Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Valorization of Agro-industrial By-products as a Filler for Polypropylene

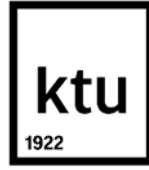Master's Final Degree Project

Sandra Chinemelum Ozohili

Project author

Prof. Virginija Jankauskaitė

Supervisor

Kaunas, 2024

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Industrial Engineering and Management (6211EX018)

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Kaunas University of Technology

Faculty of Mechanical Engineering and Design

Task of the Master's Final Degree Project

Given to the student – Sandra Chinemelum Ozohili

1. Title of the Project

Valorization of Agro-industrial By-products as a Filler for Polypropylene

(In English)

Žemės ūkio pramonės šalutinių produktų panaudojimas polipropileno užpildu

(In Lithuanian)

2. Aim and Tasks of the Project

Aim: to investigate the influence of type and surface state of the agro-industrial by-products on the morphology and properties of the polypropylene compositions

Tasks:

1. to characterize the structure and physical properties of the dispersion particles derived from agro-industrial by-products;
2. to investigate the effect of surface chemical treatment on the structure and properties of dispersion particles;
3. to investigate the effect of the surface treatment and amount of the dispersion particles on the structure and properties of the polypropylene composites;
4. to assess the managerial aspect of agriculture waste-filled PP composition product.

3. Main Requirements and Conditions

Determination of mechanical properties – standard ISO 527-2
Determination of bending properties – standard ISO 178
Water vapour and absorption tests – the samples must be dried before test

4. Additional Requirements for the Project, Report and its Annexes

Not applicable

Project author	Sandra Chinemelum Ozohili		02-10-2023
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Supervisor	Virginija Jankauskaitė		02-10-2023
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	(Name, Surname)	*(Signature)*	*(Date)*

Ozohili Sandra Chinemelum. Valorization of Agro-industrial By-products as a Filler for Polypropylene. Master's Final Degree Project, supervisor Prof. Virginija Jankauskaitė; Faculty of Mechanical Engineering and Design, Kaunas University of Technology.

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

Keywords: polypropylene; oat and spelt husks; surface silylation; structure; mechanical properties.

Kaunas, 2024. 59 p.

Summary

The aim of this study was to valorize agro-industrial by-products from cereal production, specifically oat and spelt husks as a filler in polypropylene (PP). The impact of oat and spelt husks on physical and mechanical properties of PP composite, with the morphological structure characterization, have been investigated aiming to evaluate the appropriateness of these composites for various applications. The milled oat and spelt husks surface was modified with hexamethyldisilazane (HMDS) to improve their compatibility with the polymer. Three types of PP homopolymers of different properties and melt flow index were used for investigation. PP composites filled with oat and spelt husks were mixed in a twin-screw extruder at a temperature of 190 °C, and the samples were formed by injection moulding at a temperature of 240ºC at a pressure of 700 bar. Various testing methods including scanning electron microscopy (SEM), thermogravimetric analysis (TGA), contact angle, water absorption, dynamic mechanical thermal analysis (DMTA), tensile and bending tests were carried out to study the effect of the surface treatment and filler amount on the structure and properties of the polypropylene composites. Findings showed that the influence of oat and spelt husks on the mechanical properties of the PP composites depends on the type of polymer. The water absorption of PP composites increases with increasing filler content. However, surface silylation of the filler particles reduces the water absorption. Therefore, PP composites with modified 10wt% fillers showed the lowest water absorption rate. The managerial aspect of the agriculture-waste filled PP composition product in terms of cost-effectiveness, environmental and socio-economic constraints were also analysed.

Santrauka

Šio tyrimo tikslas buvo panaudoti agrarinės pramonės šalutinius grūdų gamybos produktus, avižų ir speltos lukštus, kaip polipropileno užpildą. Buvo tiriama avižų ir speltos lukštų įtaka polipropileno (PP) struktūrai, fizinėms ir mechaninėms savybėms, siekiant įvertinti šių polimerinių kompozitų tinkamumą įvairioms reikmėms. Maltų avižų ir speltos lukštų paviršius buvo modifikuotas heksametildisilazanu (HMDS), norint pagerinti jų suderinamumą su polimeru. Tyrimui buvo naudojami trijų tipų PP homopolimerai, turintys skirtingas savybes ir lydalo takumo indeksą. PP kompozitai, užpildyti avižų ir speltos lukštais, buvo sumaišyti dviejų sraigtų ekstruderiu 190°C temperatūroje, o bandiniai suformuoti įpurškimo būdu 240 °C temperatūroje, esant 700 bar slėgiui. Užpildo paviršiaus apdorojimo ir jų kiekio poveikiui PP kompozitų tyrimams buvo naudoti įvairūs metodai, įskaitant skenuojančią elektroninę mikroskopiją (SEM), termogravimetrinę analizę (TGA), vandens absorbciją, dinaminę mechaninę šiluminę analizę (DMTA), tempimą ir lenkimą. Nustatyta, kad avižų ir speltos lukštų įtaka PP kompozitų mechaninėms savybėms priklauso nuo PP tipo. Didėjant užpildų kiekiui, didėja PP kompozitų vandens sugertis. Tačiau užpildo dalelių paviršiaus sililinimas sumažina vandens sugertį, todėl kompozitai su modifikuotais 10% užpildais parodė mažiausią vandens sugėrimo greitį. Taip pat buvo išanalizuotas žemės ūkio atliekomis užpildyto PP sudėties produkto valdymo aspektas ekonomiškumo, aplinkosaugos ir socialinių bei ekonominių apribojimų požiūriu.

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Introduction

Recently, the biobased polymer composites have garnered significant attention in the industry, primarily because of their sustainable features and economic considerations. Typically, biobased polymer composites refer to a composite that incorporates natural fibre filler as reinforcements with either thermosetting or thermoplastic materials. The biobased polymer composites are commonly utilized in various applications in the automotive, construction, interior decorations, biomedicine, packaging, and aerospace industries. The rapid expansion of the biocomposites market has raised significant concerns regarding the limitations of renewable filler resources to meet industrial demands. This is primarily because the main source of renewable natural materials to be used as fillers apart from wood is derived from agro-industrial by-products and presently these byproducts are heavily wasted globally on annual basis. Agro-industrial by-products are utilized because of the demand for bioproducts, environmental concerns and high reinforcing potential value. There are many kinds of agricultural crops ranging from cereals, fruits, oilseeds, vegetables, plants etc. that are widely cultivated and after processing, a huge amount of the byproducts or agro-waste materials including husks, hull, straws, shells, cobs etc. are wasted. Recent studies have demonstrated their utilization as fillers or reinforcements in polymer composite production. Agro-industrial waste materials are currently under research, with efforts focused on transforming them into composite materials for diverse applications. The oat and spelt husks are a significant waste byproduct in the cereal agricultural sectors representing the non-food portion of the oat and spelt grains remaining after extraction and milling process. It is estimated that 2.75–3.3 million tons of oat husks are generated as byproduct, and it typically constitutes an average of 27% of the oat grain [1]. In the past, waste from oat and spelt husks were used for animal feed and to enrich the soil and still not all the waste generated are used. Mostly, the oat and spelt byproduct wastes are burnt as a means of disposal, and this leads to negative environmental impacts. The current study underscores the utilization of oat and spelt husks as an alternative filler for polypropylene composites due to their abundance and ready availability. Based on recent EU data [2], the production of major cereals in 2022 amounted to 270.9 million tons encompassing common wheat and spelt (126.7 million tonnes) and oat (7.5 million tonnes). The use of oat and spelt husks can bring benefits to the economy, environment, and industrial sectors as there is continuous research on the development of polypropylene PP/oat and PP/spelt composites. Nevertheless, the major limitation associated with agro-industrial byproducts lies in its hydrophilic nature due to the abundance of hydroxyl groups. This characteristic may result in suboptimal interfacial compatibility between the agro-waste filler and the polymer matrix, potentially leading to a composite with poor mechanical properties and moisture resistance. The use of a silane coupling agent, HMDS for surface modification of the fillers is studied to enhance the interfacial adhesion between the hydrophobic polymer matrix and hydrophilic agro-waste fillers. The aim of this work is to evaluate the effects of surface modification on the thermal, morphology, mechanical properties and water absorption behaviour of the PP/oat and PP/spelt composites. The comparison on the properties of the composites with unmodified and modified filler particles were studied.

Aim: to investigate the influence of type and surface state of the agro-industrial by-products on the morphology and properties of the polypropylene compositions

Tasks:

1. to characterize the structure and physical properties of the dispersion particles derived from agro-industrial by-products;

2. to investigate the effect of surface chemical treatment on the structure and properties of dispersion particles;

3. to investigate the effect of the surface treatment and amount of the dispersion particles on the structure and properties of the polypropylene composites;

4. to assess the managerial aspect of agriculture waste-filled PP composition product.

Hypothesis: the use of chemically modified oat and spelt fillers improve polypropylene thermal, mechanical and water absorption behaviour.

1. Relevance of Research

1.1. Agro-industrial By-products and their Influence on Environment

The excessive reliance on non-renewable resources for plastic production has had adverse effects on the environment, particularly in relation to the problem of plastic pollution. Non-biodegradable plastics persist in the environment for extended periods, unable to naturally decompose. The excessive utilization of plastics bears significant ramifications, particularly in the context of the oceans, which regrettably have transformed into dumping grounds for immense quantities of plastic waste. Consequently, there exists a pressing imperative to advocate for sustainable alternatives, such as biodegradable plastics and environmentally friendly biomaterials. Encouraging the transition towards biodegradable plastics is pivotal in mitigating the environmental harm inflicted by non-renewable resources and synthetic materials. A feasible approach to attaining this goal involves the development of environmentally sustainable biomaterials that are environmentally sustainable, encompassing the utilization of renewable resources derived from agro-industrial by-products, such as plant-cased materials.

The polymer industry is evolving in sustainability to produce plastics, bioplastics, and biopolymers. The development of 100% biodegradable and biobased plastics can be achieved because of the need to protect the environment but there is still a small percentage of the total amount of plastics produced. According to the data from European Bioplastics [3], over 390 million tonnes of plastics are produced globally with bio-plastics accounting for 1.5% of the global production. In terms of the 2022 global production capacity of bioplastics from renewable sources, the biodegradable PBS, PLA, cellulose films and others accounts for about 51% and non-biodegradable PP, PET, PA and others accounts for 49% (Fig. 1). However, biobased non-biodegradable plastics production is predicted to reduce with an increase in biodegradable bioplastics in future. The overall production of bio-based polymers has increased continuously as the mostly used polymers for production are bio-polypropylene (PP), bio-polyethylene (PE) and bio-polyamide (PA).
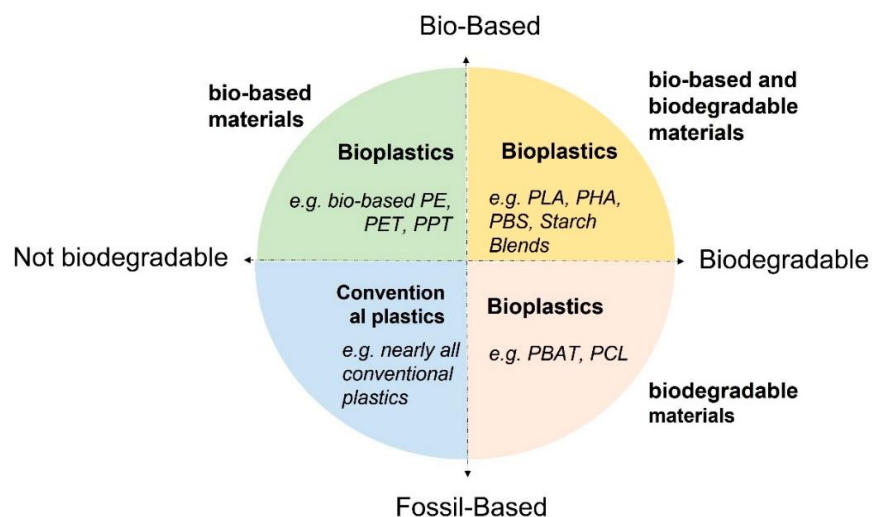
Fig. 1. Biodegradable and non-biodegradable bio-based polymers [4]

Agro-industrial by-products are produced from food waste during food milling production process of agricultural food products. Agro-industrial waste encompasses materials that are generated as by-products in the agricultural sector and related industries. These materials result from various

processes associated with the production of agricultural products such as fruits, vegetables, cereals, and legumes. It usually includes stems, peels, husks, straws, stalks, hulls, chaff etc. derived from the leaves, seeds, or fruits of plants. In the biocomposite industry, the most used agricultural products are fruits, vegetables, crop residues, legumes, and cereals as presented in Fig. 2. The processing of these products often results in waste or by-products. The primary activities resulting in by-products (stems, stalks, straw, leaves, etc.) are through sorting, collection, and harvesting the crops.
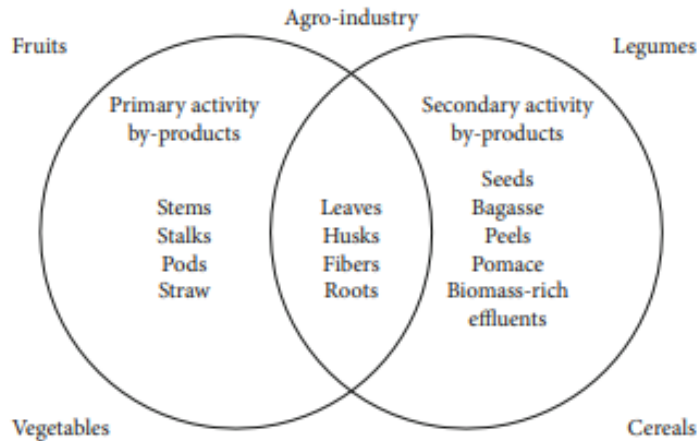
Fig. 2. Agro-industrial by-products [5]

Numerous crops yield byproducts that consist predominantly of cellulose (Fig. 3.). These by-products generate a significant amount of waste globally thereby causing environmental pollution. Based on their moisture content, these by-products can be classified as either dry or green. The by-products with high water content usually degrade in the field because while the dry by-products have low moisture content and are mostly used as fertilizers or feed. The secondary activities of industrial production processes result to by-products like seeds, peels, biomass etc. A vast number of by-products are produced annually by the agroindustry. Some are used in conventional applications such as fertilization, animal feeds and production of value-added food ingredients. Agro-industrial by-products are used in the production of biofuels, antibiotics, enzymes, phytochemicals, biofertilizers and utilization as the substrate for solid state fermentation [6]. Agro-industrial by-products offer significant opportunities for the extraction of bioactive compounds through various promising and inventive techniques.
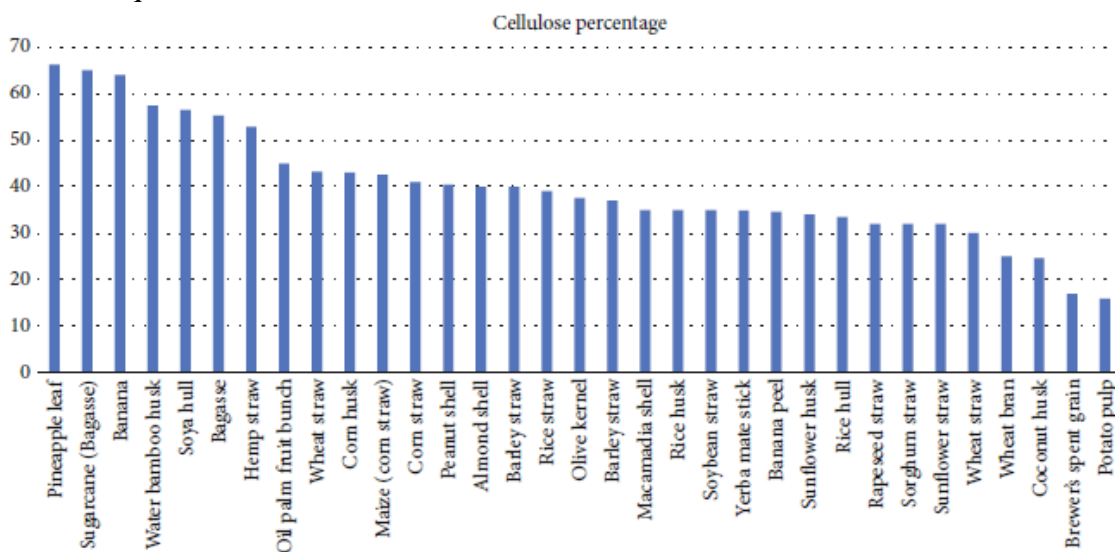
Fig. 3. Agricultural wastes and byproducts cellulose composition [7]

Most of these by-products are wasted either through disposal in landfills or by incineration. Their improper disposal negatively impacts the environment. Due to the growing emphasis on adopting a circular economy approach in the industrial sector, which considers ecological, economic, and social dimensions, a biorefinery serves as a strategic tool for advancing the concept of a circular bioeconomy [8]. Within this framework, it becomes evident that, in alignment with the core principles of a circular bioeconomy, the extraction of bioactive compounds should be achieved using cost-effective, environmentally friendly, minimal carbon footprint and sustainable technologies [8]. Methods of reducing environmental pollution caused by these by-products such as to reuse, recycle, or renew these materials to produce biomaterials has proven effective but the rate of production of agricultural products surpasses the rate of their consumption which leads to more waste by-products. Due to the substantial yearly volumes of agro-industrial by-products worldwide, significant residue will inevitably persist following the extraction process. Consequently, it becomes imperative to explore the adoption of a closed-loop system that is efficiently sustainable in the circular economy. The longer the by-products are kept in the loop to be reused, reprocessed, and renewed, the better as wastes are eliminated and the natural resources are conserved and used to produce bioproducts. Also, to control these wastes, it is imperative to implement a large-scale extraction unit [8] as this plays a crucial role to mitigate the spoilage and excessive energy expenditure associated with the storage of agro-industrial by-products. The polymer industry is increasingly focused on utilizing more environmentally sustainable resources for production in response to growing environmental and ecological apprehensions. Hence, the valorisation of agro-industrial by-product opens new opportunities to produce entirely sustainable materials.

The valorisation of agro-industrial by-products to produce biopolymers has some advantages and drawbacks. As per the Food and Agriculture Organization (FAO) 2019 annual report, global agrifood production amounted to approximately 1.3 billion tons [4]. Agro-industrial by-products present various possibilities for utilization and value enhancement because of their composition, potential for stabilization, ready availability, and storage. These options encompass repurposing them as fillers to their utilization in the plastic sector to obtain biopolymers and bioplastics that are biodegradable and eco-friendly. These by-products contain protein and polysaccharide which allow for environmentally bioplastics to be produced from these renewable sources such as lignocellulosic residues, peels, pulps, bagasse, sugarcane, starch etc. Polyesters, polyurethanes, polyamides, and polyolefins are some of the main polymers obtained from agro-industrial wastes. The manufacturing of bio-based polymers from sustainable origins and through microbial synthesis offers benefits such as cost-effectiveness, scalability, and a reduced environmental impact compared to the chemical synthesis of plastics derived from fossil sources [4].

