



Physical, chemical and surface properties of wheat husk, rye husk and soft wood and their polypropylene composites

Andrzej K. Bledzki^a, Abdullah A. Mamun^{a,*}, Jürgen Volk^b

^a Institut für Werkstofftechnik, Kunststoff- und Recyclingtechnik, University of Kassel, Mönchebergstrasse 3, 34125 Kassel, Germany

^b IGV GmbH, Arthur-Scheunert-Allee 40/41, 14558 Nuthetal-OT Bergholz, Germany

ARTICLE INFO

Article history:

Received 18 June 2009

Received in revised form 4 December 2009

Accepted 7 December 2009

Keywords:

A. Grain by-products

D. Chemical analysis

D. Surface analysis

B. Mechanical properties

ABSTRACT

The main objective of this research was to study the potential of grain by-products such as wheat husk, rye husk as reinforcements for thermoplastics as an alternative or together with wood fibres. Thermal degradation characteristics, bulk density, water absorption and solubility index were also investigated. The particle morphology and particle size was investigated by scanning electron microscopy. Water absorption properties of the fibres were studied to evaluate the viability of these fibres as reinforcements. The chemical composition of fibre such as cellulose, hemicellulose, lignin, starch, protein and fat were also measured. Surface chemistry and functionality of grain by-products was studied by EDX and FT-IR. Polypropylene composites were fabricated using a high speed mixer followed by injection moulding with 40 wt.% of fibre load. Tensile and Charpy impact strength of resulting composites were investigated.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Manufacturing of high performance engineering materials from renewable resources is one of ambitious goals currently being pursued by researchers all over the world. Also, the ecological benefits of renewable raw materials are clear: they are valuable, environmentally friendly and do not cause health problems. Natural fibres have already established a track record as reinforcing material in automotive parts and spreading up with high growth rate to packaging, construction and household utility based small industries because of their light weight, low cost, and environmental friendly nature [1–3].

In recent years, a special concern has been manifested towards “green composites”. Some of the effort has been based on the use of new waste sources, with the aim to obtain biologically active compounds which can be applied in different fields and applications. These natural lignocellulosic cereal residues (by-product) are compatible with the environment and could provide the sources for specialty chemicals [4]. Cereal waste product is an annually renewable fibre and is available in abundant volume through out the world. The traditional use of these husk and straws includes bedding for animals and livestock feeding. According to April 2009 the world production of wheat was 682 million metric tons, where 150 million metric tons produced by the European Union. The world production of rye was 17 million metric tons where the production in European Union was 9 million metric tons [5].

Wheat (*Triticum spelta*; German name is Dinkel) is the most common and important human food grain and ranks second in total production as a cereal crop. Wheat grain is a staple food used to make flour for leavened, flat and steamed breads; cookies, cakes, pasta, noodles and couscous; and for fermentation to make beer [6] alcohol or biofuel. Wheat is planted to a limited extent as a forage crop for livestock and the straw can be used as fodder for livestock or as a construction material for roofing thatch. Wheat husk is a lignocellulosic waste product which is about 15–20% of wheat and some extents of wheat husk uses as cattle food and fuel [7,8].

Rye (*Secale cereale*) is a cereal grown extensively as a grain and forage crop. It is a member of the wheat tribe (Triticeae) and is closely related to wheat. Rye grain is used for flour, rye bread, rye beer, whiskies, vodkas, and animal fodder. Non-food part of rye is agro waste which is about 15–20% of rye [7,9].

The use of the cereal residues or by-products as a filler or reinforcement in the production of plastic composites alleviate the shortage of wood resources and can have the potential to start a natural fibre industry in countries where there are little wood resources left. The composite industries are looking into alternative low cost lignocellulosic sources, which can decrease overall manufacturing costs and increase properties of the materials.

Cereal husk raw material could be a potential alternative replacing wood for making composites material particularly for automobile, packaging and construction applications. Last couple of years, cereal lignocellulosic raw material (straw, cornstalk, husk, begases) has been used for making composites with polypropylene, polyethylene, polyester, polyvinyl acetate, polyurethane, poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and Novolac resin

* Corresponding author.

E-mail address: kutech@uni-kassel.de (A.A. Mamun).

[10–22]. It can also be pointed out that the development of biodegradable packaging materials from renewable natural resources has received widespread government support in the EU countries and many national or international organisations have been established to facilitate the development in this area [23]. Apart from composite materials, the particleboards from cereal by-product could be another potential alternative [24–26].

The main factors that restrict the use of the cereal by-product, straw and other agricultural residues in composites, have associated with collection, storage, transportation of these materials and economics for the overall production of composites. However, it is believed that the research focused at the use of these materials could follow a developmental market at the same time can lead to a new market opportunity for these surplus inexpensive field crop husk.

The final properties of composites material depend on fibre properties (morphology, surface chemistry, chemical composition and crystalline contents) as well as matrix properties (nature and functionality). The adhesion between the reinforcing fibre and the matrix in composite materials plays an important role. The wetting of the fibre is an integrated step in the adhesion process. The interface depends on complex thermodynamics of fibre and matrix. Fibre properties, i.e. composition, surface roughness and surface polarity have important contribution to fibre wettability and adhesion in composites. There is contradictory evidence regarding the influence of surface chemistry of the reinforcements on the mechanical properties of the composites. For instance, it was reported by Han et al. that wood fibre surface with relatively low concentration of hydroxyl groups produced relatively high performance composites when used as reinforcing filler in non-polar polymers [27]. On the other hand, Beg et al. found that removing lignin from wood fibre provides higher amount of free hydroxyl group on the cellulose which results better interfacial bonding with the polymer matrix [28]. However, Kazayawoko et al. reported that surface chemistry of the fibres has no direct influence on the mechanical properties of the composites [29]. But it is an important to define the fibre exploring physical, chemical and thermal properties before it is using as reinforcement.

Wood fibre is the most widely used lignocellulosic natural fibre for reinforcing plastics. The demand of wood plastic composites (WPC) is increasing steadily with new application window in North America as well as Europe [30]. Considering economic and ecology, wood fibre plastic established itself as standard material but unfortunately raw wood fibre price increased 25–30% compared to last year price [31]. Therefore, scientist from all over the world are searching new source which could be the proper alternative of wood fibre. According to source and availability, wheat husk and rye husk are getting interest in the region of Asia, Europe and North America. The abundance of cereal by-product is eco-friendly, available, cheap and which is complicated in term of cell geometry, morphology and chemical composition. It also has created an environmental issue such as fouling and attraction of pests. Cereal by-products, i.e. wheat husk, rye husk are waste product of food processing from grain and have sufficient fibre value. So proper utilization of those waste materials will provide cheap engineering materials as well as help to waste management. The quality, fibre contents and chemical composition of cereal by-products depend on the grain collection process from the field and on food processing process.

