continuous PP phase is visible in the case of addition of the compatibilizer (Fig. 40, b). Fig.40 and 41 illustrated the effect of surface treatment of the surface of wheat waste on the interaction mechanism with the PP matrix. It was evident that filler particles are distributed in the PP matrix without aggregation. Besides, no space or any other fault is evident in the broken area. Surface treated wheat waste particles show high adhesion interaction with PP matrix. Increasing adhesion at the interface was a reason to increase in mechanical property.

4. The management part of agriculture waste-filled PP composition product

The main aim of the work is to make an alternate for fully composed PP stoppers to agriculture waste-filled PP stopper.

PP stopper:

The stopper is mostly used in laboratories. The main purpose of the stopper to create a block for the liquid or material inside the test-tube, and flask. It will create an airtight seal that will help not to spill. This was made by PP. The stopper has property like chemical resistance. PP also has good chemical resistance.

Agriculture waste:

According to an article written in the International Council of Clean Transportation [26], in 2013 the crop residue in the EU was 122 million tonnes per year based on estimation it would be 139 million tonnes per year in 2030. In 2013 the wheat production in the EU was 122.1 million tonnes [26] among that ratio of the field residue was 0.94% that means approximately 1 million tons become residue. Mostly the residue was used to feed the livestock. It was used for energy production also but due to the concern about CO₂ emission that also stopped. So, most of the residue becomes waste. Hence the goal of the work is to analyze the agricultural waste-filled PP composition product.

Based on the above research and result, it was clearly shown that wheat waste-filled PP composition has shown good results. It has all the properties to be a product like a stopper. In the composition the maximum amount of percentage was held by PP hence it has all the properties of PP also, during the mechanical test and surface morphology analysis of wheat waste composition was good enough.

Environmental and Economic Benefits:

If the wheat waste composition of PP is used instead of PP, that would reduce the total amount of PP used to make the stoppers hence, it will reduce the PP usage. Decomposition year for PP is 20-30 years typically hence reduction of usage of PP would provide many environmental benefits.

The average weight of plastic stopper = 10grams

If 10% of the wheat waste composition is used instead of PP that would reduce the amount of PP used to 9 grams. This is for one stopper if a company making 1000 then it will reduce 1000 grams of PP usage.

Table. 7. Cost estimation

Materials	Kilograms	Cost (Euros)
25 kg of PP	25	2
100 kg of PP	100	8
Wheat husk (24 metric tonnes)	22000	60
100 kg of Wheat husk	100	0.2

From the above table it was visible that for example if a company using 100 kg of wheat waste composition instead of PP, they could save up to €7.8. Economically this might seem low but environmentally company is reducing the 100 kg of PP.

Conclusions

The influence of silylated wheat waste on the interaction with polypropylene and its influence on the composite structure and properties was investigated.

1. Cellulose, hemicellulose, and lignin comprise the main components of the wheat waste such as sieves, and the husk. Additionally, the sieves have a high amount of starch.
2. Wheat waste was silylated to increase the compatibility of the composite. The silylation is proved by the appearance of the Si-C bond on the husk surface.
3. After silylation treatment, there was no change in the shape of lignocellulosic waste particles. However, the amount of silicon on the sieves (30%), and the husk (90%) was increased after treatment.
4. After treatment, the increasing repulsion between the particle was found that reduce the bulk density of the waste samples. Also, after treatment, the contact angle was increased by 32% for the sieves and 59% for the husk.
5. Due to the high content of hemicellulose wheat sieves show about 3 times higher ability to absorb water vapor compare to that of wheat husk. Silylation decreases the water vapor absorption degree of wheat waste particles: wheat sieves – by 56 %, wheat husk – by 12 %.
6. Silylated wheat sieves and the husk particles show a high dispersion degree and compatibility with the PP matrix. Therefore, the effective amount of these particles increases the tensile strength of PP composites by 8%.
7. The addition of wheat sieves and the husk particles markedly decreases deformability of PP composite by 30-50% this is due to the low mechanical strength of wheat waste.
8. The probability of the wheat waste-filled PP stopper was high because it has all the properties of the PP stopper, as well as the strength of the wheat waste composition, which was higher than the PP. The economic and environmental benefits of the wheat waste composition were discussed.

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