Bioplastics derived from agro-food waste find widespread applications in areas such as coatings, food packaging, scaffolds, absorbent materials, hygiene products and additionally, they are used in various sectors including construction, agriculture, medical and automotive. However, there are some limitations associated with bioplastics despite their broad range of applications. The natural biopolymers used for their production have high affinity for water since natural fibres are hydrophilic in nature, therefore the lifecycle of the bioplastic may be impacted as a result. Huge quantities of agro-industrial by-products are required for the production of biopolymers, the collection and sorting process still pose a challenge as there is no streamlined organization. There are a high production cost of biopolymers and sustainability plays a huge role in selection of the type of by-products to be utilised [4]. The accessibility of biomass of the agro-industrial by-products is closely associated with

the variations in different geographical regions which is primarily influenced by the local crops grown in different countries. The most cost-effective and eco-beneficial lignocellulosic fibres are typically sourced from agricultural and food industry solid by-products. Utilizing these fibres as fillers in biocomposites also contribute to waste reduction. Fig. 4 illustrates the process of upcycling these by-products into fillers for use in biocomposite production. These agro-industrial by-products are extracted in form of cellulose biomass and used as fillers in polymer composites.
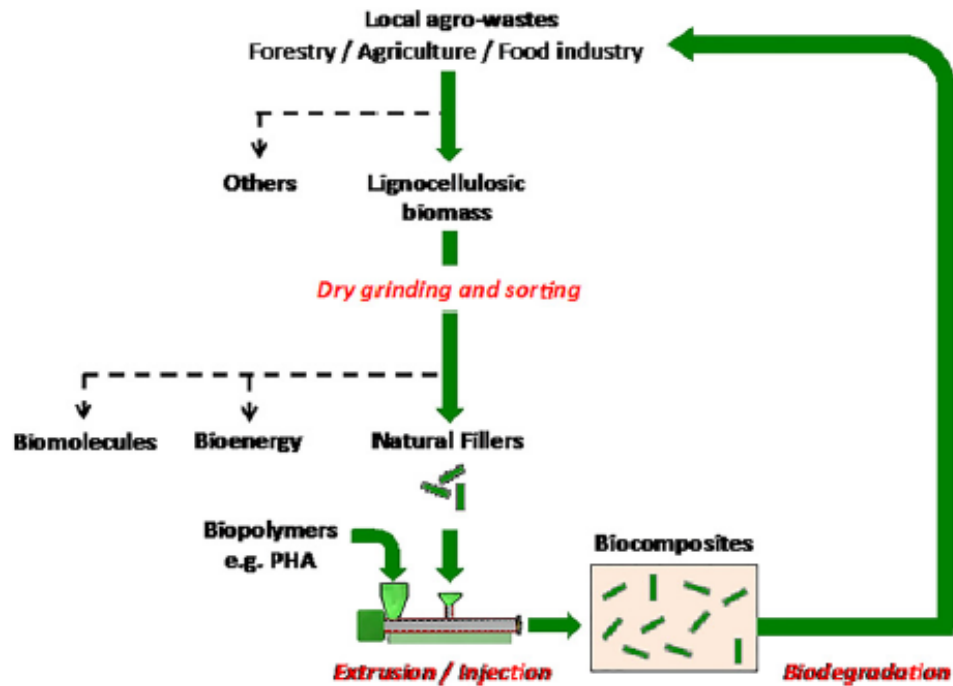
Fig. 4. Upcycling of agro-industrial byproducts for biocomposite production [9]

The investigation of agro-industrial by-products as sustainable fillers for polymers is garnering growing attention, primarily because of its positive impact on environmental sustainability within the plastic industry. Most of the organic fillers employed in biocomposites, which include both biobased and non-biobased materials, are sourced from renewable origins and typically consist of cellulose-rich materials [10]. Sources of organic fillers shown in fig. 3 are either derived from lignocellulosic feedstock or agri-food waste and by-products. Studies have shown the use of natural cellulose fibres like jute, kenaf, coir, sisal, flax, wheat bran, oat husks and may others as fillers in different polymer composite materials. They are utilised as a substitution for synthetic and inorganic fillers because of their renewability, biodegradability, low cost and ability to enhance properties of these natural fibre-based polymer composites. These by-products are used as fillers in biopolymers to produce bioplastic materials and this addition reduces the amount of plastics used in the process.

Fig. 5. Organic fillers [10]

Fillers have a wide range of mechanical and surface characteristics, varying chemical compositions, sizes, and forms have been thoroughly investigated in recent studies as reinforcements in polymer composites. Modification of these fillers either physically or chemically have shown to improve mechanical, thermal and water absorption properties od polymer composites. This study [11] used oat husk fibre as a filler for a poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) to obtain a bio-based polymer composite material. The findings demonstrated a small increase in the mechanical properties and that the oat husk fillers can be utilized in the natural state without requiring additional functionalization. This approach helps reduce both processing time and costs. This valorisation is valuable as it contributes to the effective utilization of agro-food industrial waste instead of incurring disposal costs. The effect of wheat bran agro-industrial by-product as a filler for the fabrication of a fully biodegradable and bio-based mycelium-based composites was studied [12]. The wheat bran was used as reinforcement to modify the mechanical behaviour of the composites which showed an increase in flexural strength and modulus. Research has indicated that agro-industrial by-products can serve as an effective filler in polypropylene, enhancing its properties while simultaneously reducing the overall plastic output. Studies suggest that agro-industrial by-products may hold a significant role in the prospective development of sustainable polypropylene production.

In the polymer, industry, PP is one of the most widely used polymer as it accounts for 16% of the overall plastics industry [13]. Within non-fibre plastic production since the 1950s, PP occupies the second place after PE in terms of versatility, reaching around 21% of non-fibre plastic production [14]. The production of PP has seen a rise in recent years to about 55 million tons since 2015 and it continues to rapidly increase due to its use in a wide variety of applications [15]. PP is one of the most promising polymers due to its physical properties, adaptability, dimensional stability, and environmentally friendly record. There is a growing concern regarding thermoplastic reinforced

composites like polypropylene that incorporate various lignocellulosic fibres derived from agro-industrial by-products. The properties of PP composites reinforced with fillers can be affected in terms of exhibiting an increase, decrease or unsignificant changes in these properties. This changes on properties depends on type of modification treatment, type and composition of filler, filler loading proportion, polymer matrix and other factors. This study [16] involved the characterization of novel composite materials that are based on polypropylene (PP) and filled with both acetyl treated or untreated coffee husk waste. The study focused on the physical and mechanical properties exhibited by composite materials composed of polypropylene and agricultural waste fillers. The process of acetylation performed on the filler enhanced the adhesion between the matrix and the fibre thereby increasing mechanical properties. Another research [17] enhanced the value of bagasse by-products by utilizing them in the creation of novel bio composite material. This biocomposite was based on PP and strengthened with various cellulose derivatives. The reinforced composites demonstrated a decrease in thermal stability, enhanced hardness and increase in tensile strength. Utilizing cellulose by-products as fillers is a promising approach for efficiently manufacturing polymer composites. This not only adds value to industrial by-products but also facilitates their practical utilization in various applications.

1.2. Agro-industrial By-products Applications: Past, Present and Perspectives

The utilization of agro-industrial by-products gradually became a viable alternative in most sustainable technological industries due to the awareness of environmental and economic problems caused by conventional synthetic sources. The stages of industrial revolution have seen the development and use of fossil fuels, petroleum products, organic and inorganic fibres for plastic production. These have highly beneficial properties of high durability, dynamic applications, high strength and contribute immensely to the growth of the industrial economy. However, there is poor environmental impact associated with these products due to impossibility to recycle and renew these synthetic products. Hence, the need to apply agro-industrial by-products to develop sustainable materials and bioproducts. Fig. 4 presents timeline evolution of different usage of agro-industrial by-products.
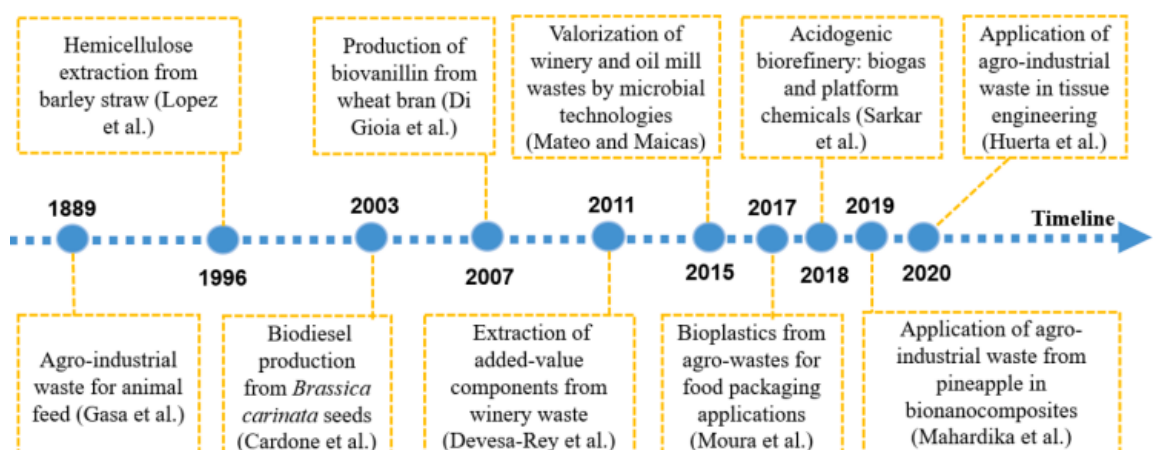

Fig. 6. Evolution of different application of agro-industrial by-products [18]

The past research on sustainability and possible use of natural resources led to the use of organic materials derived from lignocellulose by-products. During food production, these materials such as husks, hulls, grains, cobs, peels, stalks etc. were generated and used to manufacture various value-

added compounds. The production of these compounds commenced in the 1920s – 1980s with the need to continuously improve the processes to achieve quality compounds with more value. This study [19] reviewed different past research done within this period and specifically, most of these investigations into the utilization of agro-food by-products focused on thermodynamic and pyrolysis process. The next era proceeded with various research in the creation of eco-friendly products from food by-products using environmentally conscious processes. There was a need to transform the conventional approaches into innovative, environmentally friendly, and cost-effective methods for the production and reclamation of these food by-products. One method studied was the biological processes occurring in nature that allow for the extraction of value-added products using gentle and appropriate methods instead of extreme temperatures and time-consuming procedures. The solid-state fermentation biotechnology technique emerged as a better process of obtaining valuable molecules, devoid of pollutants and potentially harmful substances that can adversely affect human health. Table 1 shows the most frequently generated food by-products based on past applications.

Table 1. Some agro-industrial by-products usage from the last years [19]

Agro-industrial by-products	Process	Value-added compounds and resources
Corncobs, cornstalk, corn-by products	Digester, high-pressure steam, cobs and caustic soda fusion, destructive distillation process, traditional Soxhet system	Furfural, glue, acetic acid, xylose, lactic acid, menthol, acetone, soluble tar, formic acid, carotenoids for animal feed
Pear by-products	Commercial pectic enzymes	Sugars,
Citrus by-products	Fermentative process	2, 3-butylene glycol
Lignocellulosic biomass	Solid state fermentation	Pigments, enzymes, antioxidants
Sweet potato residue	Solid state fermentation	protein
Citrus by-products	Solid state fermentation	pectinase

Presently, it is estimated that approximately 1.3 billion tons of food by-products are produced globally but ultimately wasted by food processing industries [19]. At present, by-products from food agro industries represent significant sources of pollution. Therefore, the focus of current studies is geared towards the renewability, recyclability, and valorization of these agro-industrial by-products to gain valuable products and minimise detrimental effects. Recently, research studies are exploring creative innovative technological solutions by harnessing these sources within the field of soft chemistry to produce wide range of bio-products through less use of toxic substances while reducing energy consumption [19]. The nutritional value and nutricine (elements found in animal feeds that have a positive impact on health, distinct from their direct nutritional contributions) components of agro-industrial by-products have led to their application as feeds for animals [20]. The application of by-products like stalks and residues as feeds in poultry, pigs and ruminant animals have also become a route for sustainable development. In recent times, agro-industrial waste has been utilized in different industrial sectors to produce a vast range of applications as seen in table 2.

Table 2. Some recent applications of agro-industrial by-products [18]

Industry	By-products	Applications
Pharmacology	Silk waste residue	Drug delivery system
	Cocoa bean hulls	Nutritional pharmacology
	Citrus waste	Biological activities in drugs

Industry	By-products	Applications
Food production	Fruit residues (lemon, tomato, apple, grapes etc.)	Natural antioxidants
	Pomegranate peel, orange, goji berry, soybean residues	Functional components
	Mushrooms residue	Polysaccharides
Biomaterials production	Lignocellulosic materials (rice husk, corn straw, wheat husk, Sugar bagasse, corn leaf residues, eucalyptus cellulose, pineapple residue, rice straw, celery cellulose, cellulose nanofibres, lettuce leaves etc.)	Bioaerogels Biofilms Bionancomposites Hydrogels. Biopolymers
Tissue engineering		Scaffolds
Energy production	Woody and non-woody biomass	Thermal energy, power generation, gasification technology, combustion

From the perspective of the circular bioeconomy, there is the need to continue developing innovative solutions and results for the application of agro-industrial by-products. Biorefining is an integrated processing approach and the goal of biorefining is to maximize the utilization of plant-derived materials by systematically extracting and enhancing their constituent elements, thereby yielding bioenergy, biofuels, as well as biobased chemicals and materials [8]. These resources are abundant and hold immense potential as cost-effective biomass for biorefinery applications. The use of supercritical and subcritical fluids for biomass hydrolysis and the extraction of bioactive compounds from waste materials is now an established and practical technology [18]. The utilization of supercritical fluid technology represents an innovative and emerging approach. The pretreatment of by-products is done by an alternative method, eutectic solvent technology [18] which has the versatility to be applied across a wide range of waste processing scenarios. There has been a significant shift in expectations surrounding the development of cost-effective and environmentally friendly energy production methods using residues of agro-industrial by-products. A notable aspect of the current landscape in waste reuse is the increasing interest from numerous companies and biorefineries in creating processes for sustainable energy production. In Europe, over 40 biorefineries were identified as utilizing lignocellulosic materials for the generation of sustainable energy, highlighting the growing momentum in this field [18].

1.3. Hydrophilization of Lignocellulosic Materials (Physical and Chemical)

The utilization of lignocellulose materials such as natural fibres in the polymer industry is attributed to their abundant availability, biodegradability, biocompatibility, cost effectiveness, recyclability, and eco-friendliness. However, lignocellulose materials exhibit lower strength and modulus, and their hydrophilic nature, characterized by a strong attraction to water, represents a significant drawback. The inherent hydrophilicity of natural fibres is linked to the existence of hydroxyl groups, particularly within the crystalline cellulose region. This hydrophilic nature can pose challenges when these natural fibres are combined with certain hydrophobic thermoplastic polymers, as the weak interfacial adhesion and bonding in the matrix can result in water absorption [21]. This water absorption, in turn, can lead to swelling and a reduction in the strength of the composite materials. The hydrophilic nature of cellulosic fibres, such as those derived from cellulose, lignin, and hemicelluloses, which are the primary components of cellulosic fibres, may be ascribed to the hydroxyl groups found within these constituent components. In simpler terms, the capability of lignocellulosic materials to attract and

retain moisture stems from the presence of hydroxyl groups within these components, which can form hydrogen bonds with water molecules. These hydrogen bonds are numerous among the large molecules within the cell wall of the fibres, making them inherently hydrophilic. When moisture comes in to contact with the fibres, these hydrogen bonds can break, and the hydroxyl groups create new hydrogen bonds with water molecules. Therefore, it can be concluded that cellulosic fibres primarily absorb water through the hydrophilic -OH groups present in their structure [22].

Incorporating lignocellulosic materials in natural fibre-polymer composites can result in a substantial increment in water adsorption, particularly in moist conditions or when these composites are immersed in water. This heightened water absorption is primarily due to the hydrophilic nature of natural fibres, which contain polar groups, such as hydroxyl groups [22]. The chemical constituents found in lignocellulosic fibres are responsible for this moisture uptake. Natural fibres tend to absorb water primarily through hemicellulose, amorphous cellulose, lignin, and crystalline cellulose [22]. To mitigate this moisture absorption, chemical modification processes can be employed to significantly reduce the presence of lignin, hemicelluloses, and the amorphous cellulose region, which are the main culprits behind moisture absorption [22]. Moisture absorption can also be influenced by various tribological factors, including surface modifications, polarity, permeability, degree of crystallinity, cross-linking, viscosity, fibre orientation, interfacial adhesion bonding, volume fraction, and the inherent properties of natural fibres. This moisture absorption can have detrimental effects on the mechanical properties and dimensional stability of composites. To address this issue, techniques such as physical and chemical surface modifications can be employed to significantly reduce the water absorption capacity of natural fibres. A study [23] analysed the impact of surface treatment modification on the water absorption properties of sisal fibre. The sisal fibres that were modified with acetyl and alkali showed a substantial enhancement in sisal fibre hydrophilicity. Compared to pure sisal fibre, the modified sisal fibres exhibited a reduction in water absorption ranging from 28% to 42% [23].

Physical treatments applied to lignocellulosic materials do not alter the fundamental structural composition of the fibres; instead, they exclusively modify the surface properties while increasing the hydrophobicity of these materials [24]. This, in turn, leads to improved mechanical bonding between the lignocellulose materials and the matrix, ultimately enhancing the overall properties of the composite. There are various physical treatment methods that can be employed for the purpose of imparting hydrophobic properties. These approaches include heat treatment, plasma treatment, corona treatment, thermal treatment, ultraviolet (UV) treatment and electric discharge treatment [24]. Corona and UV treatment, for instance, enhance the compatibility of hydrophilic fibres with the matrix, elevate the polarity of the material surface, and increase composite strength. In the case of heat treatment, fibres are subjected to heating at temperatures just below their degradation point. This treatment affects water content of the materials, mechanical, chemical, and physical properties [25].

Plasma as a physical technique for surface modifications is eco-friendly as it eliminates the need for solvents in its processes. This approach involves the use of plasma to both physically and chemically alter surfaces. In the plasma state, ionized molecules are capable of enhancing surface roughness through etching and grafting [26]. These processes exclusively impact surface properties and can effectively enhance the hydrophobic characteristics of cellulose fibres. This research [27] demonstrated the use of oxygen plasma treatment on bacterial cellulose which is a lignocellulose

material to increase hydrophobicity. This surface modification led to the creation of a hydrophobic bacterial cellulose membrane that can endure wet conditions and high stable when stored in water.

Lignin can also be utilized to decrease hydrophilicity in most cellulosic materials, including natural fibres, nanocelluloses and sheets. Coatings derived from lignin have been employed to enhance the hydrophobicity of cellulosic materials. However, in certain instances, the natural lignin content within the raw materials has proven adequate to confer improved hydrophobic properties upon the materials [26]. This study [28] synthesized hydrophobic lignin derivatives through esterification with oleic acid. These esterified lignin compounds were then applied to bleached kraft pulp sheets and wood using a spray and spin-coating method. As a result of these coating processes, the contact angle of the pulp sheets increased significantly, going from an initial angle of 80° to a range of 122°–123°. Similarly, the contact angle of the wood, initially measured at 68°, increased to 147° when sprayed and 137° when spin-coated with the esterified lignin derivatives. Agricultural derived lignin was used as a filler in polylactic acid (PLA) matrix to reduce hydrophilicity [29]. The lignin was purified, treated through acetylation, and blended with the PLA. The contact angles of the PLA acetylated lignin composites increased from 73.4° to 81.7° when compared to the pure PLA and PLA lignin composites. Acetylated lignin exhibits enhanced hydrophobicity due to the substitution of hydrophilic OH groups with less polar acetyl groups.

Chemical reactions serve to enhance the adhesion between the matrix and cellulose fibres when these fibres undergo chemical modification. Numerous chemical treatments have been explored for this purpose, including benzoylation, the use of alkali, silane, acetic anhydride (acetylation), and the use of coupling agents. One of the most used chemical methods to decrease the hydrophilicity of lignocellulose materials is esterification. Acetylation modification is an esterification process that changes the structure of the cellulose materials, and the reaction involves the interaction between the hydroxyl groups present in the cellulose materials and acid anhydrides, acyl chloride or carboxylic acid [30]. This reaction causes the presence of ester groups into the cellulose molecule. The hydrophilic nature of the cellulose materials diminishes during acetylation treatment due to the interaction between acetyl groups (CH_3CO) and hydroxyl groups (-OH), resulting in the removal of water [22]. In this study [31], cellulose esterification was conducted in a solid-state approach, capitalizing on the water content on the surface of the cellulose fibres. The acetylation reaction was carried out using N-acetylimidazole as the reagent and imidazole as the catalyst. Importantly, the acetylation process had no discernible impact on the structure of the fibres. As a result, the water contact angle of the fibres saw a significant increase, rising from an initial 12° to approximately 134°. Silylation is another technique for cellulose chemical modification where a coupling known as silane is utilized. The silane treatment process involves three key stages: hydrolysis, condensation, and the formation of chemical bonds on the cellulose fibres. It has been observed that employing a silane coupling agent is an effective method for improving the bonding interface between the cellulose - fibres and the matrix, ultimately reducing the propensity of the fibre to absorb water.