In this study the investigation was carried out on the morphology, composition, the surface chemistry and thermal degradation characteristics of the wheat husk and rye husk with a view to explore the suitability in processing and producing composites. In addition, investigation was also carried out to explore the potential of wheat husk and rye husk as a possible reinforcement for thermoplastic and as a substitute for wood flour in wood plastic composites.

2. Materials and methods

Wheat husk and rye husk are light yellow colour fibres. Fibres were grown up in Germany, 2006 and were collected via IGV Institute, Germany.

Soft wood fibres (WEHO 500) are light yellow colour fibres and were supplied by Jelu-werk Ludwigsmühle, Rosenberg, Germany.

Polypropylene (Sabic PP 575P) was provided as granules by Sabic Deutschland GmbH & Co. KG, Duesseldorf, Germany. Its melting temperature was 173 °C and melting index was 10.5 g/10 min at 230 °C. Its density at room temperature was 0.905 g/cm³.

A commercially available maleic anhydride–polypropylene copolymer (Licomont PP MA 6452) with an acid number of 37–43 mg KOH/g was used as a coupling agent. It was obtained from Clariant Corp., Frankfurt, Germany. Its softening point was 153 °C and density was 0.89–0.93 g/cm³.

2.1. Thermal property

The thermal gravimetric analysis (TGA) was conducted by thermal gravimetric analyser (TGA Q500), supplied by the TA Instrument. The samples were heated up; steady state 20 °C/min from 25 °C to 600 °C in nitrogen medium and 600–850 °C in air medium. Analysis has been done two times for each sample.

2.2. Physical property

2.2.1. Particle geometry

Particle geometry has also been investigated by SEM, MV2300, CamScan Electron Optics. A little amount of black adhesive was placed on small metal plate and smoothening surface by clean glass needle. Then fibres were distributed on a metal surface carefully and then the fibre geometry was investigated after being sputter coated with gold.

2.2.2. Water absorption

Water absorption studies were performed following the EN ISO 62 (method 3) standard test method for water absorption of fibres. Two samplings from every fibre were placed in considering cabinet at 23 °C and relative humidity of 65% and 95%. The samples were removed from the considering cabinet after certain periods of time, weighed with a high precision balance to find the amount of moisture taken up, and then replaced in considering cabinet.

2.2.3. Bulk density

Bulk density values were measured using gravimetric method in g/cm³ by Geopyc 1360, Micromeritics, Germany. A known inner volume of glass cylinder was taken which is directly connected to the precious balance for measurement. The glass cylinder was equipped with two automatic sensors which control the cylinder full or empty. Fibre samples were dried at 80 °C for 48 h before measurement. The dry sample mass was taken while glass cylinder was full. The bulk density was calculated by dividing the dry mass of each sample by the known volume of glass cylinder.

2.2.4. Water absorption index and solubility index

The water absorption index equalled the weight of gel obtained per gram of dry sample for measuring swelling of material. About 2.5 g sample of ground product (mesh 60–200) was suspended in 30 ml of water at 30 °C in a 50 ml centrifuge tube, stirred intermittently over a 30 min period and centrifuged at 3000g for 10 min. The supernatant liquor was poured carefully into a tarred evaporating dish. The remaining gel was weighed and the water absorption index was calculated from its weight. As an index of water solubility, the amount of dried solids recovered by evaporating

the supernatant from the water absorption test as described above was expressed as percentage of dry solids in the 2.5 g sample.

2.3. Chemicals content

2.3.1. Fat contents

The pre-dried samples were weighed and dissolved in hydrochloric acid and then filtered. The filtrate was washed with hot water several times till completely acid free. The filtrate was dried and extracted using benzene. After distil off the solvent, filtrate was dried and weighed. The fat content is taking account of weight loss from the difference between initial and final weight.

2.3.2. Protein contents

The samples were dissolved in concentrated sulphuric acid in presence of catalyst. The total protein content was oxidised and produced ammonium sulphate. The reaction product $(\text{NH}_4)_2\text{SO}_4$ was treated with sodium hydroxide. Then the solution (NH_4OH) was filtered and titrated with hydrochloride acid. The concentration of NH_4OH was calculated from titration results and successively the protein content was calculated.

2.3.3. Starch contents

The sample was extracted by 10% ethyl alcohol for removing optically active substance. Then the solution was filtrated and then the filtrate containing starch was dissolved in hot hydrochloric acid. The Carrez solution was added to the solution where dissolved protein was precipitated. The solution was filtered and measured the starch concentration in solution by V-630 UV-VIS spectrophotometer, Jasco, Germany.

2.3.4. Lignin contents

Two grams of sample were placed in a flask and 15 ml of 72% sulphuric acid was added. The mixture was stirred frequently for two and half hours at 25 °C and 200 ml of distilled water were added to the mixture. Then the mixture was boiled for next two hours and cooled. After 24 h, the lignin was transferred to the crucible and washed with hot water repeatedly until becoming acid free. The collected lignin was dried at 105 °C and cooled down in desiccator and weighed. The drying and weighing were repeated until constant weight.

2.3.5. Holocellulose contents

Three grams of air dried samples were weighed and placed in an Erlenmeyer flask and then, 160 ml of distilled water, 0.5 ml of glacial acetic acid and 1.5 g of sodium chloride were added successively. The flask was placed in water bath and heated up to 75 °C for an hour and then additional 0.5 ml of glacial acetic acid and 1.5 g of sodium chloride were added. The additions of acetic acid and sodium chloride were repeated two times hourly. The flask was placed in an ice bath and cooled down below 10 °C. The holocellulose was filtered and washed with acetone, ethanol and water, respectively and at the end; sample was dried in oven at 105 °C before weighed.

2.3.6. α -Cellulose contents

Two grams of holocellulose were placed in a beaker and 10 ml of sodium hydroxide solution (17.5%) was added. The fibres were stirred up by glass rod so that they could be soaked with sodium hydroxide solution vigorously. Then sodium hydroxide solution was added to the mixture periodically (once every 5 min) for half an hour and the mixture temperature was kept at 20 °C. About 33 ml of distilled water was added in the beaker and kept it for an hour. The holocellulose residue was filtered and transferred to the crucible and washed with 100 ml of sodium hydroxide (8.3%), 200 ml of distilled water, 15 ml of acetic acid (10%) and again

water successively. The crucible with α -celluloses was dried and weighed.

2.3.7. Hemicellulose contents

Hemicellulose = Holocellulose – α -cellulose

2.4. Elementary analysis

The composition of the surface of the fibres was evaluated by energy dispersive spectroscopy (EDS). The technique is suitable because localized analyses are possible, which is very important, considering the size of the fibres. The peak positions are then used to determine the elements present in sample and the peak intensities are related to the amounts present. Whereas, there are several problems associated with the analysis for instance, fibre surface geometry and homogeneous at the micron level. An experienced operator can usually overcome these obstacles and reproducibility can be overcome by repeating the analyses.

All samples were analysed by the combination of a scanning electron microscope and an EDS electron microprobe analyser, Röntec, Germany. The sample was coated with carbon to ensure the sample is conductive can prevent X-ray penetration. The surface elements were identified and quantified with compare to known standard sample. Samples were analysed at the pressure 10^{-8} Torr with pass energy 30 eV. The spot size was about $250 \mu\text{m}^2$.

2.5. Fourier-transform infrared spectroscopy (FT-IR)

A Nicolet 6000 FT-IR, Thermo Scientific, UK was used to obtain spectra for the wheat husk and rye husk. KBr disk sample preparation method was followed in taking infrared spectra. Fibres were ground and mixed with KBr at the ratio 1:99 then the mixer was pressed under vacuum to form pellets. FT-IR spectra were recorded in a range of $4000\text{--}400 \text{ cm}^{-1}$ at a resolution of 4 cm^{-1} with 64 scans.

2.6. Processing

2.6.1. Mixer-injection moulding

Fibres with polypropylene were mixed by high speed cascade mixer (Henschel heat-cooling mixer system, type HM40-KM120). Fibres were dried at 80 °C in an air circulating oven for 24 h (moisture content <0.5%) before mixing. The fibre at 40 wt.% proportion and polypropylene was placed into hot mixer and heated to the melting temperature of polypropylene (173 °C) and then hot agglomerate granules were transferred to the cool mixer where hot agglomerate granules were cooled down to room temperature by the cold water supply. Then cold agglomerate granules were dried again (80 °C, 24 h) before the sample preparation by injection moulding process. Additionally coupling agent was accounted for 5 wt.% with respect to fibre content. It means that the fibre and matrix contents were taken always 40:60 ratio and after then coupling agent was added [2]. Test samples were prepared from dried agglomerate by injection moulding process at temperature zone 160–180 °C, mould temperature of 80 °C and under an injection pressure 20 kN/mm^2 .

2.7. Characterization of composites

2.7.1. Mechanical properties

Tensile test was performed at a test speed of 2 mm/min according to EN ISO 527 for fibre–polypropylene composites with and without coupling agent on a Zwick UPM 1446 machine. All tests were performed at room temperature (23 °C) and at a relative humidity of 50%. Charpy impact test was carried out using 10 notched samples according to EN ISO 179. In each case a standard

deviation <5% (drop weight) was used to calculate the Charpy impact strength.

3. Results and discussion

The feature of thermal analysis result of wheat husk, rye husk and soft wood fibre shown in Fig. 1. The Table 1 shows decomposition temperatures, initial moisture content, organic content and residues of wheat husk, rye husk and soft wood fibre. Organic content indicated the total amount of cellulose, hemicellulose, lignin, starch, protein, fat and others. Residues pointed out total amount of inorganic content (Si, Mg, Al, S, P, K, and Ca) and ash. It was observed that the initial moisture content of wheat husk and soft wood are nearly same which is 6% and the moisture content by rye husk is about 8%. The DTG curve of all fibres showed an initial peaks between 30 °C and 130 °C, which corresponds to the vaporization of water. After this peak, the curve for rye husk exhibits single decomposition step and the decomposition peak temperature is at 306 °C. On the other hand, the curve for wheat husk exhibits two decomposition steps and the decomposition peaks temperature are at 309 °C and at 367 °C. The DTG curve of soft wood exhibits single decomposition step and the decomposition peak temperature is at 383 °C. The decomposition start temperature of rye husk, wheat husk and soft wood found to 180 °C, 205 °C and 210 °C, respectively. The decomposition peak at around 300 °C is due to the thermal decomposition of hemicellulose and the glycosidic linkage of cellulose. The peak in the range 350–390 °C is due to α -cellulose decomposition. Lignin degrades first and at a slower rate than the other constituents. The peak corresponding to the lignin is slightly broader and it appears in the range 190–500 °C with maximum value at about 350 °C. So it is overlapped with the hemicellulose and cellulose peaks.

The TGA program was associated with two steps. The first step is 25–600 °C in inert medium and second step is in oxygen

medium. The sudden step down at about 600 °C is because of sudden oxidation of fibre contents.

Fibre sizes and shapes are one of most important factor for composite materials. The effective surface area which may have influence on mechanical properties inversely depends on particle size and shape. Its mean that the same amount of smaller particles expose more effective surface area than the bigger particles if the particle has same shape. Fig. 2 shows particle size and shape of wheat husk, rye husk and soft wood. There are different types of fibre shape observed. Most of the particles are round and angular shape and small amount of particles are longitude shape. Particle size (length) distribution is shown in Fig. 3. It was observed that 80–85% of all fibres were distributed in the range of 50–300 μ but distribution is not same. The aspect ratio of soft wood was 2–5.8 whereas the aspects ratio of wheat husk and rye husk were 1.4–4.6 and 1.2–4.8, respectively. It was also observed that a portion of rye husk and wheat husk found to nearly bimodal distribution.

The fibre surface morphology plays a vital role in case of composite materials. Every fibre has unique surface properties. External surface features of fibres such as contours, defects and damage and surface layer are observed in the SEM (Fig. 4). The fibre surface layer is relatively minor portion of fibre but it plays an important role in wettability and surface tension. It has long been postulated that the cereal fibre surface contents lipid and proteinaceous compound and the lipid molecule is usually bonded to the protein molecule by ester or thioester bond [32]. The amount of lipid on the fibre surface has influence on hydrophobicity and surface tension. The more amount of lipid on the fibre surface means the more hydrophobic and more surface tension as well as smoother the fibre surface forming a thin film. Fig. 4a–c represents the wheat husk, rye husk and soft wood fibre surface, respectively. It can be pointed out that the rye husk fibre surface is smoother than wheat husk and the defects and damages were observed on the fibre surface in the both cases. Soft wood fibre surface is rough and a lot of defect and fibre damage were observed on the surface.