This study holds significance in assessing how these agro-industrial byproducts affect the physical, mechanical, and chemical properties of polypropylene. The outcomes of this investigation will provide valuable insights for manufacturers to enhance the performance of polypropylene materials by incorporating these agro-industrial by-products. This can eventually lead to a reduction in the quantity of polymer plastic used and contribute to cost-effectiveness. Such formulations may find application in food packaging due to their enhanced biocompatibility. The research findings are

expected to contribute to the environmental sustainability of polypropylene production. Finally, this research aims to advance sustainability by promoting the reusing of oat and spelt husks, thereby reducing the reliance on plastics, and improving overall environmental impact.

1.4. Chapter Summary

Agro-industrial by-products and their impact on the environment delves into the significance of these by-products, which result from agricultural and industrial processes, and explores their various environmental implications. The production and disposal of agro-industrial by-products can contribute to environmental issues such as pollution, waste management challenges, and ecological imbalances. Also, potential solutions or strategies to mitigate the negative environmental effects associated with these by-products were discussed. One of these strategies is to utilize agro-industrial by-products as a filler for polymer composite production thereby reducing wastage and overreliance on synthetic resources for plastic production. The application of agro-industrial by-products, tracing their utilization through past, present, and future perspectives explore the historical context of how these by-products have been employed in various industries and agricultural practices. The evolution of techniques and technologies for utilizing agro-industrial by-products over time was presented. The present applications and their significance in contemporary practices were highlighted, including their role in sustainable agriculture, resource efficiency, and economic considerations. The application of these by-products provides insights into future perspectives, emerging trends, innovations, and potential advancements in renewable biopolymer production. The hydrophilization of lignocellulosic materials, covering both physical and chemical aspects of the process explores methods to enhance the hydrophilic nature of lignocellulosic materials, which are derived from plant cell walls. Physical hydrophilization methods involve altering the surface properties of these materials without chemical reactions, potentially through physical treatments or coatings. Chemical methods involve the use of chemical agents to modify the structure of lignocellulosic materials, making them more water-resistant. There is need to enhance the hydrophobicity lignocellulosic materials in terms of their applications and benefits as this leads to improved performance in polymer composite processes, increased compatibility with polymer matrix and enhanced interface interactions between the fibres and polymer matrix.

2. Experimental

2.1. Materials

Polymers: 3 polypropylene (PP) homopolymers were used:

- PPH HN5046 (Slovnaft, Solvakia Republic) possessing high fluidity and a narrow molecular weight distribution with a high melt flow index (MFI) of 50 g/10min
- PPC 9712 (TotalEnergies, Belgium) which is a heterophasic copolymer with an MFI of 25 g/10min
- PPC 10642 (TotalEnergies, Belgium) which is a nucleated antistatic heterophasic copolymer with a high MFI of 44 g/10min

Fillers: Two agro-industrial by-products were applied for polypropylene modification. Oat husks and spelt husks were sourced from Malsena Plius UAB, Lithuania. They are lignocellulose natural fibres and were ground using ball mills to reduce particle size. The oat and spelt husks used for investigations are presented in Figs. 7 and 8.


Fig. 7. Oat husk before (a) and after (b) milling

Fig. 8. Spelt husk before (a) and after (b) milling

Compatibilizer: Improving the interfacial interaction characteristics in composite materials containing lignocellulosic fillers is more effective when utilizing a compatibilizer, leading to enhanced properties in PP composites. The coupling agent chemically functionalized polypropylene-graft-maleic anhydride (PP-g-MA) Orevac CA 100 (Palmer Holland, USA) with a melt flow rate of 10 g/10 min, a melting point of 167˚C and a density of 0.91 g/cm^3 was used to improve the adhesion of PP/ waste composites. Structure of PP-g-MA:
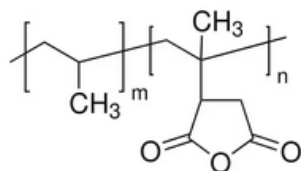

The incorporation of grafted maleic anhydride increases polarity to the polypropylene, resulting in exceptional adhesion characteristics to natural fibres and lignocellulose fillers.

Modifier: Hexamethyldisilazane (HMDS) was used to modify surface of filler particles. HMDS is a colourless liquid possessing a pungent odour reminiscent of ammonia and the principal utilization lies in serving as a surface modifier and adhesion enhancer across a range of applications. HMDS is an N-silyl compound. It is obtained from ammonia by replacing two hydrogens with trimethylsilyl groups:

Antioxidant: Mileox AO-B215 PD is a specialized system used in polyolefins for both processing and long-term thermal stabilization. It consists of a combination of phenolic antioxidant (AO 168) and phosphate antioxidant (AO 1010), (Fig. 9) which provides processing stability and long-term thermal protection throughout the service life of a material. This antioxidant was added to the PP composition to safeguard against plastic degradation when subjected to elevated temperatures during the processing phase.
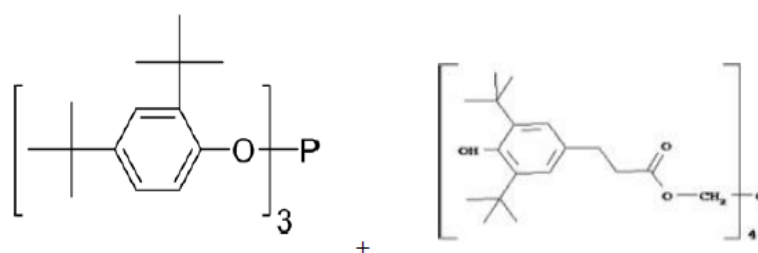
Fig. 9. Structure of AO-B215

2.2. Filler Particles Modification Procedure

The filler particles were subjected to HMDS vapor using a chemical vapor deposition technique, and this process was carried out without the use of a catalyst at an elevated temperature. The filler powder was positioned on porous filter paper within a sealed chamber, which also contained an open vessel holding approximately 120 mL of liquid HMDS for a duration of 6 hours at a specified temperature. 120ºC [32].

2.3. Composition Preparation Procedure

The composites where prepared by different stages of filler preparation, filler surface modifications and finally composite preparation. The flow chart of the composite preparation procedure is presented in Fig. 10. The oat and spelt husks were cleaned and sieved to separate the husks from foreign materials. The husks were now dried to remove any moisture content. The cleaned and dried husks were then subjected to milling process to be ground into filler consistency. Fillers were then modified by silylation to enhance their interfacial adhesion in the polymer matrix. Different formulations of the unmodified and modified fillers amount where then mixed with the polymer. This polymer matrices were then mixed with a compatibilizer and antioxidant to improve matrix interaction and thermal stabilisation respectively. All components of PP composites were mixed in a twin-screw extruder at a temperature of 190 °C. The samples for mechanical testing were formed by injection moulding at a temperature of 240ºC at a pressure of 700 bar.
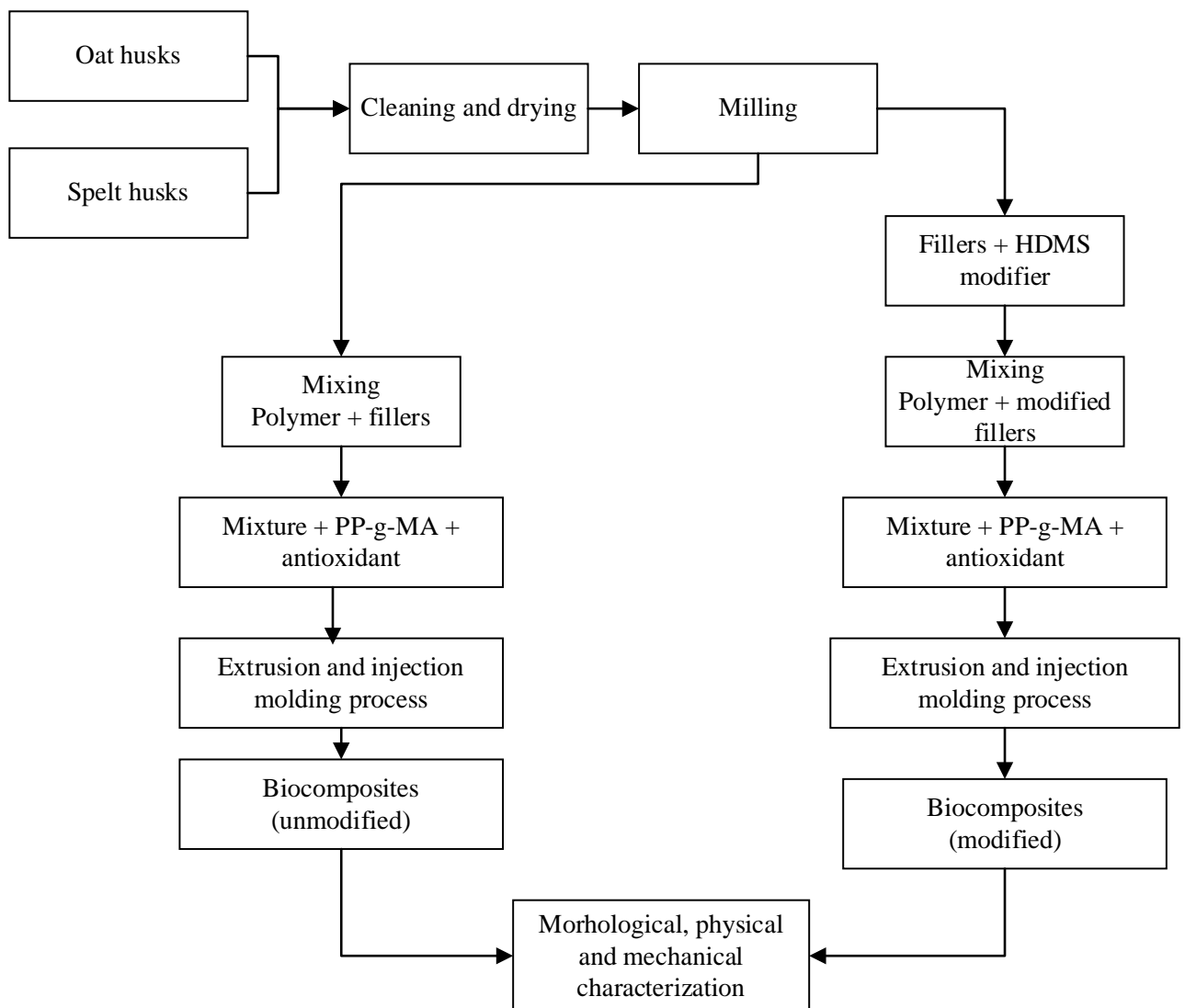

Fig. 10. Flowchart of oat and spelt husks PP biocomposites preparation

2.4. Methods of Morphological Characterization

Scanning electron microscopy (SEM) characterizes the surface morphology, shape, particle size of lignocellulosic oat and spelt filler particles and the morphology of PP composite. Quanta 200 FEG

microscope (FEI, Eindhoven, The Netherlands) was used. The samples were analysed under low vacuum conditions at 20.0 kV employing an LDF detector. Before this, the fracture surface of the samples was covered with a thin layer of silver.

Thermogravimetric analysis (TGA) is a technique used for investigating the thermal degradation and stability of composites containing fillers. TGA measures the percentage of weight change or loss in response to an increase in temperature. TGA was performed using a Perkin Elmer instrument TGA 4000. The analysis was performed within a temperature range of 30–600°C at a heating rate of 10°C/min (flow 20 cm^3/min) under a nitrogen and oxygen atmosphere.

2.5. Methods of Determination of Physical Properties

Contact angle measurement is a method for assessing the level of surface wetting. The measurement was conducted using a pocket goniometer (PG2, Rycobel NV, Deerlijk, Belgium) at room temperature, employing the sessile drop method. A drop of controlled volume deionized water (~ 5 µL) was placed on the test surface and the contact angle were measured (measurement time 5 s) at five different sample locations to calculate the arithmetic mean of the measurements. The measurement of CA (Contact Angle) was carried out using a technique based on active contours to investigate the wetting properties of the filler particles, tablets were prepared by compressing the particles at 3 MPa for 3 min.

Water vapour absorption (WVA) test is done to assess the quantity of water vapour a sample material can absorb within a defined timeframe. The samples were dried in the oven at 60°C for about 48 hours to eliminate moisture and weighed before the WVA test. Subsequently, the samples were positioned inside a desiccator filled with water as presented in Fig. 11 to achieve a relative humidity (RH) of 100% and then subjected to an extended period within an oven set at 40°C. At defined intervals of 24 hours, samples were weighed, and the mass of the sample at the specific time, denoted as Wt, was recorded. The calculation of WVA is performed in accordance with Eq. 1.

$$WVA = [(Wt-Wo)/Wo] * 100 \qquad\qquad (1)$$

Fig. 11. Specimens of oat and spelt placed in the desiccator for water vapour absorption analysis

Water absorption test is used to assess the rate at which composites absorb water or moisture when they are exposed to a wet environment. Prior to commencing the water absorption tests, the samples were subjected to desiccation for about 48 hours in the oven at 60°C to eliminate moisture. Then the

samples were placed in containers filled with distilled water and placed in an oven set at 40°C for a long period of time as presented in Fig. 12. The weight of the test samples was initially measured, and any subsequent weight increase for each sample was recorded at regular intervals of 24 h. The water absorption test was conducted over duration of over 1400 h, as the maximum water absorption was reached during this period. Fourteen distinct PP compositions were employed for the investigation as presented in Table 3. The percentage (%) of water absorption is expressed in Eq 2.

$$WA\ (\%) = [(M_f\text{-}M_i)/M_i] * 100 \tag{2}$$

Fig. 12. Samples of PP composites placed in the oven for water absorption analysis

Table 3. Polypropylene compositions used for investigation

	Composition, wt%:													
	unmodified								modified by HMDS					
PPH HN 50 46							74.8	74.8					74.8	74.8
PPC 9712			54.8	54.8	44.8	44.8					54.8	54.8		
PPC 10642	54.8	54.8							54.8	54.8				
Oat husk		30	30			40		10		30	30		10	
Spelt husk	30			30	40		10		30			30		10
Orevac CA 100	15	15	15	15	15	15	15	15	15	15	15	15	15	15
Mileox AO-B215	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	100	100	100	100	100	100	100	100	100	100	100	100	100	100

Bulk density of the filler particles was calculated based on their volumes and masses. In this instance, a plastic container with a volume of 50 ml was filled with the lignocellulosic sample and weighed with a precision of 0.001 g (Fig. 13). The average of three measurements was employed.

The bulk density was calculated according to the Eq. 3:
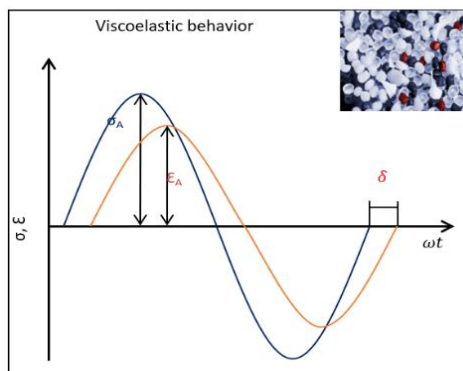
$$\rho = V/M \tag{3}$$

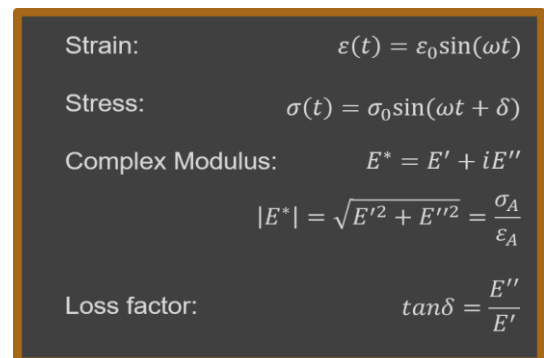**Fig. 13.** Determination of bulk density of filler particles

2.6. Mechanical Properties Determination Methods

The test specimens for mechanical testing were fabricated at Vilkritis UAB in Vilnius. Polypropylene was blended with husks at a temperature of 190°C using a twin-screw extruder. Dog-bone-shaped specimens for the tensile test were fabricated from PP/husk composite pellets through injection moulding (at a temperature of 240ºC at a pressure of 700 bar).

Dynamic Mechanical Thermal Analysis (DMTA) was employed to assess the viscoelastic properties of the PP composites. A specimen of the material to be examined is subjected to a certain sinusoidal stress or strain (axial or torsional deformation), and the reaction of the material is measured (Fig. 14, a). The mathematical definitions of important DMTA parameters are depicted in Fig. 14, b.

a

Strain: $\varepsilon(t) = \varepsilon_0 \sin(\omega t)$

Stress: $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$

Complex Modulus: $E^* = E' + iE''$

$$|E^*| = \sqrt{E'^2 + E''^2} = \frac{\sigma_A}{\varepsilon_A}$$

Loss factor: $tan\delta = \frac{E''}{E'}$

b

Fig. 14. Stress, strain, and phase shift behaviour of viscoelastic material (a) and mathematical definition of important terms for DMTA measurements [33]

The tests of PP composite samples were performed with an Anton Paar (Graz, Austria) rheometer MCR302 in the shear mode, raising the temperature from –75 to 200 °C at a heating rate of 2 °C/min. The storage (elastic) modulus G' (or E'), loss (viscosity) modulus G'' (or E'') and damping/loss factor tanδ were measured. Storage modulus G' is measure for the stored energy during the load phase, while loss modulus G'' is measure for the (irreversibly) dissipated energy during the load phase due to

internal friction. The ratio of the loss to the storage is tanδ and is often called damping and it is a measure of the energy dissipation of a material.

***Tensile testing*** was performed utilizing an H25KT universal testing machine (UTM) from Tinius Olsen (Salfords, UK), equipped with a 1 kN load cell and a cross-head speed of 50 mm/min. The test samples (Fig. 15.) conformed to the specifications outlined in the LST EN ISO 527 standard, which is typically employs 5 samples for tensile measurements.
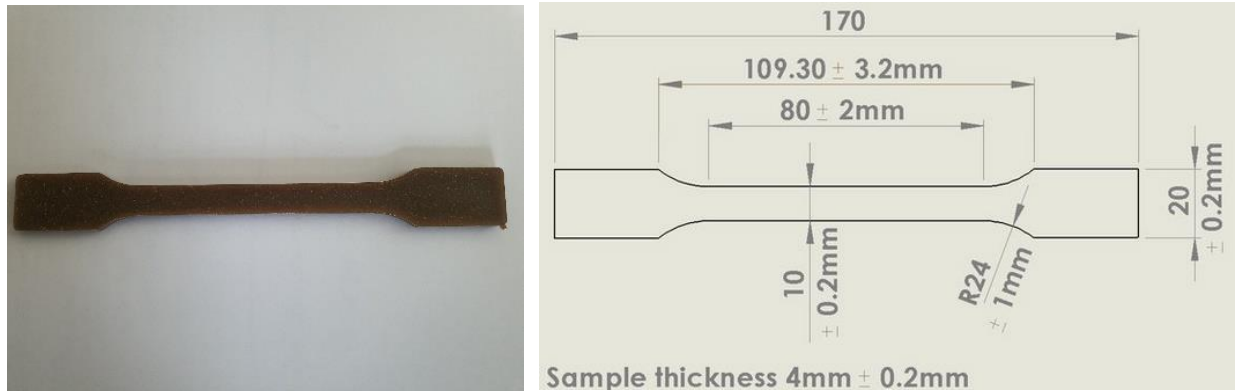
Fig. 15. Composite sample for tensile testing according to ISO 527

A vernier calliper was used to measure the thickness of the specimens at three different areas of each specimen and the average thickness was calculated. The specimens had a width of 10mm and the working zone was 100mm on the UTM used to investigate the tensile strength as presented in Fig. 16, a. Tension is then applied to specimens on both ends.

a   b
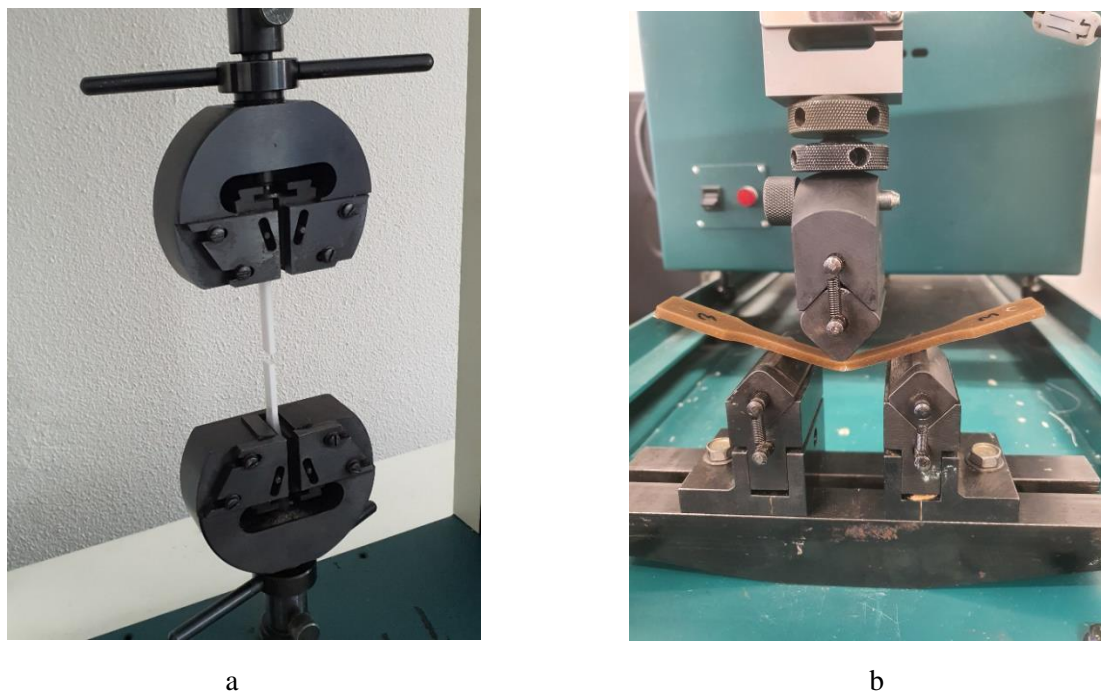
Fig. 16. Tensile test (a) and 3-point bending test until test sample fracture (b)

The stress, strain, and Young's modulus are determined using the machine's software application. Stress is defined as the ratio of the applied force to the initial cross-sectional area, represented by (Eq. 4)

$$\sigma = F/A0 \tag{4}$$

Strain measures the deformation of the sample and is calculated using the (Eq. 4), where L represents the final length, and Lo represents the original length.

$$\varepsilon = (L - Lo)/ Lo \tag{5}$$

Young's modulus, denoted as E, is the ratio of stress to strain, expressed as (Eq. 5). It also corresponds to the slope of the stress-strain curve.

$$E = \sigma/\varepsilon \tag{6}$$

A three-point bending test was conducted for the composites according to the requirements of ISO 178 standard. The flexural strength and flexural modulus were determined. Bending test was performed utilizing an H25KT universal testing machine (UTM) from Tinius Olsen 25KT (Salfords, UK), equipped with a 1 kN load cell and a cross-head speed of 20 mm/min. Length of span between supports was 64 mm and radius of loading edge was 5 mm. Sample undergoing testing is presented in Fig. 16, b.

2.7. Chapter Summary

The description of experimental materials and methods of how different properties are measured and evaluated is outlined in this section. Filler particle preparation with oat and spelt husks which is modified to enhance compatibility properties in the polymer matrix. Polymer composition is prepared with three different PP and mixture with compatibilizer and antioxidant to enhance interface interaction and thermal stability respectively. SEM and TGA techniques are utilised to characterize the morphology and thermal behaviour of the materials respectively. The physical properties like density, wetting and moisture behaviour of the filler particles and composites are determined. The contact angle tests, bulk density, water vapour absorption and water absorption tests are employed for this purpose. The mechanical properties and characteristics like the elasticity, tensile and flexural strength is determined by tensile and a three-point bending tests. DMTA is also a method utilised to determine the stiffness, loss and storage modulus of the composites.

3. Results and Discussions

3.1. Oat and Spelt Husks Particles Characterization

The chemical composition of the waste fillers utilized in this research is shown in Table 4. Oat husk has a slightly higher cellulose content than spelt husk which means oat husk as evaluated can have a better reinforcing potential of polymer matrix theoretically. Oat husk also has higher lignin content and lower hemicellulose content compared to the spelt husk. Both constituents significantly contribute to the thermal and moisture stability of the filler, with lignin as the most resistant and hemicellulose as the least resistant constituents playing crucial roles.

Table 4. Chemical composition of oat and spelt husks [34, 35]

Constituent (%)	Oat husk	Spelt husk
Cellulose	37.3	37
Hemicellulose	34.4	40
Lignin	21.8	20

The process of treatment by silylation of the surface of waste particles and the effect of this treatment was investigated by SEM analysis. SEM was used to observe the particle size, morphology and shape of the oat and spelt particles. The obtained images of the untreated and silylated spelt particles are presented in Fig. 17 and Fig. 18 respectively at different magnifications. The shapes of the untreated spelt particles look irregular, rectangular like shapes with varying aspect ratios. There are also many smaller particles that sizes are varied from about 10 μm to 100 μm with a heterogeneous surface. Also, holes and formations of various sizes are evident on the surface of the spelt husks. The silylated spelt particles have less irregularities and compact sizes (Fig 18). There are less smaller particles, almost homogenous surface with little or no holes formation on the surface of the spelt husks.
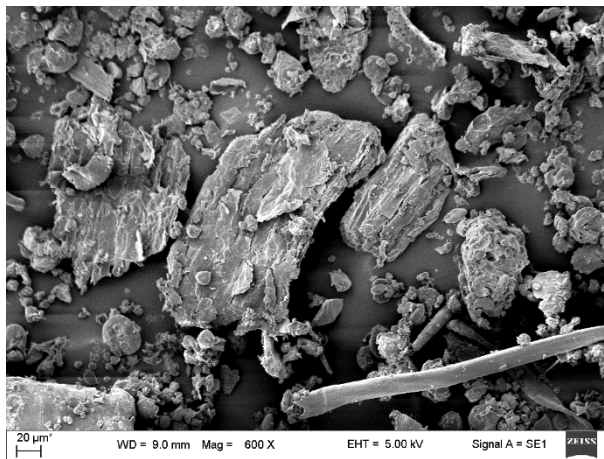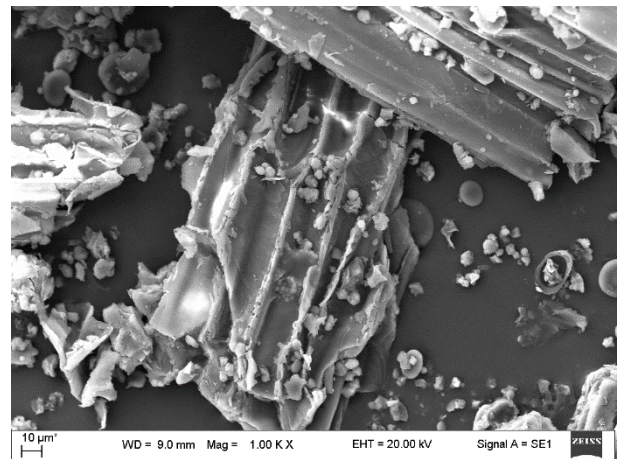
a   b

Fig. 17. SEM images of spelt particles at different magnifications: a – 600×; b – 1000×; c – 2000×; d – 3000×

Fig. 18. SEM images of silylated spelt particles at different magnifications: a – 600×; b – 1000×; c – 2000×; d – 3000×

SEM images of both untreated and silylated oat particles are illustrated in Fig. 19 and Fig. 20, respectively, at different magnifications. The untreated oat particles exhibit rough, irregular, rectangular-like shapes with varying aspect ratios as observed in Fig 19. Additionally, there are numerous smaller particles with size ranging from about 10 µm to 100 µm. Holes and formations of

various sizes are visible on the surface of the oat husks. The surface of silylated oat particles is smoother, less irregular (Fig. 20). There are fewer smaller particles, and the surface appears almost homogeneous with little or no formation of holes on the surface of the oat husks.
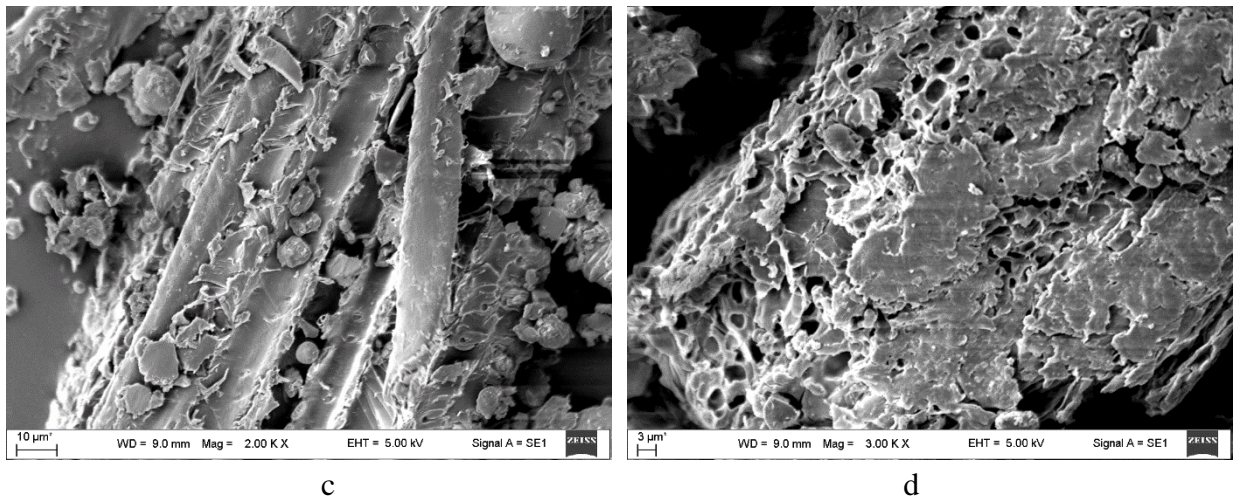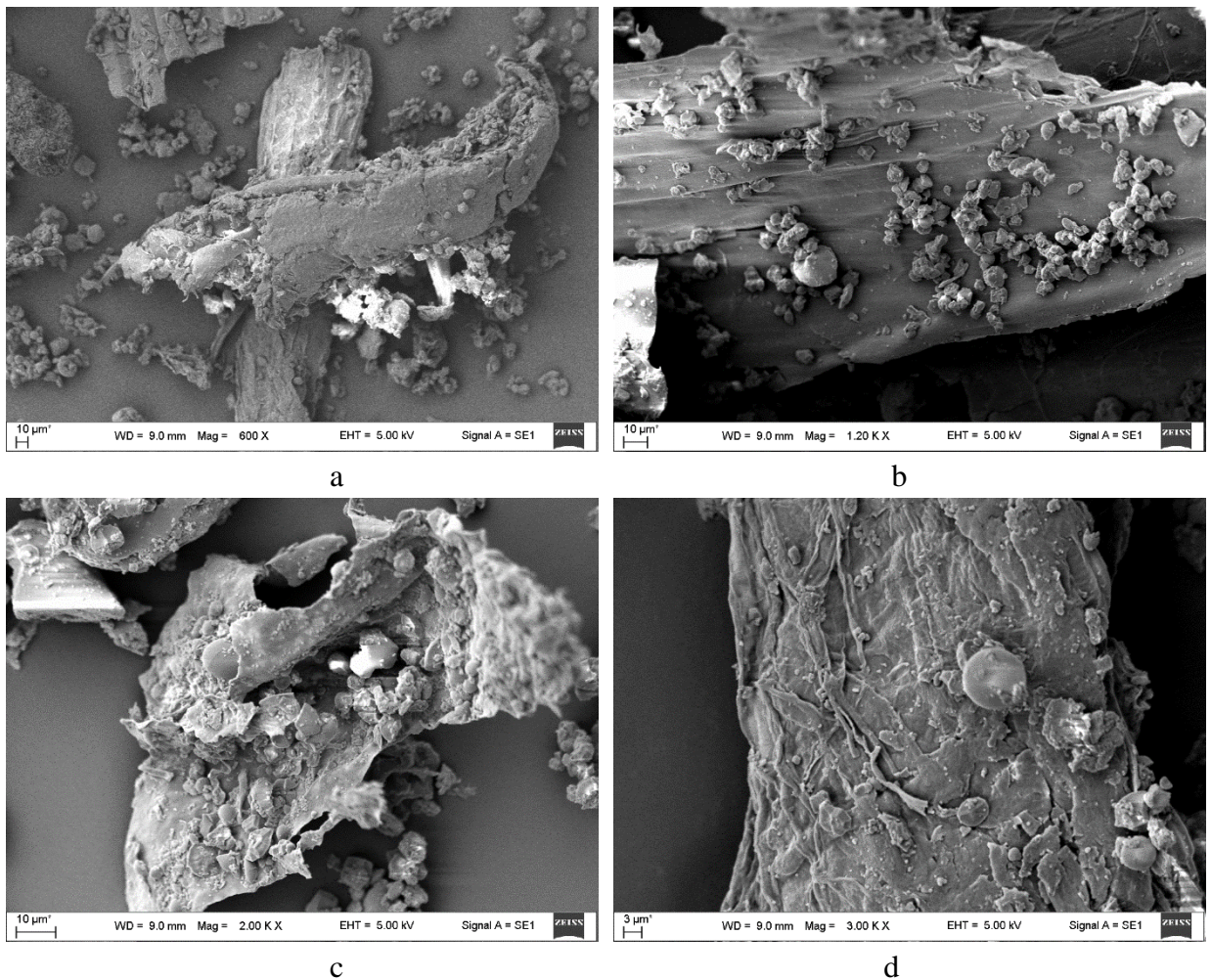

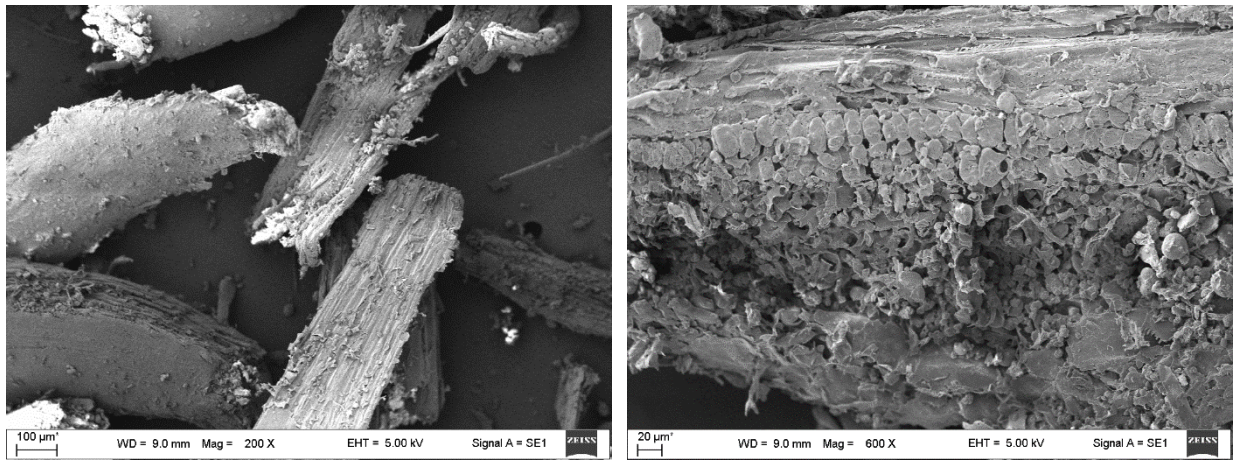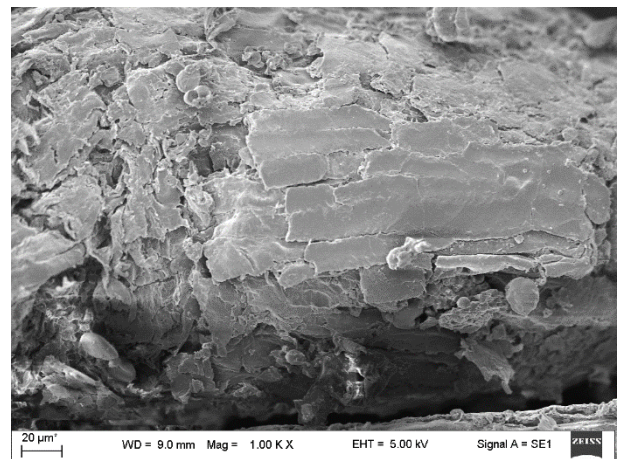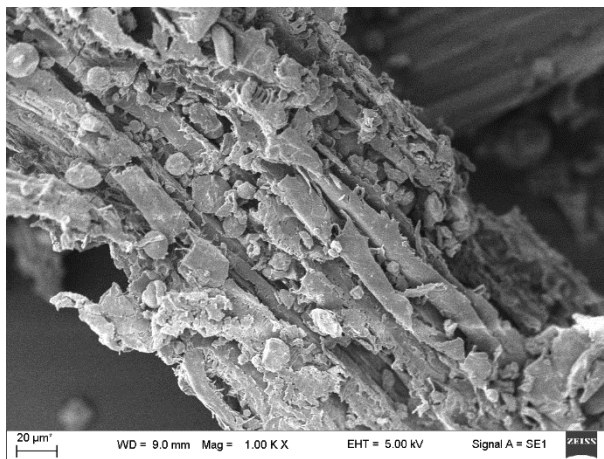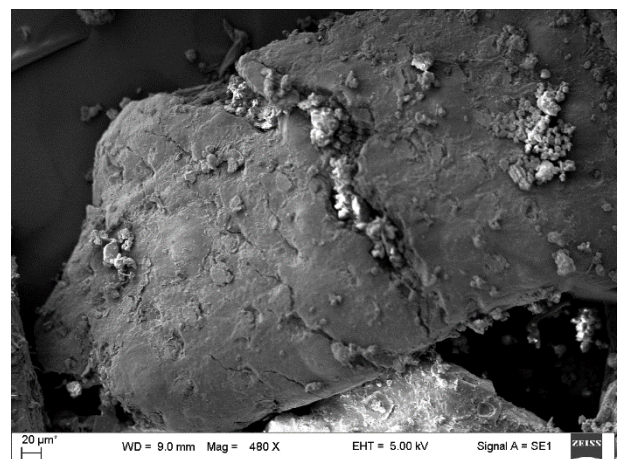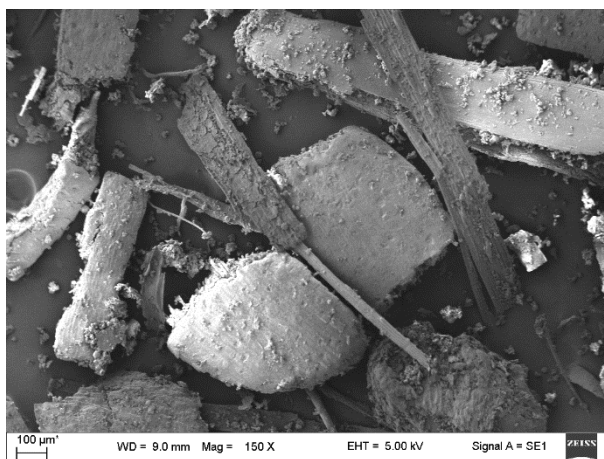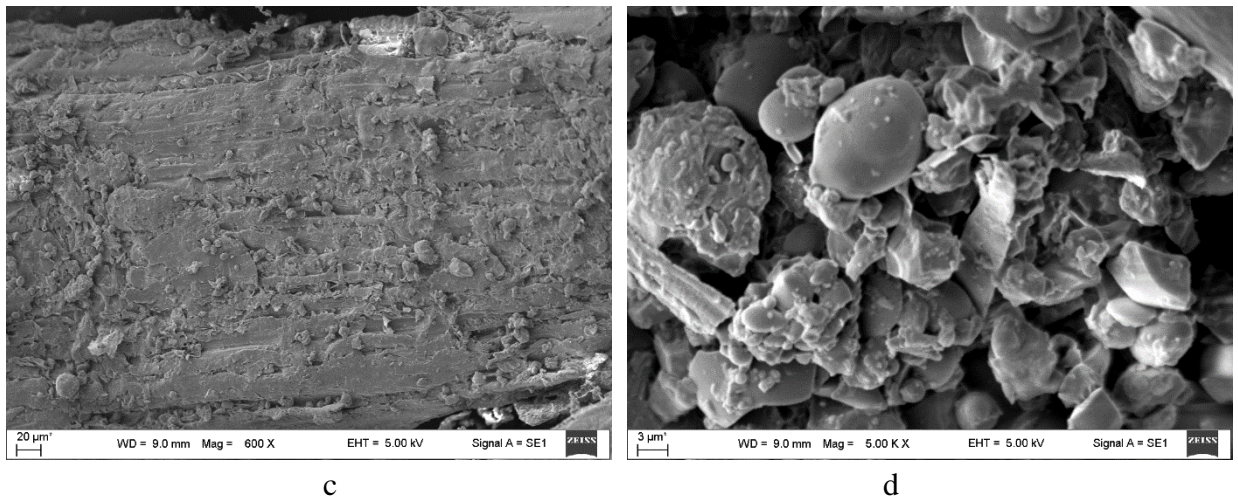**Fig. 19.** SEM images of oat particles at different magnifications: a – 600×; b – 1000×; c – 2000×; d – 3000×d – 1000×

c   d

Fig. 20. SEM images of silylated oat particles at different magnifications: a – 150×; b – 480×; c – 600×; d – 5000×