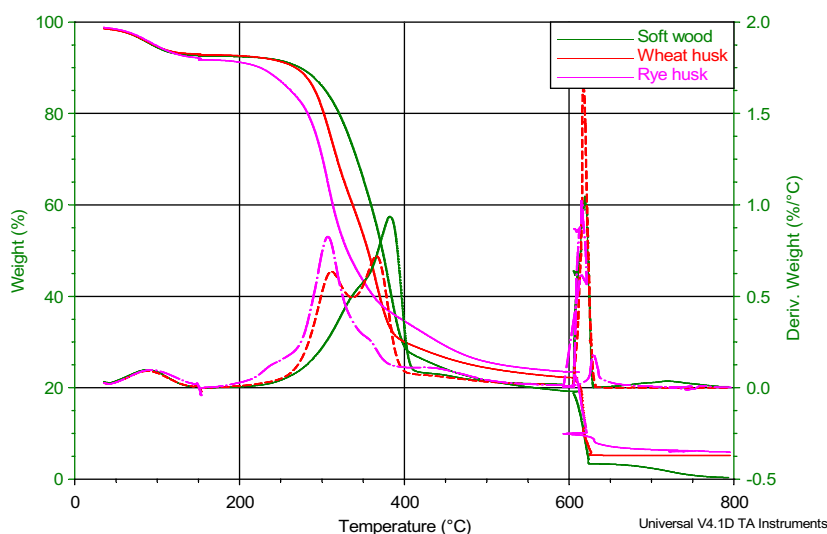


Fig. 1. TGA of wheat husk, rye husk and soft wood fibre.

Table 1

Thermal analysis of wheat husk, rye husk and soft wood.

Fibre	Deco. beg. temp. (°C)	Deco. peak temp. (°C)	Moisture (%)	Organic (%)	Residue (%)
Wheat husk	205	309/367	6	87	7
Rye husk	180	306	8	81	11
Soft wood	210	383	6	89	5

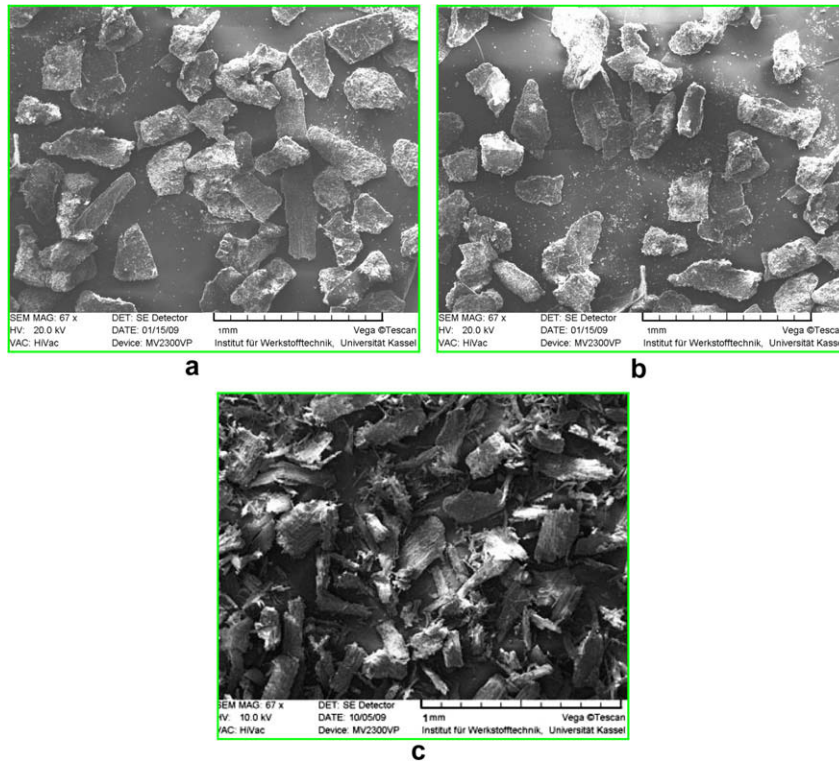


Fig. 2. SEM microgram of fibre geometry: (a) wheat husk, (b) rye husk and (c) soft wood.

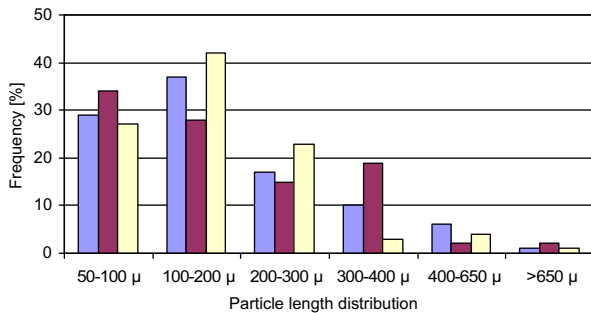


Fig. 3. Particle size (length) distribution of wheat husk, rye husk and soft wood.

The bulk density, water absorption and solubility index of grain by-products shown in Table 2. It was observed that the bulk density of wheat husk was found to be higher than rye husk and the bulk density of rye husk was found to be higher than soft wood consequently. It means that the same weight of husk needs lower storage and transportation space which provides low cost handling. The water absorption and solubility index of fibres are temperature dependent and viscosity related which could have influence on process parameter during the composites preparation. Soft wood fibre showed lower water absorption and solubility index than wheat husk and rye husk. On the other hand, water absorption and solubility index of wheat husk found to be lower than rye husk.

Cereal husk fibres as well as natural fibre are three dimensional, polymeric composites made up primarily of cellulose, hemicellulose, lignin and small amount of protein, starch, fat and ash. Fibres change dimensions with changing moisture content because the cell wall polymers contain hydroxyl and other oxygen containing groups that attract moisture through hydrogen bonding. The hemicelluloses are mainly responsible for moisture sorption, but the

accessible cellulose, noncrystalline cellulose, lignin and surface of cellulose also play a major role.

Fibres are degraded biologically because organisms recognize the carbohydrate polymers mainly by hemicellulose in the cell wall. Biodegradation of the high molecular weight cellulose and hemicellulose weaken the fibre cell wall and fibre strength is lost as the fibre cellulosic polymer undergoes degradation through oxidation, hydrolysis and dehydration reactions. The photochemical degradation takes place primarily in the lignin component, which is responsible for the characteristic colour changes. The lignocellulosic fibres burn with increasing temperature because the cell wall polymer undergoes pyrolysis reactions to give off volatile and flammable gas. The fat, starch and protein polymers are degraded by heat, much before the cellulose and hemicellulose. So, it is obvious that the chemical composition and amount plays a vital role of fibre properties as well as composites properties [33,34].

The chemical compositions are presented in Table 3. It can be seen that the structural material cellulose contents by soft wood is 42%, by wheat husk 36% and by rye husk 26%, whereas, another structural material starch contents by rye husk is 17%, by wheat husk is 9% and by soft wood is less than 1%. It is also observed that wheat husk and rye husk contain 6% and 10% of protein and 5% and 7% of fat, respectively. On the other hand fat and protein content by soft wood are less than 0.5%. The rest of the compositions of fibres are inorganic and ash contents. The analytical results have done two times, its may need to regard as 5% standard deviation.