Previous studies have shown that the surface energy state of lignocellulosic particles is altered after silylation with HMDS [32]. The contact angle of water drop on the spelt and oat husks surface before and after their modification are shown in Fig. 21. The contact angle after HMDS treatment of spelt husk increased from 48° to 80.6° which is approximately about a 68% increase in surface hydrophobicity. The low contact angles of the surfaces exhibit a hydrophilic nature but after modification, the contact angles increased which shows a more hydrophobic property of the husk surface. As can be seen from Fig. 21, the treatment did not alter the surface characteristics of the oat husks. This shows no significant change in the hydrophilic nature of the husks even after modification.
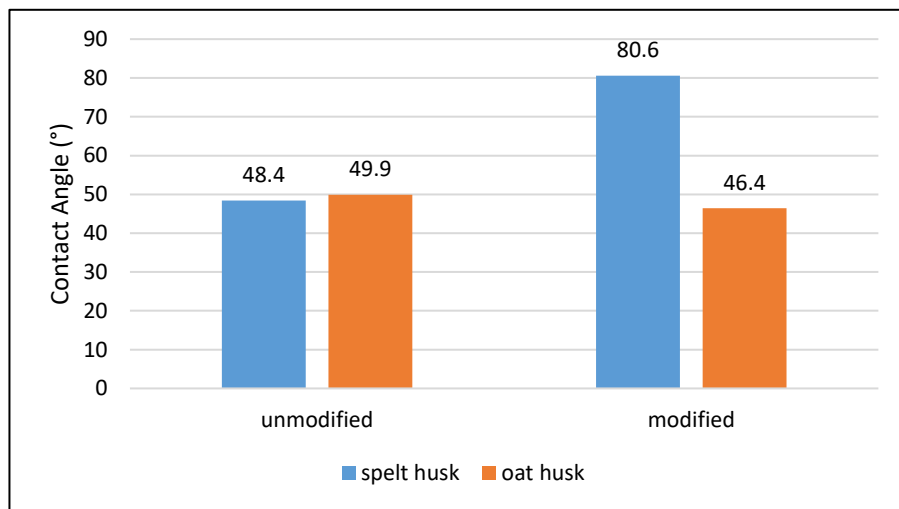
Fig. 21. Influence of the silylation on the wettability of oat and spelt husks

However, studies on bulk density have contradicted these results. The variation in bulk density of oat and spelt husks (modified and unmodified) is presented in Fig. 22. Unmodified oat husk particles bulk density is 0.8 g/ml, but it decreases down to 0.5 g/ml (i.e. about 62%) after treatment with HMDS. Oat particles are highly hydrophilic, for aggregates or agglomerates, but after treatment the surface hydrophilicity of these particles decreases, and the repulsion of particles take place. Therefore, the bulk density decreases markedly. In the case of spelt husk, no appreciable change in bulk density was obtained after their surface treatment (only in 5%).

35
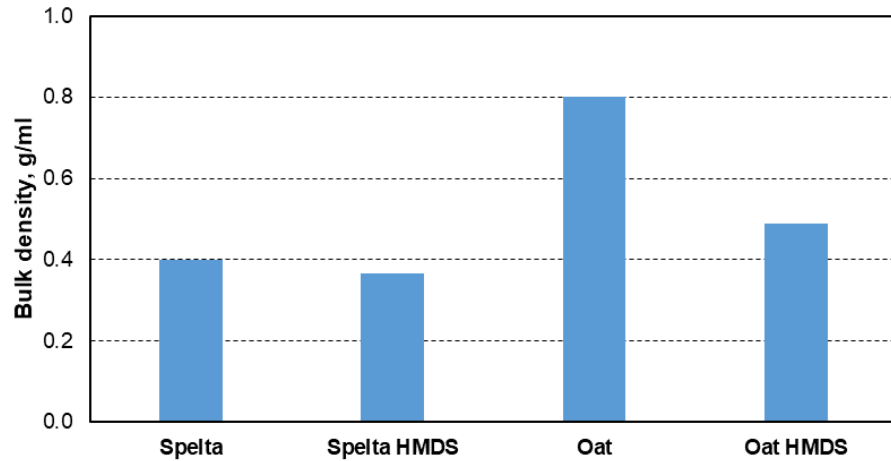
Fig. 22. Dependence bulk density of oat and spelt husks upon surface properties

The maximum water vapour absorption rate of the filler particles during the first 48 h at RH=100%. Thereafter, the WVA is almost independent on the duration of storage in a humid environment. Fig. 23 shows the water vapour absorption as a function of the square root of time of oat and spelt husks. Initially, the rate of absorption was almost same until after 48 h, oat husks absorbed more water vapour than the spelt husks. At 72 h the rate of absorption started to decline for both samples with inconsistency in different time durations. There was no significant change in absorption rate of untreated and HMDS treated oat samples. The rate of absorption for the untreated spelt husk was slightly lower than the HMDS treated spelt husks as time duration increased.
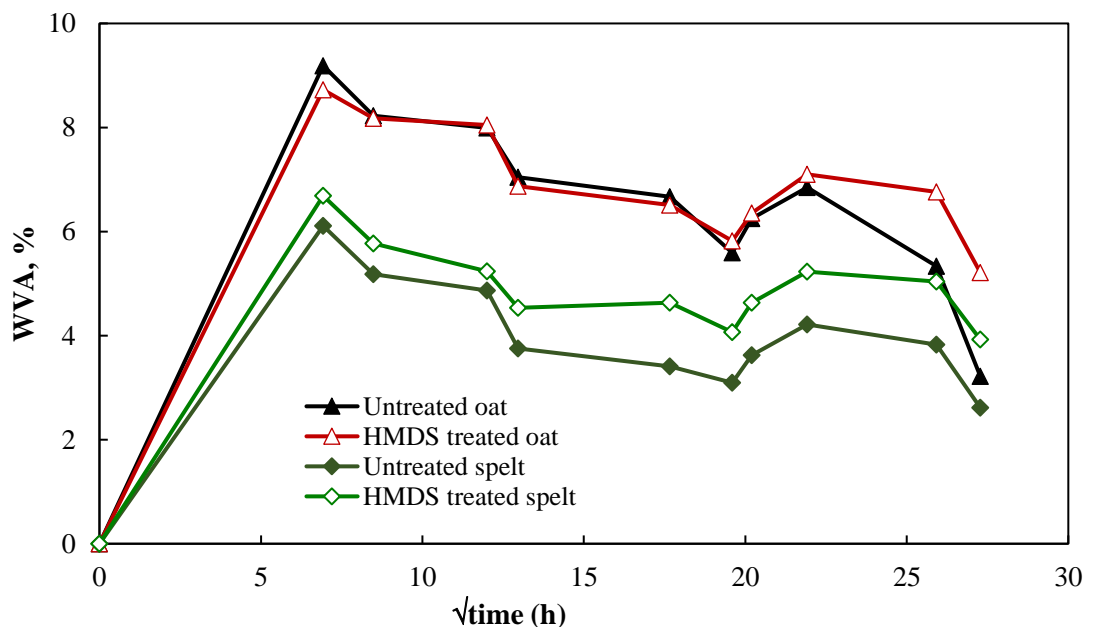
Fig. 23. Water vapour absorption as a function of the square root of time of oat and spelt husks

3.2. The Effect of Filler Particles Surface Treatment on Polypropylene Composite Structure and Properties

TGA curves were employed to determine weight loss and identify the decomposition behaviour of the composite samples at different temperatures. The thermal investigation of the PP/30% oat and PP/30% spelt composites, heated to the temperature of 1000 °C in nitrogen environment, is depicted in Figs. 24 and 25. As can be seen, the type of filler has practically no influence on the thermal degradation processes of PP composite. Fusion of PP crystallites is seen on both heat flow curves at 165-166ºC. The PP composites started to decompose at about 300ºC (with oat at 297ºC and with spelt at 302ºC). However, at this stage, the mass loss is higher for PP/30% oat (~19%) compare to that of PP/30% spelt (~13%). The ignition of composites is expressed in a strong exothermic peak in the DTA curves at a temperature ~470ºC. The residue at 1000ºC is 11% for composites with oat husks, compared with only 4% for composites with spelt husks.
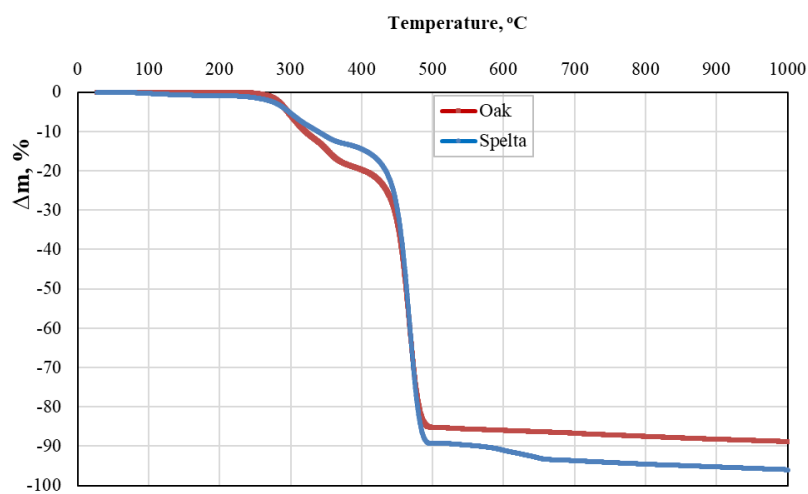
Fig. 24. TGA curves of the PP/oat and PP/spelt composites
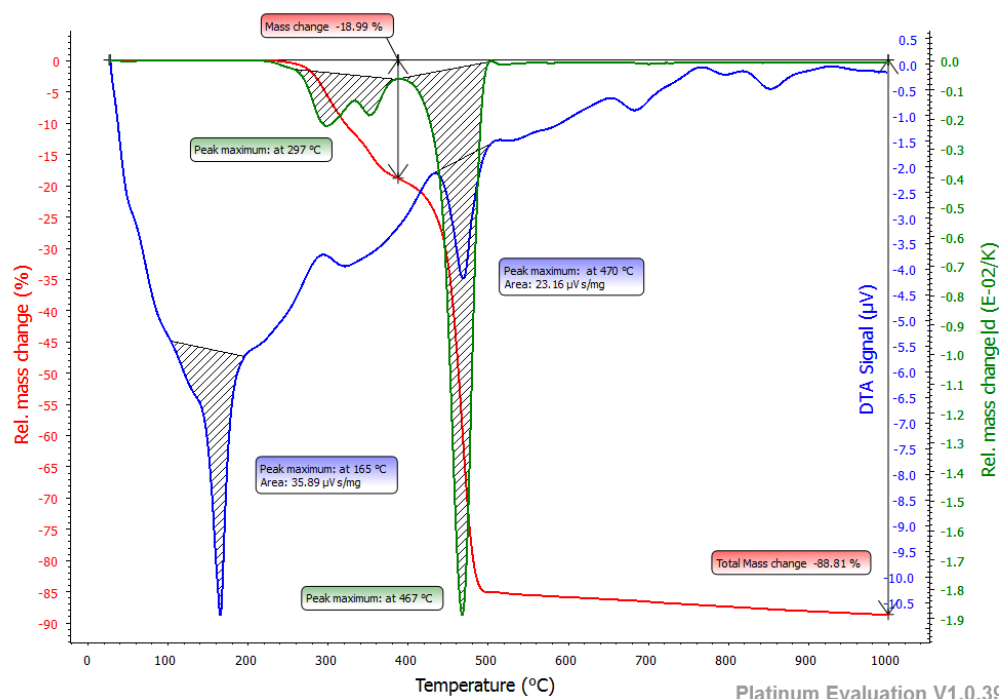
a
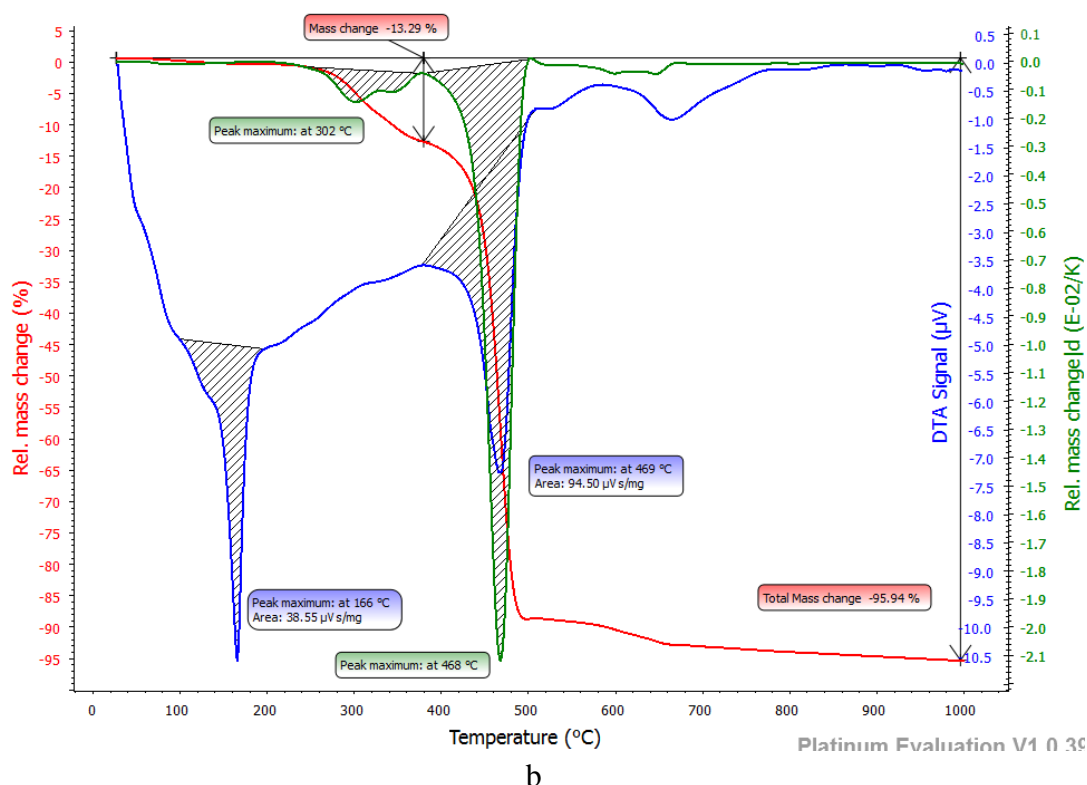
Fig. 25. Thermogravimetric decomposition process of PP filled with untreated husk particles: a – oat; b – spelt

DMTA investigations were used to investigate the viscoelastic properties of the PP composites change as a function of temperature. PP composite samples to be used for investigation are listed in Table 5.

Table 5. Glass transition and melting points of the samples tested

Samples	Glass transition temperature T_g, ºC	Melting point T_m, ºC
PPC10642 homopolymer	0	
Untreated PP/30% oat (R73)	0	
Untreated PP/30% spelt (R74)	0	~170 – 175
HMDS treated PP/30% oat (R77)	0	
HMDS treated PP/30% spelt (R80)	25	

The glass transition (T_g) and melting point (T_m) of the samples were determined from the maxima of the tanδ curves. The tanδ curves or loss factor of pure PP, modified and unmodified composites are presented in Fig. 26. The tanδ is the damping or loss factor that serves as a responsive indicator for mechanical or thermal conditions that lead to substantial intermolecular rotation and bond friction within the material. Tanδ is influenced by the matrix type, modifier, oat, and spelt contents. The change in the peak height of tanδ indicated inclusion of fillers to the PP matrix and different variations in the strength of interactions between the polymer matrix and fillers with modification affecting the glass transitions regions. Glass transition temperature T_g was determined from the β peak and the second peak is the α peak. From results presented in Table 5 it is evident that T_g is practically independent of the composition of the PP and is close to 0. Only in the case of PP/30% spelt treated T_g= 25ºC, which may be related to the heterogeneity of the sample. The tanδ curves do not show a

clear peak of T_m because the thickness of the sample decreases during the tests due to melting, therefore the apparatus does not accurately record other parameters. The analysis showed that PP composites have a melting point in the range 170-175℃.
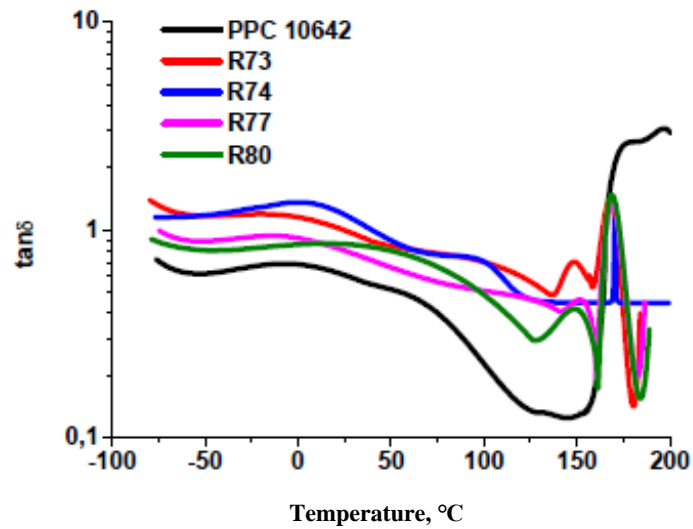
Fig. 26. Dependence of tan δ on the composition of PP composites

The storage modulus, G′ is indicative of the mechanical energy stored by a material during a loading cycle. As a result, it is directly associated to the shape recovery and stiffness of the polymer composites during loading. Fig. 27 shows the variation of storage modulus of pure PP and unmodified or modified PP/oat and PP/spelt composites as a function of temperature. In Fig. 27, b is compared storage modulus of unmodified PP/oat (R73) and modified PP/oat (R77) with the neat PPC10642. At low temperature (–75℃) the storage modulus was increased from 74 MPa to 120 MPa and 135 MPa with addition of 30wt% oat untreated and treated one, respectively. This indicates improved stiffness due to the filler modification of the composite. Untreated oat particles enhanced the stiffness of the composites by 62%, while treated with HMDS – by 82%. In the case of PP/spelt composites, no effect of modification on storage modulus was observed, which may be related to the inhomogeneity of the PP composite samples.
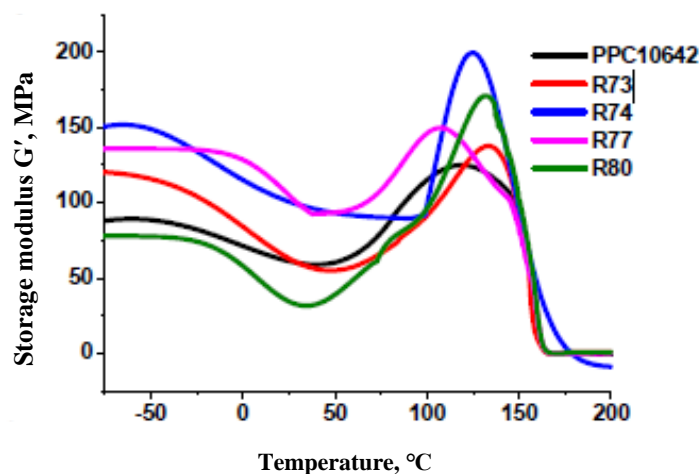
a
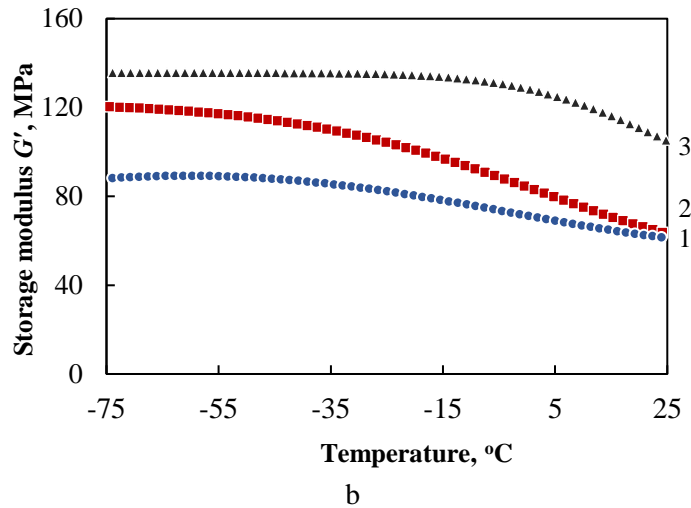
Fig. 27. Dependence of storage modulus G′ on the composition of PP composites: a – all PP samples; b – stiffness comparison of PP samples (1 – PPC; 2 – untreated PP/30% oat (R73); 3 – treated PP/30% oat (R77))

The loss modulus G'' characterizes viscous nature of a polymer material, reflecting its ability to dissipate mechanical energy. It is controlled by the motion of the chain segments, therefore, the addition of filler to the PP can lead to a reduction in the activation volume because the filler particles restrict the movement of the molecular chain segments. Fig. 28 shows the changes in loss modulus of PP/composites after incorporation of unmodified and modified oat and spelt particles. The loss modulus G'' of PP composites increase with incorporation oat and spelt fillers due to the increase in the viscosity of composites. For example, in the case of the unmodified and modified oat, G″ increases from 60 MPa up to 125 MPa and 175 MPa, respectively.
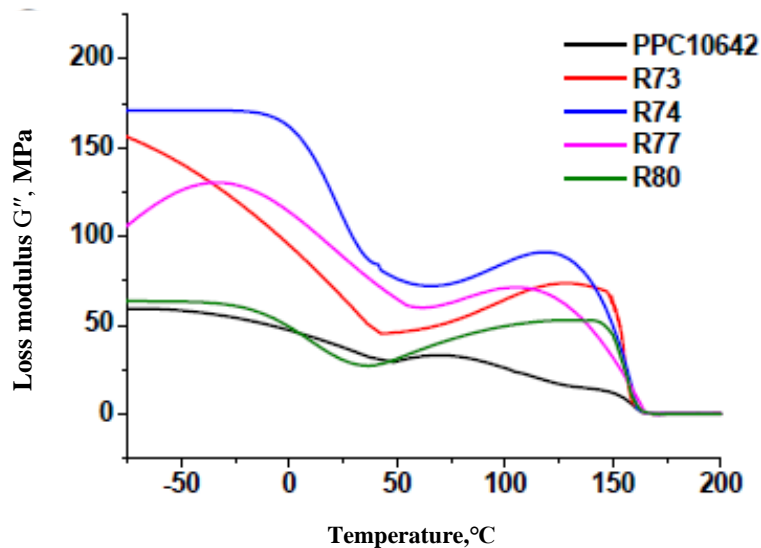
Fig. 28. Dependence of loss modulus G″ on the composition of PP composites

In further studies, it was decided to compare the influence of the filler nature (oat, spelt) and its surface state on the PPs with different mechanical and rheological properties. For this purpose, three types of PP homopolymers with different melt flow index MFI (*see* subchapter 2.1) were chosen: PPH HN5046 (MFI = 50 g/10min), PPC 9712 (MFI = 25 g/10min) and PPC 10642 (MFI = 44

g/10min). The viscosity of PPH HN5046 and PPC 10642 are polymers of similar viscosity, while PPC 9712 has a viscosity 1.8-2.0 times higher. As can be seen from Fig, 29, these homopolymers also have different strength properties and deformability. PPC 9712 shows the lowest ultimate strength (1.3-1.8 times lower than for other homopolymers), but the highest deformation ability (36%), i.e. strain at break is 3.6-4.5 times higher than for other homopolymers. Besides, for PPC 9712 is characteristic elastic behaviour with neck formation, when remaining polypropylenes exhibit plastic behaviour during deformation.

a

b
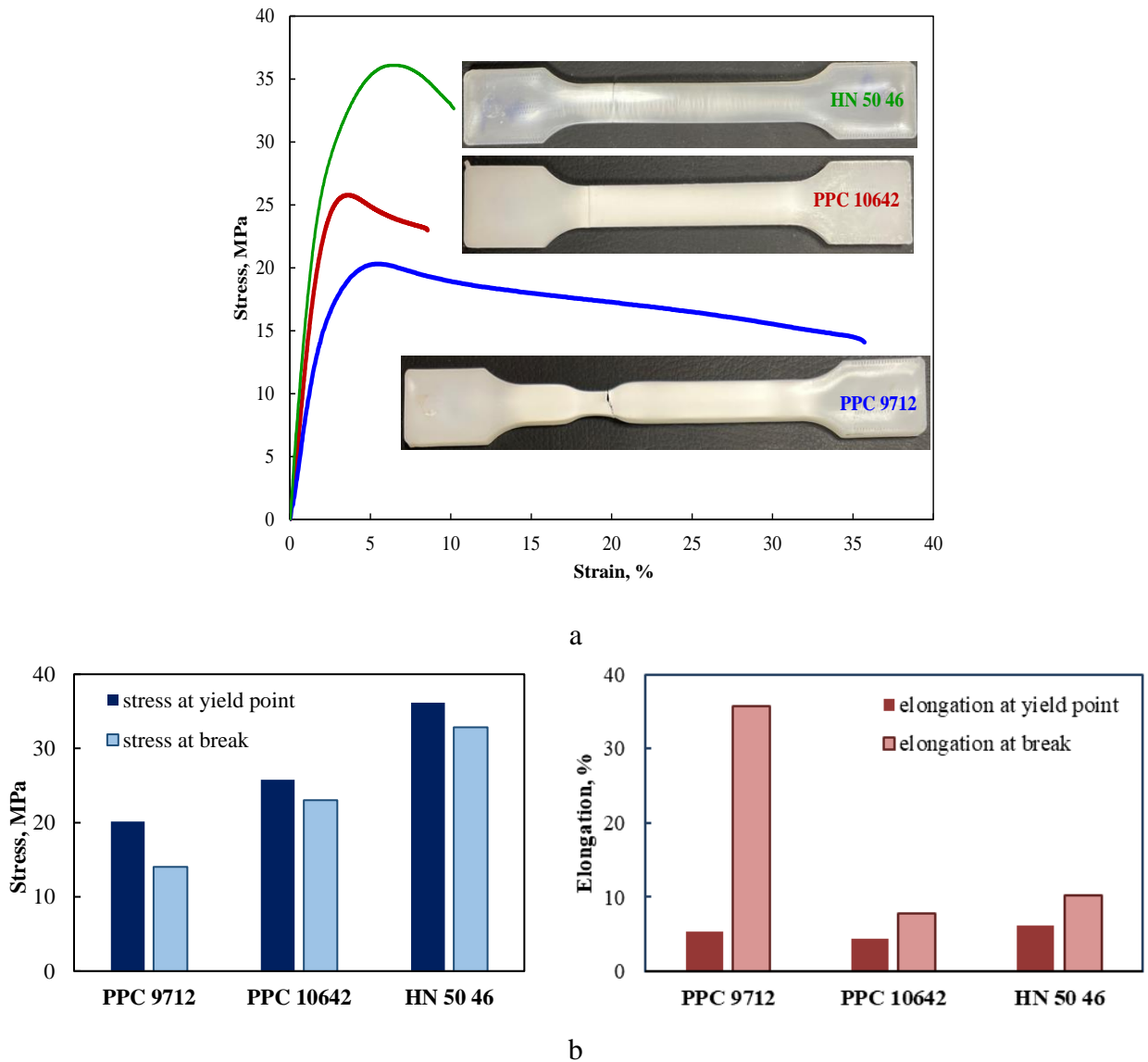
Fig. 29. Mechanical properties of different PP homopolymers: a – averaged stress-strain curves; b – strength and elongation properties of PP homopolymers

The addition of filler such as oat or spelt husks changes the mechanical properties of PP. The filler content was varied in the range 10 – 40 %. In the case of PPH HN 5046, only 10% of filler was added, because higher content of filler drastically worsens the polymer properties. Mechanical properties at tension of PP/oat husk composites are presented in Fig. 30. Comparison of the results with those shown in Fig. 29 suggests that in the case of PPC 10642 and PPH HN 5046 polymers the unmodified filler has only minor effect on the tensile strength (decreases by 6 % of PPC 10642, increases by 1 % of PPH HN 5046), whereas in the case of PPC 9712 it increases the tensile strength by >20%. In addition, increasing the oat husk content from 30% to 40 % increases the tensile strength of PPC 9712

from 25,2 MPa to 27,9 MPa. The silylation of the oat husk surface also increases the tensile strength of PP composites by 5-20% (except for PPH HN 5046) compared to PP composites with unmodified filler (Fig. 30, a).

OAT HUSK_Tensile strength, MPa

a

OAT HUSK_Elongation at break, %

b

OAT HUSK_Young's modulus, MPa
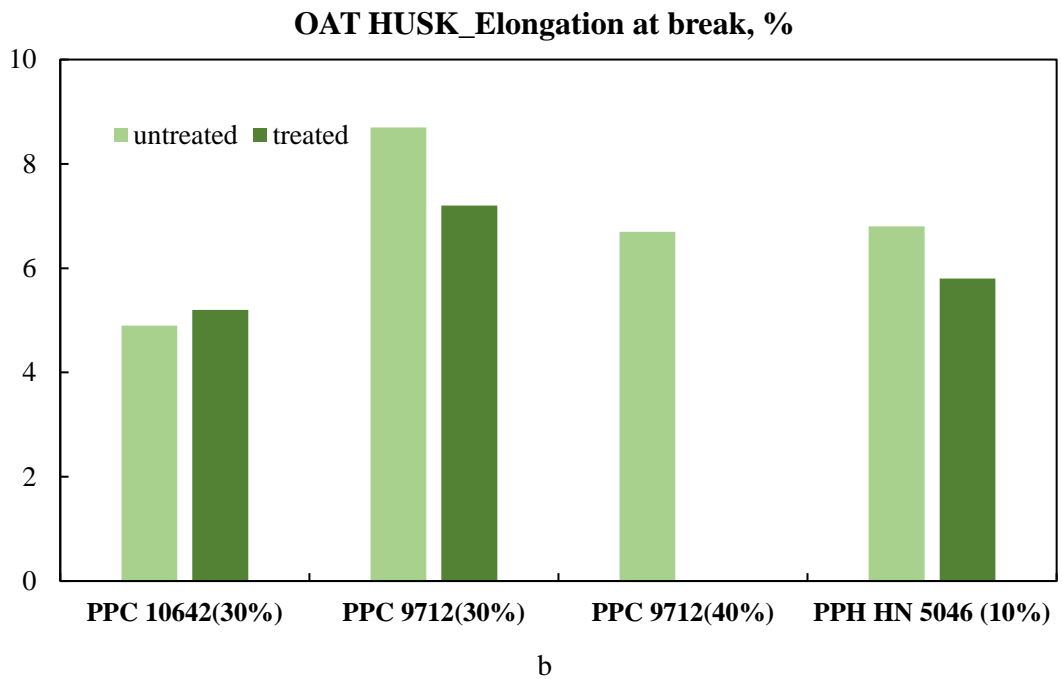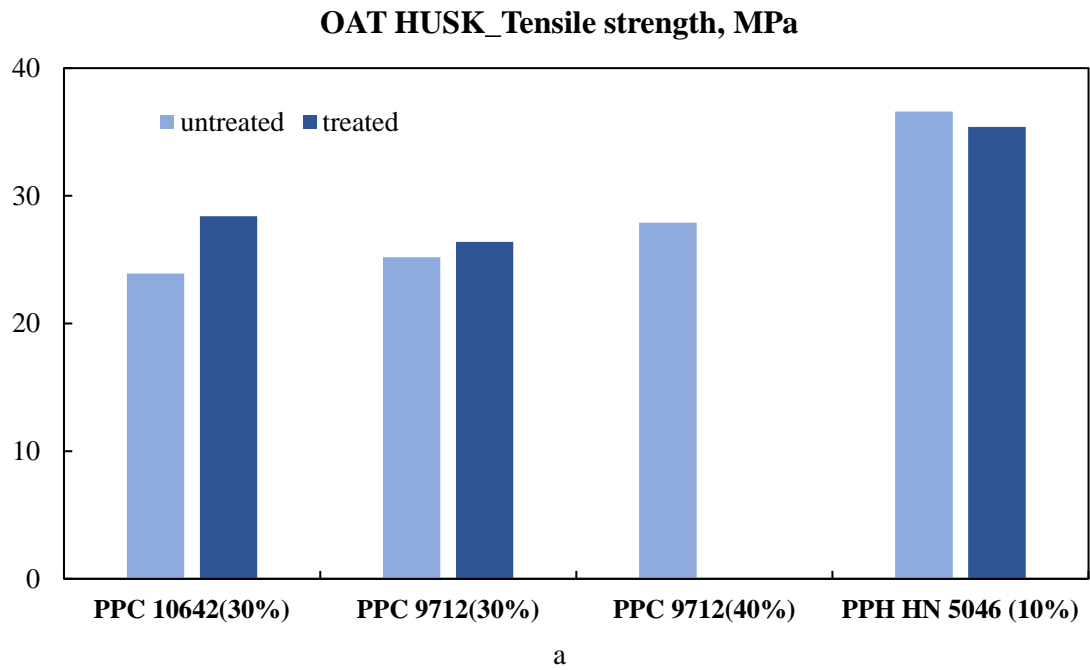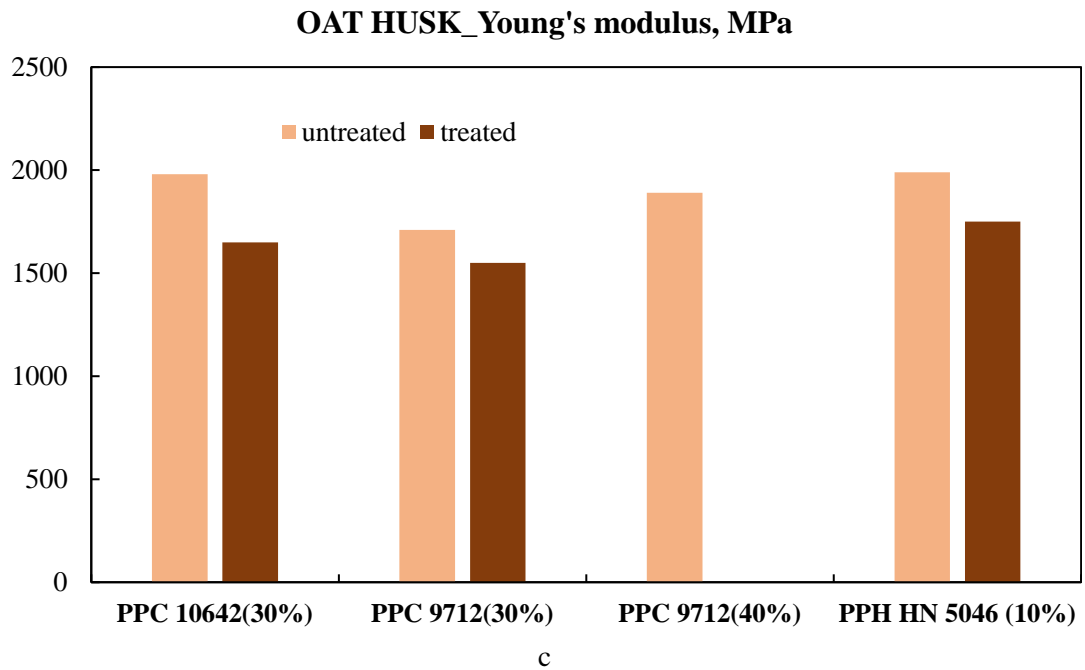
Fig. 30. Influence of oat husk amount and surface state on the mechanical properties of PP/oat composites:
a – tensile strength; b – elongation at break; c – Young's modulus

The changes of elongation at break of the PP composites with the addition of filler is completely different. Independent on the PP type, the deformability decreases with the addition of oat husk. This is particularly evident in the case of PPC 9712 homopolymer, where the elongation at break decreases from 36 % to 9 % (4 times). This may be related to the increase in stiffness of the PP samples and the formation of defects due to the not always good dispersion of the filler particle in the PP matrix. Silylated oat husk further reduce the elongation at break of PP (Fig. 30, b). Addition of oat husk markedly increases PP composites stiffness and Young's modulus arise in 20 – 50% (Young's modulus of PPH HN5046 homopolymer is 1686 MPa, PPC 9712 homopolymer – 1123 MPa).

The influence of unmodified and modified spelt husk on the mechanical properties of different PP composites is presented in Fig. 31. As can be seen, tensile strength of PP composites with spelt husk mechanical behaviour is close to PP composites with oat husk. In comparison to PP composites with unmodified spelt fillers, the silylation of the spelt husk surface increases the tensile strength of PPC 10642 and PPC 9712 composites by 19.7% and 2.2.% respectively (except for PPH HN 5046) (Fig. 31, a). The influence of filler amount on the tensile strength of the PP composites can also be observed. Increasing the spelt husk content from 30% to 40 % increases the tensile strength of PPC 9712 from 25,7 MPa to 26.7 MPa.
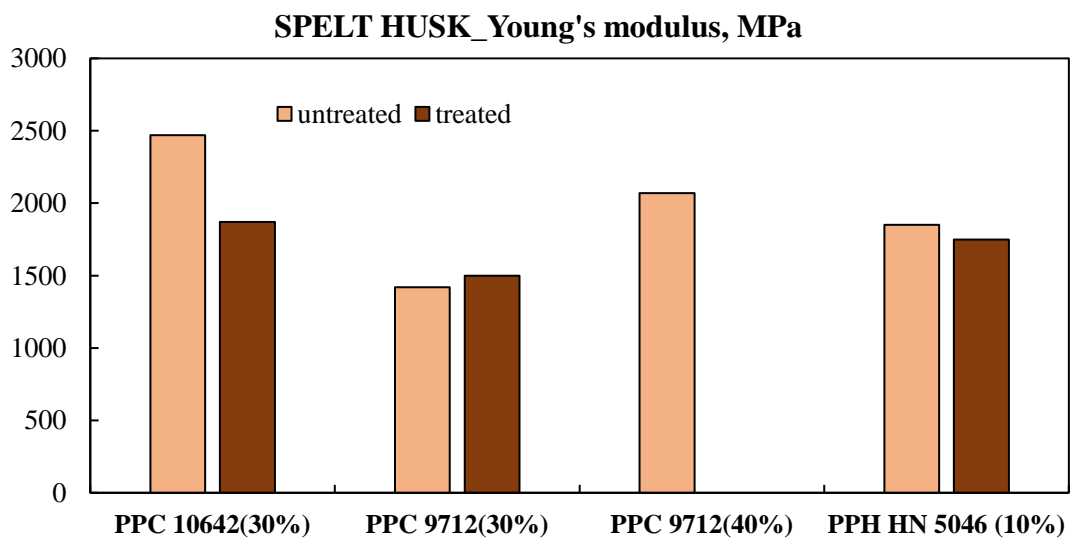
Fig. 31. Influence of spelt husk amount and surface state on the mechanical properties of PP/spelt composites: a – tensile strength; b – elongation at break; c – Young's modulus