The fibre on the moisture absorption properties of wheat husk, rye husk and soft wood were illustrated in Figs. 5 and 6, respectively at temperature 23 °C and different relative humidity (65%, 95%). In Fig. 5, it can be seen that for all types of fibre the moisture absorption increased with increasing conditioning period. At the early conditioning periods (till 10 days) the moisture uptake by soft wood fibre was found to be higher than moisture uptake by wheat husk and rye husk. This can be due to the different surface contents of fibres. Fat and protein bonded together covalently

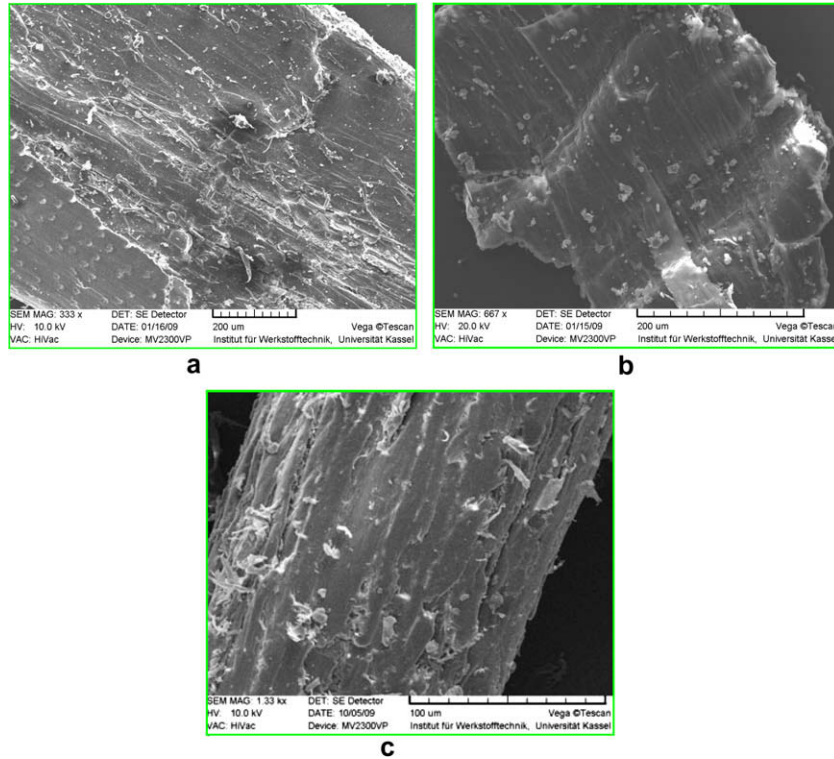


Fig. 4. Surface morphology of (a) wheat husk, (b) rye husk and (c) soft wood.

Table 2

Bulk density, water absorption and solubility index of wheat husk, rye husk and soft wood.

Fibre	Bulk density (kg/m ³)	W. absorption index (g Gel/g)	W. solubility index
Wheat husk	750	4.5	3.3
Rye husk	700	4.8	3.7
Soft wood	650	4.2	2.9

Table 3

Chemical compositions of wheat husk, rye husk and soft wood.

Compositions (%)	Soft wood	Wheat husk	Rye husk
Cellulose	42	36	26
Hemicellulose	22	18	16
Lignin	31	16	13
Starch	0.45	9	17
Protein	0.45	6	10
Fat	0.45	5	7

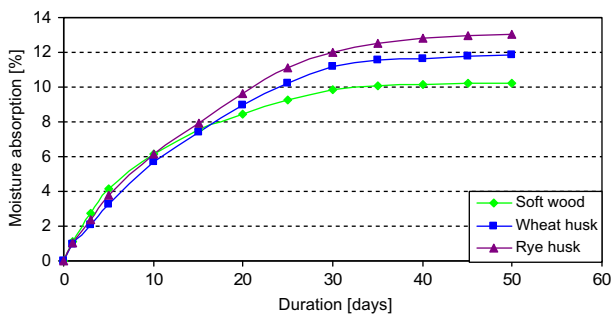


Fig. 5. Moisture absorption of wheat husk, rye husk and soft wood at RH 65%.

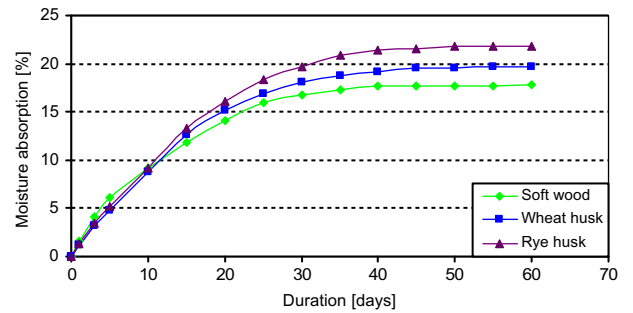


Fig. 6. Moisture absorption of wheat husk, rye husk and soft wood at RH 95%.

and make a coat on fibre surface. That is why moisture diffusion kinetic hindered and took little more time to diffuse in fibre. At the initial conditioning period moisture uptake took place by other active oxygen containing surface components of wheat husk and rye husk. On the other hand soft wood contains very little amount of fat and protein on the surface and without initial hindering moisture uptake took place depending on the overall chemical contents of soft wood fibre. Moisture uptake takes place mainly by hemicelluloses, starch, accessible cellulose, noncrystalline cellulose, lignin and surface of cellulose contents. The moisture uptake for all types of fibre was found to be equilibrium after 45 days of conditioning periods. The equilibrium moisture content of wheat husk and rye husk are 16% and 27% higher than moisture uptake by soft wood fibre, respectively. The same tendency was observed in Fig. 6. The moisture uptake for all types of fibre was found to be equilibrium after 55 days of conditioning periods and the equilibrium moisture content of wheat husk and rye husk were 11% and 22% higher than moisture uptake by soft wood fibre, respectively.

Natural fibres consist of a number of elementary fibres that are bound together by lignin or hemicellulose matrix. The fibre

consists of mainly cellulose ($O/C = 0.83$), hemicellulose (polysaccharides with a range of monomers, where $O/C = 0.83$), lignin ($O/C = 0.35$), pectin (O/C similar to hemicellulose), and wax [35]. The greater proportion of cellulose lies within the elementary fibre in the form of crystalline and amorphous cellulose. Therefore, it can be expected that the fibre surface will be enhanced in lignin and hemicellulose material, which helps bind the fibres together, and wax, which acts as a natural barrier to the environment for the plant stem.