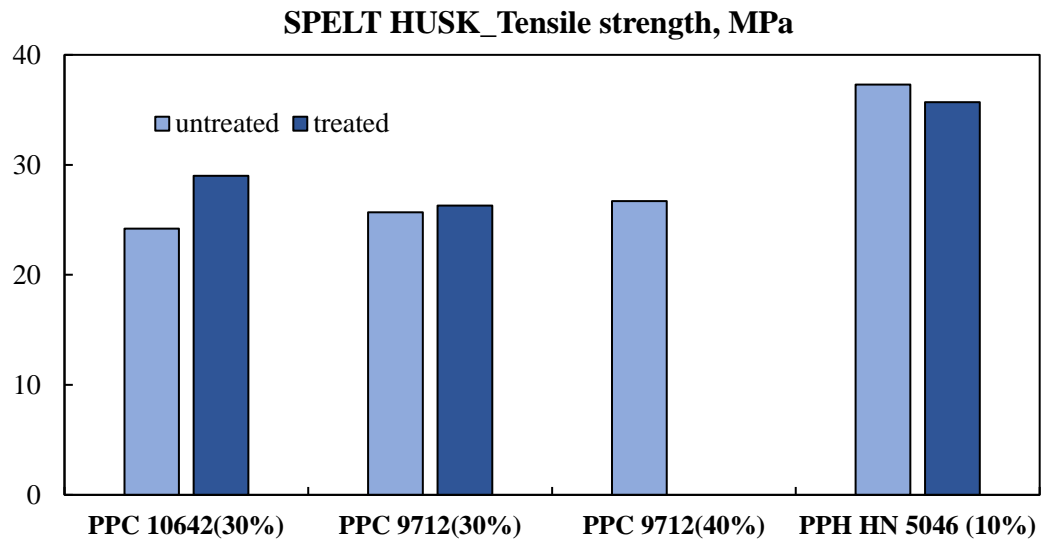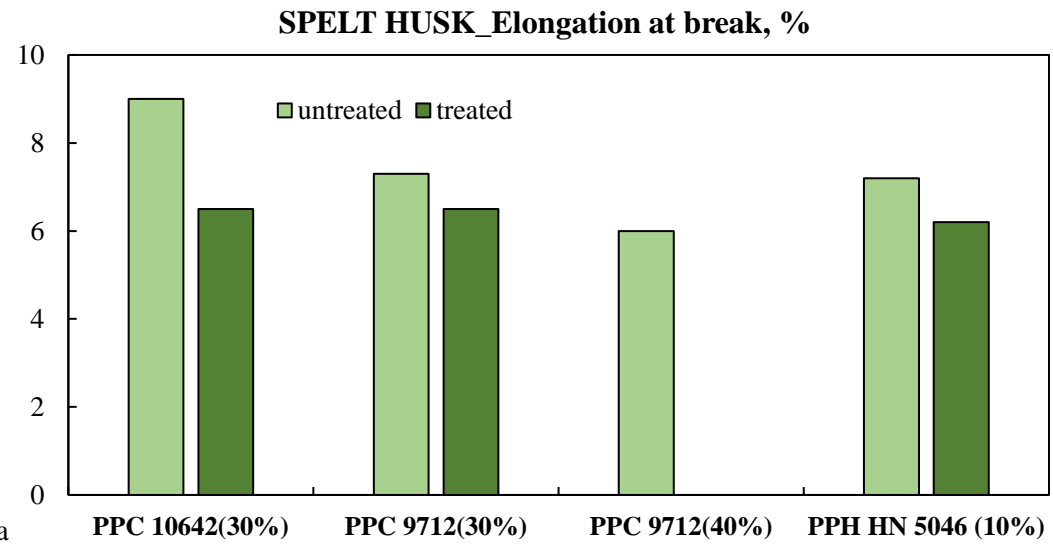The changes of elongation at break of the PP composites with the addition of spelt filler is comparison to the addition of oat filler is not much of a difference. Independent on the PP type, the elongation at break decreases with the addition of spelt husk. This is particularly evident in the case of PPC 9712 homopolymer, where the elongation at break decreases from 36 % to 7.3%. This may be related to the increase in stiffness of the PP samples and the formation of defects due low interaction of dispersion of the filler particle with the PP matrix. Silylated spelt husk further reduce the elongation at break of PP (Fig. 31, b). Addition of spelt husk markedly increases PP composites stiffness and Young's modulus arise in 10 – 50% when compared to the PP homopolymers. Young's modulus of PPH HN5046 increased by 9.7% and PPC 9712 increased by 26% - 84% with the increase of filler amount from 30wt.% to 40 wt.%.

The flexural strength of PP composites reinforced with untreated and treated oat husk fillers is presented in Fig. 32a. The obtained results show a decrease in flexural strength even after modification of the oat particle surface. This is because of the increase in the sample brittleness. In terms of PP type, PPH HN5046 demonstrates better flexural strength. Comparing same filler amount of 30wt% in different PP types, PPC 10642 exhibited better strength than PPC 9712 in both untreated and treated samples. This means that flexural strength can be dependent on filler amount and polymer type. An increase in flexural strength from 204.4 MPa to 220.16 MPa was observed for PPC 9712 when the filler amount was increased from 30wt.% to 40wt.% respectively. The flexural modulus of PP/oat composites is presented in Fig. 32b. An increase in flexural modulus indicates that a material is more resistant to bending. Addition of oat husk markedly increases PP composites resistance to bending and flexural modulus increases to about 40% (flexural modulus of PPC 9712 homopolymer – 1050 MPa).

a
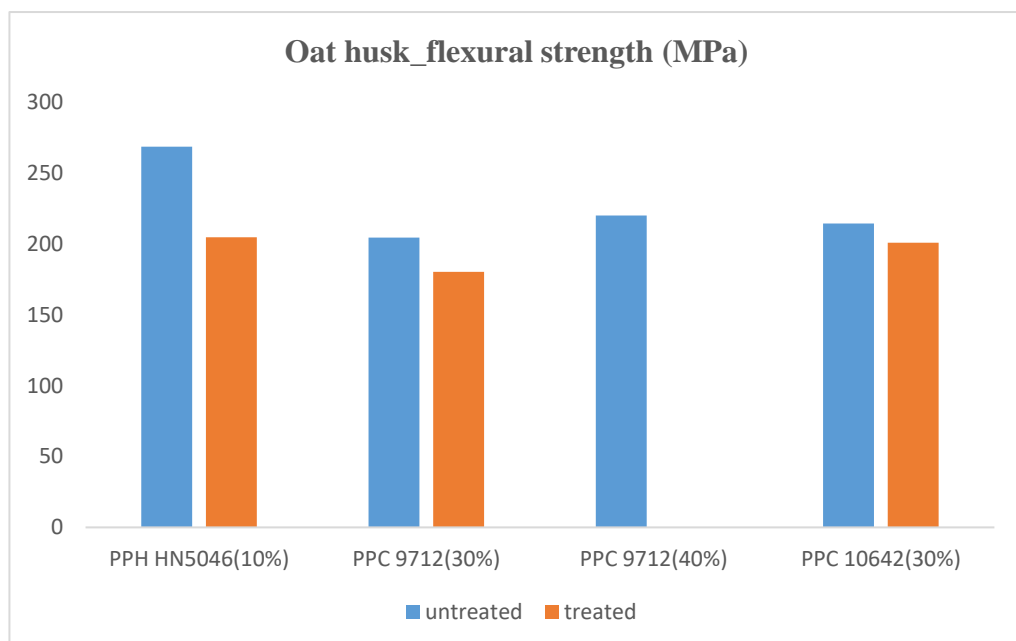
Oat husk_flexural modulus (MPa)
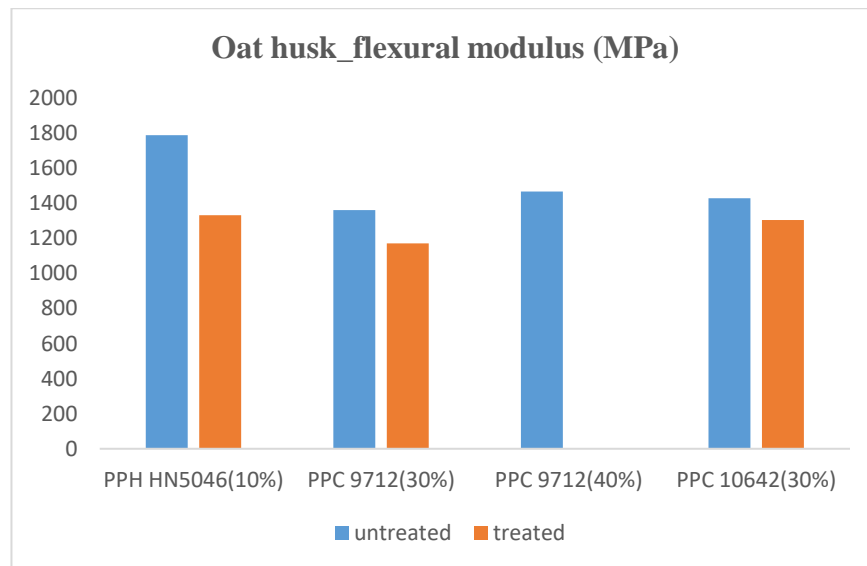
b

Fig. 32. Influence of filler type, amount, and surface state on the flexural strength of PP/oat composites: a –
flexural strength; b – flexural modulus

The flexural strength of PP composites reinforced with untreated and treated spelt husk fillers is
presented in Fig. 33a. The obtained results show decrease in the flexural strength of PPH HN5046
and PPC 9712 composites after modification of the spelt particle surface. This is because of the
increase in the sample brittleness. However, about 2% increase in flexural strength was observed for
PPC 10642 from 201.28 MPa to 204.79 MPa after modification. Comparing the addition of same
spelt filler amount of 30wt% in different PP types, PPC 9712 exhibited higher strength than PPC
10642. This means that flexural strength can be dependent on filler amount and polymer type. An
increase in flexural strength from 217.2 MPa to 234.08 MPa was observed for PPC 9712 when the
filler amount was increased from 30wt.% to 40wt.% respectively. The flexural modulus of PP/spelt
composites is presented in Fig. 33b. An increase in flexural modulus indicates that a material is more
resistant to bending. Addition of spelt husk markedly increases PP composites resistance to bending
and flexural modulus increases to about 1% - 49%, (flexural modulus of PH HN 5046 homopolymer
– 1800MPa, PPC 9712 homopolymer – 1050 MPa).

Spelt husk_flexural strength (MPa)

a

Spelt husk_flexural modulus (MPa)

b
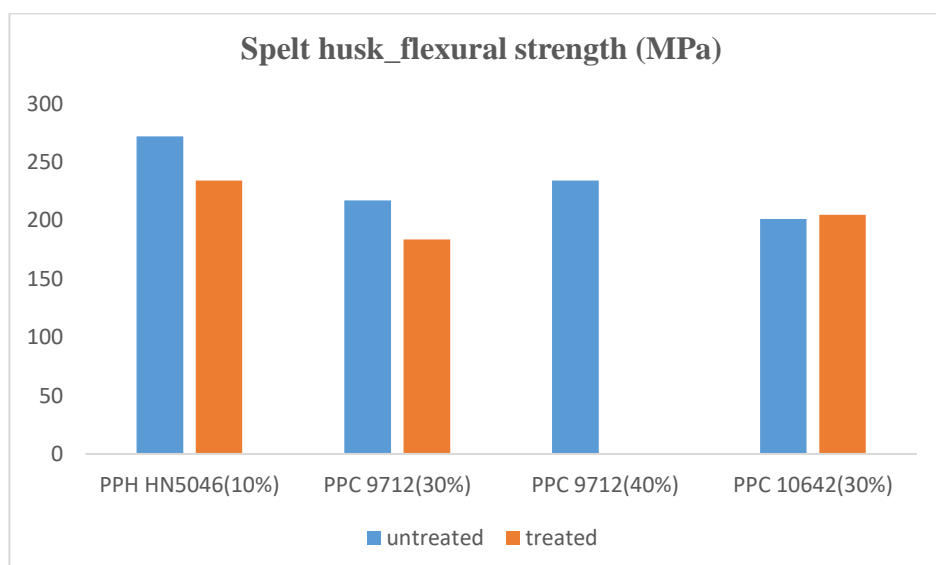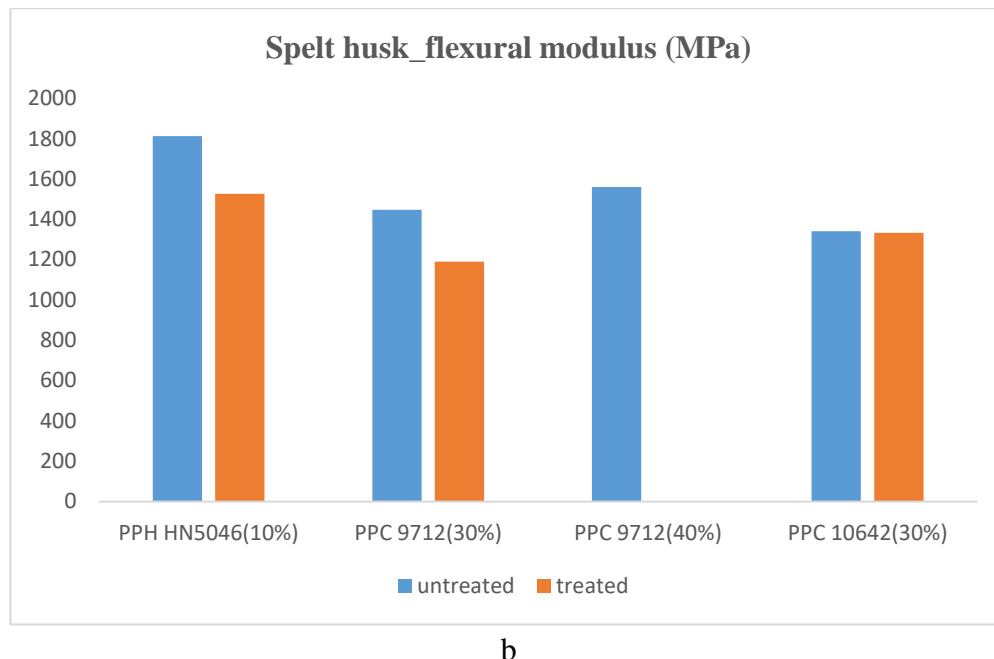
Fig. 33. Influence of filler type, amount, and surface state on the flexural strength of PP/spelt composites: a – flexural strength; b – flexural modulus

For polymers it is important to study water absorption behaviour. Previous studies have shown that PP homopolymers have a water absorption of 0.1-0.3%. It can be proposed that addition of hydrophilic filler increase water absorption properties of PP composites. The water absorption test was conducted for the PP composites at temperature 40°C for over 1400 h. The influence of PP type, filler amount and modification on water uptake was analysed (Fig. 34). The PPH HN5046 having 10% oat or spelt husks has the lowest water uptake which is almost same results for the PP composite with modified fillers. PPC 9712, containing 30% modified oat husks, also has almost no effect on water absorption. In contrast, this polymer with 30% modified spelt husks has a lower water uptake compared to composites with unmodified spelt husk. After 1440 h of immersion, the water uptake of PP composite with silylated spelt husks is 1.4 time lower. As can be seen from Fig. 34, the highest water uptake is characteristic for PPC 10642 composites. However, the water absorption of PPC 10642 decreases in several time when modified filler particles was incorporated. Thus, the silylation of oat and spelt husk surface decrease PP composites water uptake. The unmodified filler particles are very hydrophilic in nature with very high water absorption ability, while the chemical modification markedly decrease the water absorption of the filler due to the conversion of hydroxy to trimethylsiloxy groups during silylation, which imparts hydrophobic properties to the oat and spelt surface [32].
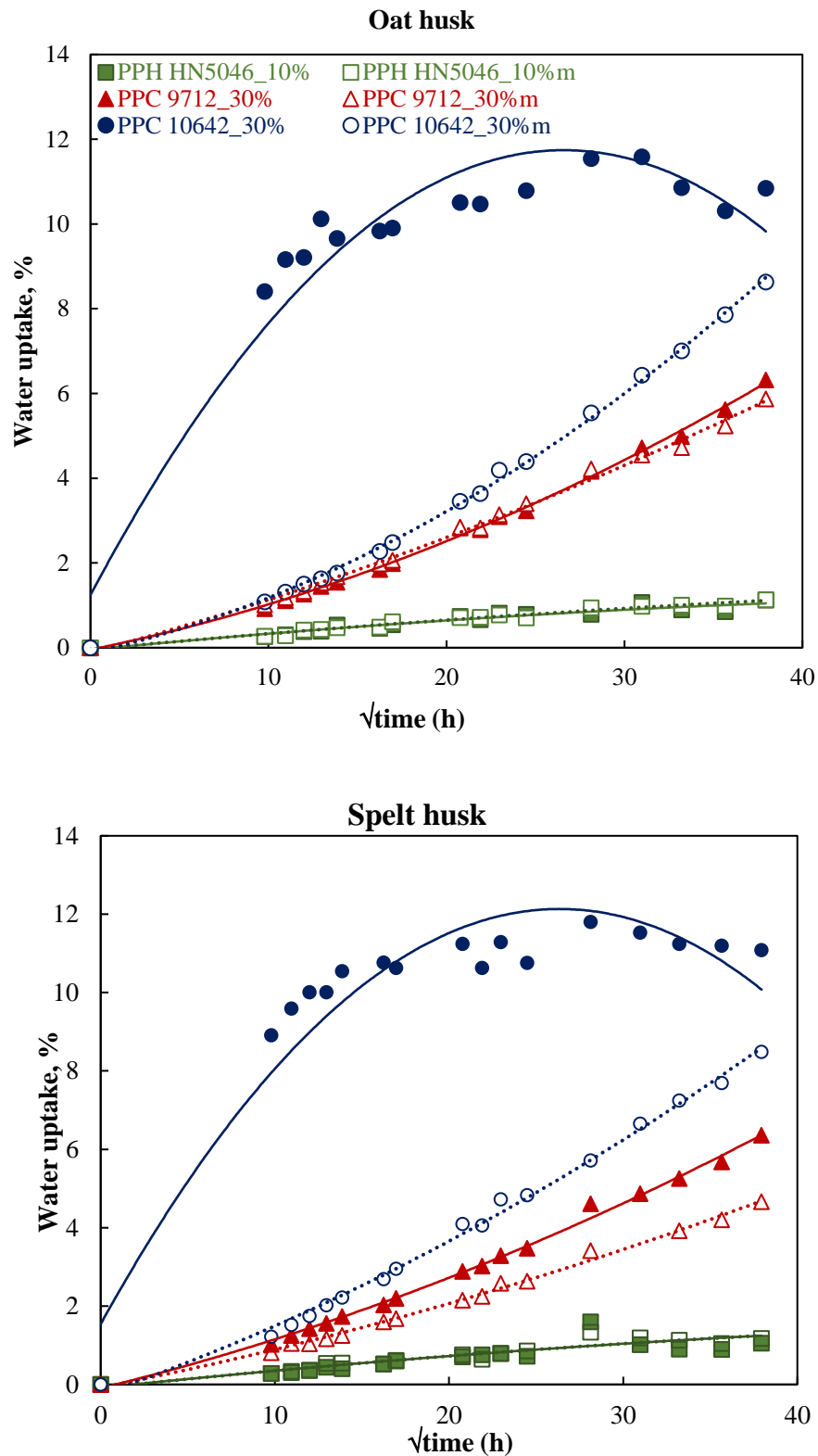
Fig. 34. Water uptake of PP composites as a function of the square root of time

The effect of filler loading (30 and 40 wt.%) and its modification on water absorption properties is shown in more detail in Figure 35. As can be seen, increase in filler amount of oat and spelt husk from 30wt.% to 40wt.% increased the water absorption capacity of the PP composites. This is because the fillers are hydrophilic in nature and the filler amount increase reduces the interface adhesion and compatibility between the polymer matrix and filler particles. A lower filler amount of

30wt.% in this case significantly decreases the rate of water absorption thereby increasing hydrophobicity of the composites.
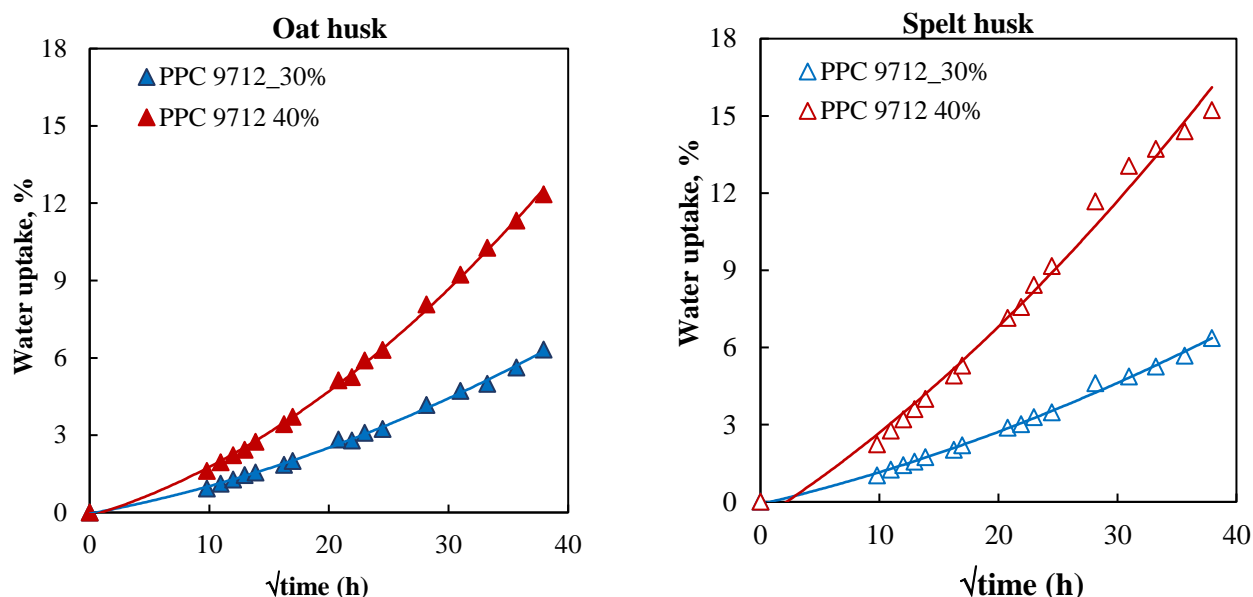
Fig. 35. Influence of filler content on water uptake of PP composites

From the water absorption results of all the samples, the PPH HN5046 composites of both oat and spelt husks demonstrates the best resistance to moisture absorption. The 30wt% of PPC 9712 showed a decrease in moisture uptake compared to the 40wt% for both oat and spelt composites. The incorporation of modified oat and spelt husks into PP composites resulted in a reduced rate of water absorption. Overall, the observed composites with low water resistance behaviour display a highly hydrophilic nature, possibly attributable to the presence of hydroxyl groups in the materials. These hydroxyl groups contribute to increased hydrophilicity, enhancing their ability to absorb and retain water. Notably, the PP/oat composites demonstrated better water absorption resistance compared to the PP/spelt composites. The water absorption capacity holds significance for the ultimate application of bioplastics, as different sectors require specific properties. For instance, in packaging, bioplastics must maintain impermeability, while in the hygienic industry, controlled absorption is often considered beneficial.