Figs. 7–9 show the inspection spectra of fibre surface elements acquired for rye husk, wheat husk and soft wood, respectively. As seen in the figure, all fibres exhibit spectra containing mainly carbon, oxygen and small amount of silicon, potassium, sulphur, phosphorous, sodium, magnesium, aluminium. The elemental compositions and oxygen carbon atomic ratio of rye husk, wheat husk and soft wood are given in Table 4. The relative atomic percent of the atoms were obtained from the peak area and corrected with an appropriate sensitivity factor.

Wheat husk and rye husk show a higher proportion of carbon atom as compared to soft wood fibre, on the other hand rye husk shows a higher proportion of carbon atom compared to wheat husk. The higher proportion of carbon in fibre can be attributed to the presence of hydrocarbon rich waxy coating on the cuticle of fibre and lignin present on the surface.

Wheat husk contains double proportion of silicon as compared to soft wood, whereas rye husk shows a little proportion of silicon compared to soft wood. The silicon contains in fibre may have the influence on the properties of fibre reinforced composites. The oxygen–carbon ratio of wheat husk and rye husk appeared lower than the soft wood fibre, on the other hand the oxygen–carbon ratio of rye husk found to be lower than wheat husk. The lower ratio of O/C in the rye husk indicated a higher proportion of aliphatic and aromatic carbons near to the surface than that of soft wood. Hence it is anticipated that rye husk has a high compatibility with non-polar polymers compared to wheat husk and soft wood fibre whereas a large number of parameter related to the compatibility.

Wheat husk and rye husk were analysed using FT-IR to know the various chemical constituents present in them. The FT-IR spectrum of those fibres is shown in Fig. 10. In the stretching region, the peaks at 3420 cm^{-1} and 2929 cm^{-1} for wheat husk and the peaks at 3402 cm^{-1} and 2929 cm^{-1} for rye husk were observed. The peak at about 3400 cm^{-1} is due to hydrogen bonded O–H stretching. The hydrophilic tendency of wheat husk and rye husk was reflected in the broad absorption band ($3100\text{--}3700\text{ cm}^{-1}$), which is related to the –OH groups present in aliphatic or aromatic alcohol and

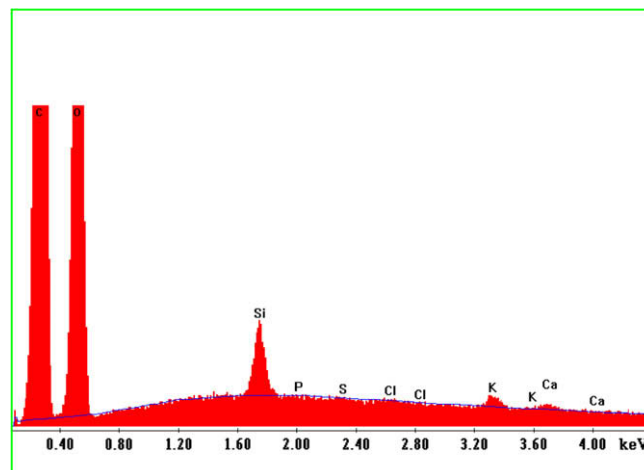


Fig. 8. Elementary analysis of wheat husk.

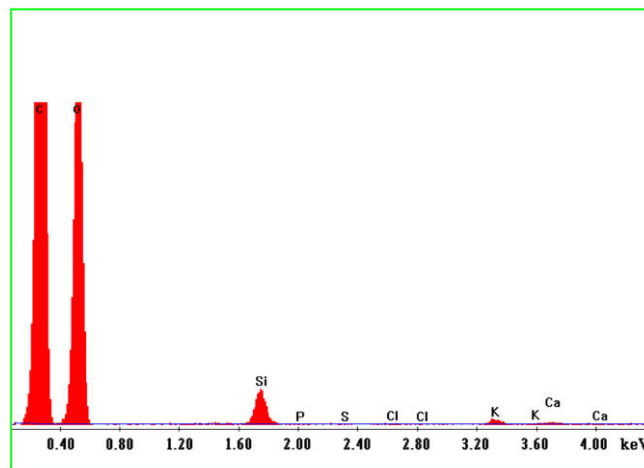


Fig. 9. Elementary analysis of soft wood fibre.

Table 4

Elementary analysis of wheat husk, rye husk and soft wood.

Fibre	C (%)	O (%)	Si (%)	K (%)	S (%)	P (%)	O/C (%)
Rye husk	75.6	18.9	0.2	3.3	1.3	0.7	0.25
Wheat husk	74.9	22.4	2.1	0.6	–	–	0.30
Soft wood	73.9	25.0	1.1	–	–	–	0.34
Cellulose ^a							0.83
Lignin ^a							0.35

^a Indicated theoretical value of O/C ratio [35].

present in their main components. The peak at about 2929 cm^{-1} is due to the C–H stretching from aliphatic saturated compounds. These two stretching peaks are corresponding to the aliphatic moieties in cellulose and hemicellulose [36]. In the triple bond region, the peaks at 2351 cm^{-1} and 2142 cm^{-1} were observed for wheat husk. On the other hand the peaks at 2368 cm^{-1} , 2346 cm^{-1} and 2142 cm^{-1} were observed for rye husk. The peaks at around 2351 cm^{-1} are attributed to the P–H stretching and P–O–H stretching. The band at about 2118 cm^{-1} is reflected Si–H stretching. It could be summarised that the bands in this region were representing the multivalent inorganic hydride or oxide [37]. In the double bond region, a shoulder peak at 1723 cm^{-1} in the both spectrums is assigned to the C=O stretching of the acetyl and uronic ester groups of hemicellulose or to the ester linkage of carboxylic group

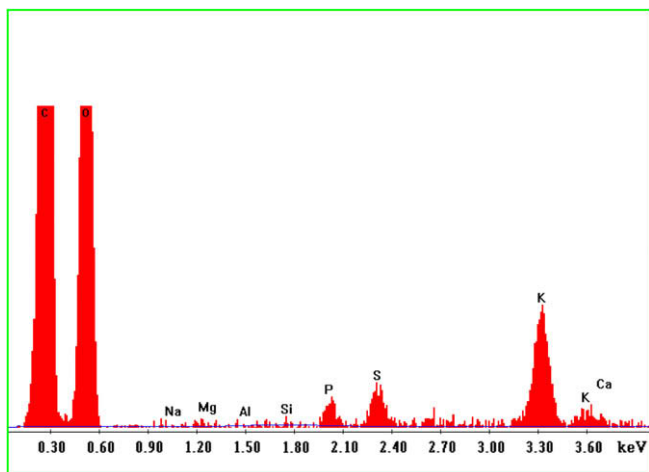


Fig. 7. Elementary analysis of rye husk.

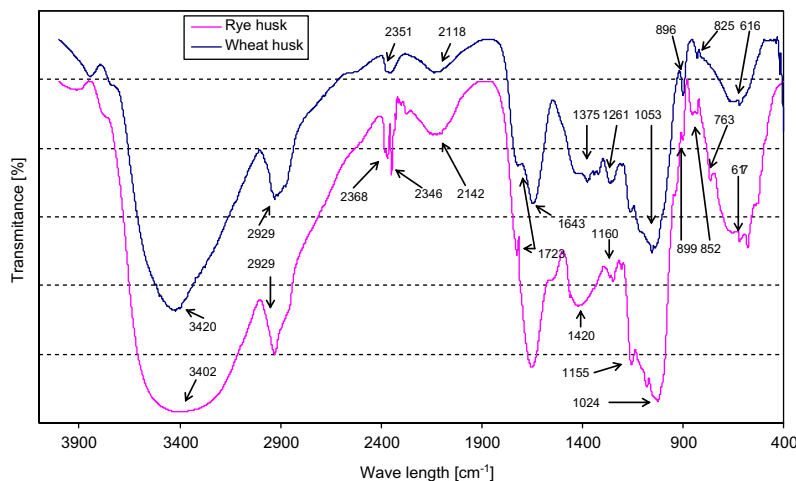


Fig. 10. FT-IR analysis of wheat husk and rye husk.

of the ferulic and *p*-coumaric acids of lignin [38]. The sharp peaks at 1643 cm^{-1} for wheat husk and at 1649 cm^{-1} for rye husk were reflected for amide I. The amide I band represents 80% of the C=O stretching of the amide group, coupled to the in-plane N-H bending and C-N stretching modes. The exact frequency of this vibration depends on the nature of hydrogen bonding involving the C=O and N-H groups and the secondary structure of protein [37]. In the fingerprint region, there are many sharp peaks were observed from the both spectrums. The bands in the range $1450\text{--}1370\text{ cm}^{-1}$ were assigned from the C-H symmetric and asymmetric deformations. The region of $1200\text{--}1000\text{ cm}^{-1}$ represents the C-O stretching and deformation bands in cellulose and lignin. A small sharp at around 900 cm^{-1} (896 cm^{-1} for wheat husk and 899 cm^{-1} for rye husk) which is indicative of the C-1 group frequency or ring frequency, is characteristic of β glycosidic linkages between the sugar units [38]. It could be noted that the both fibres content more or less similar chemical constituents but different peak area which is associated with different amounts. In many cases the peaks for same constituent were shifted, which is associated with the nature of hydrogen bonding and coupling effects.

The tensile strength property displays in Fig. 11. The tensile strength of wheat husk composites and soft wood composites found to be more or less similar with considering standard deviation. On the other hand rye husk composites showed 15% lower tensile properties in compare with soft wood composites. Due to addition of coupling agent tensile strength improved 15–35% for those fibres composites which is because of ester linkage formation via MA-PP between cellulosic filler and polypropylene molecule. It can also observed that due to addition of coupling agent the tensile strength of wood fibre composites was increased 15% and the tensile strengths of wheat husk and rye husk composites were in-

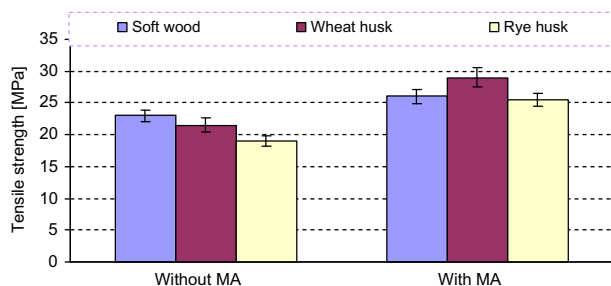


Fig. 11. Tensile strength of soft wood, wheat husk and rye husk PP composites with and without MA.

creased about 35%. There may be the reason of various structural materials cellulose and starch content, amorphous material hemicellulose, lignin and protein content. The structural materials provide reinforcing of composites with strong interlinking between fibre and matrix. On the other hand amorphous materials have less effect (positive/negative) on composites properties.

The elongation of break of different fillers composites are presented in Fig. 12. The elongation at break or strain is expressed as the ratio of total deformation to the initial dimension of the material body in which the forces are being applied. Higher elongation indicates higher ductility of material and lower elongation indicates lower ductility of materials. It is observed that rye husk polypropylene composites showed 110% better elongation at break and wheat husk composites showed 50% better in compare with soft wood fibre composites. The elongation property was remained unchanged due to addition of MA-PP for every case which is because of increase of toughness.

The impact strength of a composite is influenced by many factors, including the toughness properties of the reinforcement, the nature of interfacial region and frictional work involved in pulling out the fibre from the matrix. The nature of the interface region is of extreme importance in determining the toughness of the composite. The notched Charpy impact strength of wheat husk, rye husk and soft wood composites are presented in Fig. 13. The Charpy impact test is a standardized high strain-rate test which determines the amount of energy absorbed by a material during fracture. This absorbed energy is a measure of a given material's toughness and acts as a tool to study brittle-ductile transition. It was observed from diagram that the notched Charpy impact strength of wheat husk and rye husk composites found to be 15% and 10% better, respectively than soft wood composites. This could

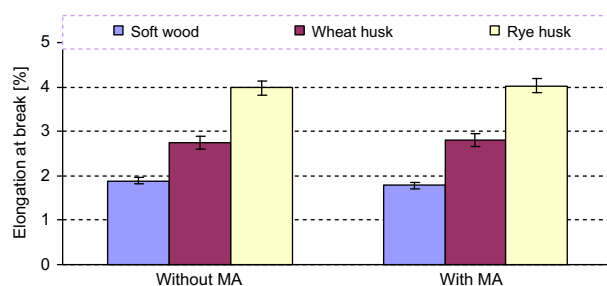


Fig. 12. Elongation of break of soft wood, wheat husk and rye husk PP composites with and without MA.

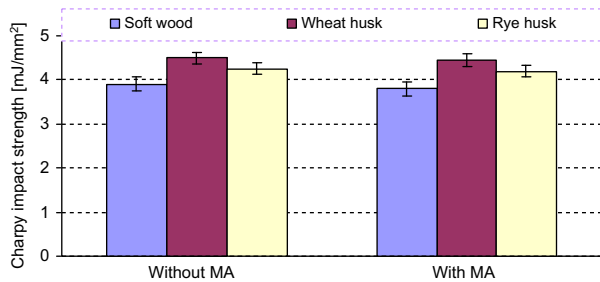


Fig. 13. Charpy impact strength of soft wood, wheat husk and rye husk PP composites with and without MA.

be explained by brittleness and local internal deformation exhibit relatively more for soft wood composites. Particle size, shape and fibre surface properties have the influence on that. It is also observed that Charpy impact strength property was remained unchanged due to addition of coupling agent.