The structure of the PP composites fracture surface is illustrated in Fig. 36. The structure of unmodified and modified PP/oat composites are compared in order to investigate the morphology and interface interaction between filler and polymer matrix. Silylated filler particles appear to demonstrate improved interfacial adhesion with the polymeric matrix compared to the unmodified filler particles. The effect of modification is evident in the reduction of holes between the PP and modified filler particles. This effect contribute to an enhancement in the tensile strength of the composites.
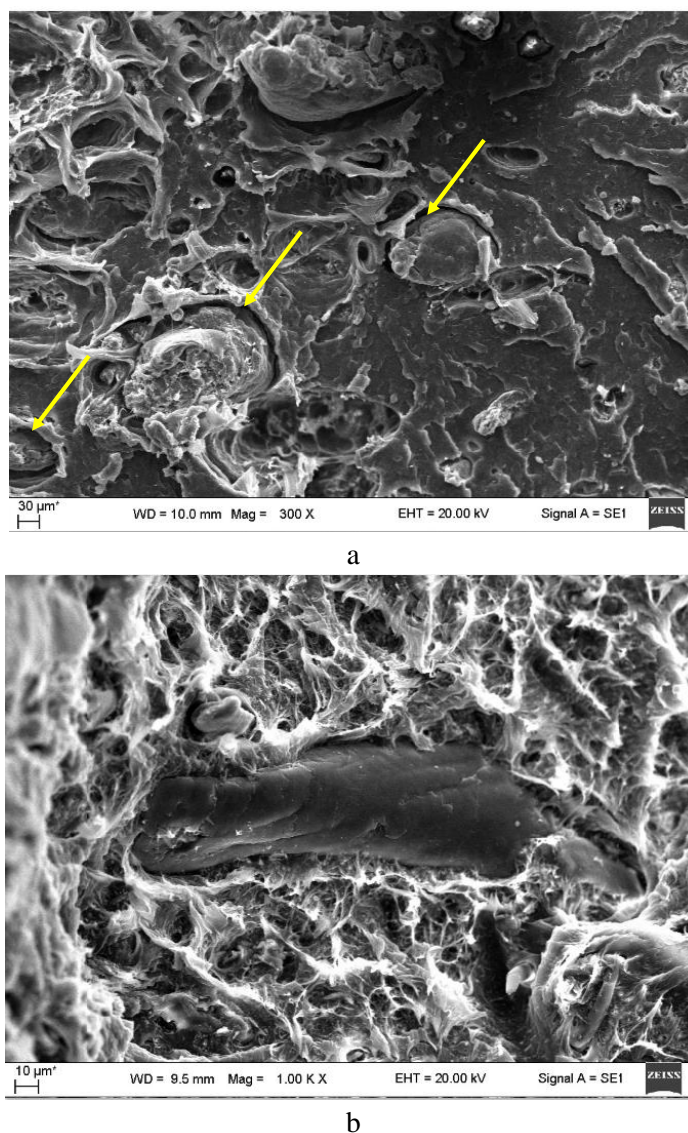
Fig. 36. SEM images of fracture surface of PP/composites with (a) unmodified and (b) modified oat husk

3.3. Chapter Summary

The structure and physical properties of the oat and spelt filler particles were characterized. The morphology is of smaller particle sizes and heterogeneous surfaces. The effect of surface chemical treatment on the structure and properties of filler particles is observed with SEM. Contact angle measurements show the influence of silylation on the wettability properties of oat and spelt husks. The effect of surface chemical treatment and amount of filler particles on the structure and properties of the PP composites is observed with TGA, DMTA, water absorption behaviour, tensile and bending test. TGA results show that the type of filler has practically no influence on the thermal degradation processes of PP composite. In the DMTA observation, T_g is practically independent of the composition of the PP, tan δ, storage and loss modulus is influenced by the matrix type, modifier, oat and spelt contents. The tensile and flexural test is analysed based on the effect of PP type, filler amount and filler modification. The viscosity of the PP homopolymers influence the strength of composites after addition of spelt and oat husks. An increase of filler amount to 40wt% show an increase in tensile and flexural strength. Composites show tensile and flexural strength increase after filler surface modification. An increase in filler amount increases the water absorption rate and filler surface modifications also show increased water resistance and hydrophobicity of the composites.

4. The Management Aspect of Agriculture Waste-filled PP Composition Product

The global bio-composites market was valued at approximately $7.7 billion in 2021. The anticipated global composite market size is expected to reach $144.5 billion in the year 2028 [36]. Projections indicate that the market size will experience a 3.4% compound annual growth rate (CAGR) from 2021 to 2027. By 2027, it is anticipated that the market will reach around $9.5 billion [37]. This depicts an uptrend towards sustainability as biocomposites are being utilized to reduce the use of synthetic based composite or be a replacement depending on the application. The use of PP in the biocomposite sector is largely in high demand because this polymer offers versatility, cost effectiveness, high resistance, and good mechanical properties. PP composite products are attracting considerable interest from various industries, including packaging, biomedical, aviation, marine, automotive, consumer goods, and construction for a wide range of industrial applications.

The market dynamics of PP composites filled with agro-industrial by-products can provide valuable insights into the drivers, restraints, opportunities, and challenges (Fig. 37) associated with this type of material. Agro-industrial by-product-filled PP composites offer several advantages in terms of sustainability and cost-effectiveness, but they also face challenges related to their mechanical properties, consistency, and market acceptance. In terms of sustainability, utilizing agro-industrial by-products in PP composites is viewed as an eco-friendly option as these products are renewable resources that reduce the environmental impact of plastics and agricultural wastes. Government regulations play a crucial role in driving this need as the European union regulates and insists on the use of bio-based materials while emphasizing the use of biodegradable and recyclable materials in industrial applications. Agro-industrial by-products are considered inexpensive and readily available making these wastes a cost-effective filler material for PP composites. PP composites are also lightweight which is beneficial in applications where weight reduction is essential like the automotive and aerospace industries. There is also the design flexibility that agricultural waste-filled PP composites offer based on customizability as their compositions can be tailored to meet specific application requirements. Depending on the choice of agricultural waste and polymer, the composites can be designed to be fully biodegradable reducing long-term environment impact.

Drivers	Restraints	Opportunities	Challenges
•Sustainability •Government regulations •Cost-effective •Lightweight •Biodegradability	•Limited mechanical strength •Moisture sensitivity •Variability •Limited durability	•Growing demand for sustainable markets •Research and innovation •Regulatory support •New applications	•Competition from traditional markets •Quality control issue •Market skepticism •Environmental regulations

Fig. 37. Market dynamics of PP/waste composites

However, there are some weakness factors or restraints associated with agriculture waste-filled PP composition products. There is the limited mechanical strength and durability because agro-industrial by-products in comparison to synthetic materials may not provide the same level of strength and durability. This limits their suitability for high-stress applications and may reduce service life of the composites. Many agro-industrial by-products are hygroscopic in nature which means high sensitivity to moisture which can lead to moisture absorption and degradation of the composite properties. There

are different types of agro-industrial by-products, and their properties can vary significantly based on the different sources leading to inconsistencies in properties of composites.

The market also creates some opportunities for agriculture waste-filled PP composition products because of the growing demand for sustainable materials in various industries. Ongoing research and innovation can lead to the development of improved processing techniques and formulations thereby providing an avenue for continuous enhancement of properties of these PP composites. Also, government regulations and incentives promoting the use of sustainable materials can provide a favourable business environment for agriculture waste-filled PP composition products. There are opportunities for new applications as the biocomposite market is growing and evolving. Agriculture waste-filled PP composites can find applications in a wide range of industries from construction to packaging as the technology and awareness of sustainable materials grow.

Some challenges that can be seen with agriculture waste-filled PP composition products is the existing competition from traditional markets. Established materials like conventional plastics and synthetic fillers may continue to dominate certain industries posing a competitive threat. There may be supply chain and quality control challenges as variability in agriculture waste properties can make consistent product performance challenging. Some customers may be skeptical about the mechanical properties and long-term performance of agriculture waste-filled PP composition product, slowing overall market adoption. Also, stringent environmental regulations, such as restrictions on certain types of biodegradable materials, can affect the market for these composites.

4.1. Environmental and Socio-economic Impacts

The environmental impacts of a product made from agriculture waste-filled PP composition depends on several factors such as the life cycle of the product and the waste materials used, in this research: oat and spelt husks waste. There are both advantages and disadvantages for the environmental constraints associated with these composite materials. The potential environment consequences of extracting and utilizing agro-industrial byproducts includes the depletion of natural resources, emissions of greenhouse gases during production and disposal, and potential impacts on local ecosystems. This study [38] conducted a comparative analysis of the carbon, ecological, and water footprints of PP based composites incorporating cotton, jute, and kenaf fibres. The findings revealed that the inclusion of 30% cotton, jute, and kenaf fibres in a PP matrix resulted in a reduction of the carbon footprint by 3%, 18%, and 18%, respectively. Per resource utilization, using agro-industrial byproducts can reduce the demand for virgin plastic and other non-renewable resources but also depending on the sources of the agricultural byproducts, the extraction and processing may have negative environmental consequences. For instance, when oat and spelt waste is used, the environmental impact would depend on the agricultural practices employed during sourcing and cultivation. In terms of energy consumption, reducing the utilization of pure PP can lower energy consumption during production but the processing and incorporation of agricultural waste may require additional energy and resources depending on the properties of the material. The use of renewable energy sources and efficient manufacturing processes can mitigate these impacts.

The life cycle assessment of agriculture waste-filled PP composition product (Fig. 39) analyses the usage and waste management are important factors to consider in relation to environmental impacts. Reducing waste by repurposing the agricultural byproducts for use in biopolymer composite

production can alleviate the burden of landfills. However, if not managed properly, the waste generated during the production process, any post-consumer waste from the product itself and end-of-life stages of the composite products can still have environmental impacts. Minimizing waste and promoting recycling or composting can help mitigate environmental impacts. The lifespan and durability of the product will impact its overall environmental footprint. A longer-lasting product reduces the need for frequent replacements thereby decreasing the demand for new raw materials. Also, how the product is disposed of or recycled at the end of its life is crucial. If the product is biodegradable or recyclable, it can reduce environmental impact. However, if it ends up in landfills, it contributes to pollution and if not managed properly, it could lead to soil degradation or other ecological issues. Some agro-industrial byproducts can enhance the biodegradability of the PP composites which can mitigate long-term environmental pollution. The biodegradability of these composites can vary; therefore, it is essential to analyse their properties to check whether they meet specific environmental requirements.
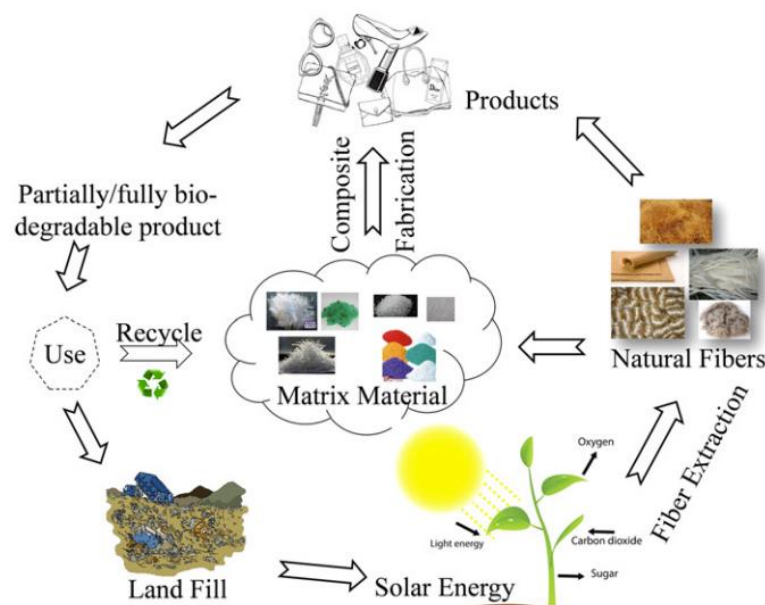
Fig. 38. Life cycle assessment of agriculture waste-filled PP composition product [39]

Socio-economic impacts include the economic viability of using agro-industrial byproducts in PP composition products, potential job creation or loss, and the overall impact on local communities and economies. The utilization of agro-industrial byproducts can provide additional income streams for farmers and local communities. Farmers producing oats and spelt may find additional revenue streams by selling their waste products to industries that use them in composite materials. Using agricultural waste in industrial processes promotes resource efficiency and circular economy principles. However, the socio-economic benefits may not be evenly distributed, and there could be negative effects if resource extraction disrupts local ecosystems or communities. From consumers perception who are highly interested in green or environmentally friendly products, a sustainable product made from agricultural waste may appeal to them potentially leading to increased sales and market share for the manufacturing firms. There is also industrial and economic growth as developing new bioproducts from agricultural waste-filled PP compositions can stimulate product innovation in industries which can lead to the creation of new job and business opportunities. Bioproducts made from these composites can gain popularity and create market demand for the waste materials thereby supporting the agricultural industries and sectors involved in the production process.

In terms of product performance and durability, the agriculture waste-filled PP composition products can provide specific advantages such as increased biocompatibility and biodegradability. However, if the products are found to be less durable or have lower quality, this can have socio-economic impacts on the manufacturers and users. The incorporation of agricultural wastes in PP composites can help companies meet environmental regulations and consumer demand for eco-friendly products but developing and optimizing these products can require significant investments in research and development costs. Overall, the success of these bioproducts depends on market acceptance and consumer preference which can be unpredictable bur ensuring the products meets regulatory standards is crucial for market success. Another socioeconomic constraint is the effect these products can have on cost and market dynamics. Agriculture waste-filled PP composition product is more likely to be cost effective than pure PP which can lower the cost of products for consumers. The availability and cost of the agro-industrial byproducts can be subject to fluctuations which may impact the stability of the supply chain causing an increase in the product price costs.

The polyethylene terephthalate (PET) bottle cap is a product that can be made with agriculture waste-filled PP composite. PP is utilized for this application because it is a non-toxic, degradable, highly versatile, eco-friendly, and recyclable material. It possesses excellent barrier properties and is chemical resistant. A PET bottle cap made from waste-filled PP is considered biobased and recyclable. Substitution of pure PP with PP/oat or PP/spelt composites in the bottle cap production will decrease the overall PP amount used, leading to less plastic pollution. The natural biodegradation period of PP is typically 20-30 years and incorporation of the waste fillers will fasten this process while offering several environmental benefits. The average weight of a PET bottle cap is 2.2g. If the PP composition has 30%wt. spelt, 1kg of PP cost 0.58€ and 1kg of spelt husk cost 1.99€, cost estimation is presented in table 6. In this case, to produce same number of PET bottle caps, it will cost 0.58€/kg for PP and 1.003€/kg for PP/spelt composites.

Table 6. Cost estimation

Material	Cost (€)	Caps
1g PP	0.00058€/g	454
1 PET bottle cap	0.001276€/cap	
30% spelt + 70% PP (g)	0.001003€/g	454
1 PET bottle cap	0.00220066€/cap	

4.2. Chapter Summary

The management aspect of agriculture waste-filled PP composition products involves analysing the market dynamics in terms of drivers, restraints, opportunities, and challenges associated with these products. Life cycle assessment is used to analyse the environmental impacts of the PP composite products from material sourcing to disposal. Efficient management practices are essential for sustainability and environmental responsibility. The market dynamics of these composites and socio-economic impacts of agriculture waste-filled PP composition products aims to create a sustainable and environmentally responsible value chain, minimizing waste, maximizing resource efficiency, and contributing to a circular economy.

Conclusions

1. The possibility to use agro-industry by-products such as oat and spelt husks for polypropylene filling was investigated:
   - Both oat and spelt husks are rich in lignocellulose and highly hydrophilic.
   - The silylation of oat and spelt husks with hexamethylenedisilazane by chemical vapour deposition alters the chemical nature of the surface by replacing some hydroxyl groups with silane groups. This reduces the surface tension of particles, resulting in a decrease in wettability and bulk density of up to 66%.

2. Dynamic mechanical analysis was used to investigate the viscoelastic properties of polypropylene (PP) filled with oat and spelt husks:
   - An increase in stiffness and an improvement in the storage modulus was obtained in the case of the PP/oat (30%) composite: untreated oat particles enhanced the stiffness of the composites by 62%, while silylated by 82%. Due to the inhomogeneity of the samples, it was not possible to determine the effect of the modification on the storage modulus of the PP/spelt composite.
   - The glass transition temperature T_g and the melting point T_m of the PP/husk composites were determined from the β peak and the α peak in the loss factor tanδ curves, respectively. These temperatures are almost independent of the PP composition: T_g is close to 0, while T_m is in the range-170-175 °C.

3. The mechanical behaviour of PP/husk composites depends not only on the type and content of the husks, but also on the properties of the PP homopolymers used:
   - Unmodified oat and spelt husks have only a minor effect on the tensile strength of composites for almost all PP. Silylation of the husk surface increases the tensile strength of PP composites by 5-20%.
   - Independent on the PP type, the addition of unmodified husks reduces the deformation properties of the composites and the elongation at break decreases by a factor of 1.5 to 4. This may be related to the increase in stiffness and defect formation of PP composites because of the low compatibility between the filler particles and the polymer matrix. However, the addition of silylated husks does not improve the deformability of PP composites.
   - Unmodified or silylated oat and spelt husks significantly increase the stiffness and Young's modulus of PP composites arises in 20 – 50%.
   - Silylation of the oat and spelt husk surface show reduction in the flexural strength and a 2% increase in respective PP composites. This may be related to the increase in samples brittleness. Unmodified or silylated oat and spelt husks significantly increase the bending resistance and flexural modulus of PP composites by 1 – 49%.

4. PP/husk composites are sensitive to moisture. The degree of water absorption depends on the type of PP homopolymer, the filler content, and the interaction between the filler and the polymer matrix. Silylation of the surface of the filler particles reduces the number of hydroxyl groups that tend to bind to water molecules and increases the resistance to water sorption up to 1.5 – 2.5 times. However, prolonged storage in a humid environment breaks down the bonds between the PP and the silylated filler particles and worsens the water resistance of the composites.

5. The inclusion of agro-industrial by-products as fillers in PP to produce biocomposites demonstrates reduction in environmental impact, cost effectiveness and biocompatibility.

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