4. Conclusions

This study inspected the feasibility of utilizing of grain by-products such as wheat husk and rye husk as alternative fillers for soft wood fibre as reinforcement in for composites material. The following conclusions could be drawn:

- Wheat husk and rye husk are thermally stable as low as 235 °C and 210 °C, respectively.
- Structural proportions (cellulose, starch) contained by wheat husk and rye husk are 45% and 43%, respectively on the other hand 42% contained by soft wood.
- More carbon rich surface was observed for rye husk and wheat husk compared to soft wood fibre.
- Wheat husk contained more surface silicon than soft wood fibre.
- Wheat husk composites showed 15% better Charpy impact strength than soft wood composites.
- Rye husk composites showed 110% better elongation at break than soft wood composites.

References

[1] Suddel BC, Evans WJ. In: Mohanty AK, Misra M, Drzal LT, editors. Natural fibers biopolymers and biocomposites. USA: Taylor & Francis; 2005. p. 231–59 [chapter 7].

[2] Bledzki AK, Faruk O, Mamun AA. Abaca fibre reinforced PP composites: influence of fibre length and compounding processes on the mechanical properties. *J Polimery* 2008;53(2):42–53.

[3] Puglia D, Biagiotti J, Kenny LM. *J Nat Fibers* 2004;1(3):23–30.

[4] Mohanty AK, Misra M, Drzal LT. Sustainable bio-composites from renewable resources: opportunity and challenges in the green materials world. *J Polym Environ* 2002;10:19–26.

[5] World production data sheet. USA: Foreign Agricultural Service, United States Department of Agriculture, <<http://www.fas.usda.gov>>.

[6] Cauvain SP, Cauvain P. Bread making. Boca Raton (FL): CRC Press; 2003. p. 40.

[7] Smith AE. Handbook of weed management systems. Marcel Dekker; 1995. p. 411.

[8] Daniel Z, Maria H. Domestication of plants in the old world. 3rd ed. Oxford: University Press; 2000. p. 75.

[9] Duke JA. Handbook of edible weeds. Boca Raton (FL): CRC Press; 1992.

[10] White NM, Ansell MP. Straw reinforced polyester composites. *J Mater Sci* 1993;18:1549–56.

[11] Hornsby PR, Hinrichsen E, Trivedi K. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibers. Part 1. Fiber characterization. *J Mater Sci* 1997;32:443–9.

[12] Panthapulakkal S, Sain M. Injection molded wheat straw and corn stem filled polypropylene composites. *J Polym Environ* 2006;14:265–72.

[13] Panthapulakkal S, Sain M. Agro-residue reinforced high-density polyethylene composites: fiber characterization and analysis of composite properties. *Composites: Part A* 2007;38:1445–54.

[14] Yang HS, Kim JK, Son J, Park HJ, Lee BJ, Hwang TS. Effect of compatibilizing agents on rice husk flour filled polypropylene composites. *Compos Struct* 2007;77:45–55.

[15] Bledzki AK, Mamun AA, Volk J. Manufacturing of grain by-products reinforced polypropylene composite, Naro.tech. In: Exhibition and conference of renewable raw materials, Erfurt, Germany, September 6–9, 2007.

[16] Lehrack U, Volk J. The innovative potential of cereal products for technical application. In: Symposium fibre, Poznan, Poland, April 16–17, 2002.

[17] Hornsby PR, Hinrichsen E, Trivedi K. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibers. *J Mater Sci* 1997;32:1009–15.

[18] Borda J, Teskey BM. Biologically degradable fiber reinforced urethane composites from wheat straw. *Polym Compos* 1999;20:511–24.

[19] Avella M, Rota GLA, Martuscelli E, Raimo M, Sadocco P, Elegir G. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fiber composites: thermal, mechanical properties and biodegradation behaviour. *J Mater Sci* 2000;35:829–36.

[20] Patil YP, Gajre B, Dusane D, Chavan S, Mishra S. Effect of maleic anhydride treatment on steam and water absorption of polymer composites prepared from wheat straw, cane bagasse and teakwood saw dust using novolac as resin matrix. *J Appl Polym Sci* 2000;77:2963–7.

[21] Ashori A, Nourbakhsh A. Mechanical behaviour of agro-residue reinforced polypropylene composites. *J Appl Polym Sci* 2009;111:2616–20.

[22] Jahan MS, Mun SP. Studies on the macromolecular components of nonwood available in Bangladesh. *Indus Crops Prod* 2009;30:344–50.

[23] Davis G, Song JH. Biodegradable packaging based on raw materials from crops and their impact on waste management. *Indus Crops Prod* 2006;23:147–61.

[24] Han G, Zhang C, Zhang D, Umenura D, Kawai S. Upgrading of urea formaldehyde bonded reed and wheat straw particleboards using silane coupling agents. *J Wood Sci* 1998;44:282–6.

[25] Wang D, Sun XS. Low density particleboard from wheat straw and corn pith. *Indus Crops Prod* 2002;15:43–50.

[26] Karr GS, Sun XS. Straw board from vapour phase acetylation of wheat straw. *Indus Crops Prod* 2000;11:31–41.

[27] Han GS, Shiraishi N. Composites of wood and polypropylenes. *Mokuzai Gakkaishi* 1990;36:976–82.

[28] Beg MDH, Pickering KL. Accelerated weathering of unbleached and bleached kraft wood fibre reinforced polypropylene composites. *Polym Degrad Stab* 2008;93:1939–46.

[29] Kazayawoko M, Balatinecz JJ, Woodhams RT, Law S. Effects of wood fiber surface chemistry on the mechanical properties of wood fiber polypropylene composites. *J Polym Mater* 1997;37:237–61.

[30] Rowell RM. Handbook of wood chemistry and wood composite. New York (USA): Taylor & Francis Publisher; 2005.

[31] Wood fibre price and product information sheet. Jeluwerk, Ludwigsmühle 73494 Rosenberg, Germany.

[32] Negri AP, Cornell HJ, Rivett DE. A model for the surface properties of fibers. *J Text Res* 1992;63:109–16.

[33] Bledzki AK, Mamun AA, Lucka M, Gutowski VS. The effects of acetylation on properties of flax fibre and its polypropylene composites. *Express Polym Lett* 2008;2(6):413–22.

[34] Rowell RM, Stout HP. In: Lewin Menachem, editor. Handbook of fibre chemistry. New York (USA): Marcel Dekker, Inc.; 1998.

[35] Stevens MP. Polymer chemistry. An introduction. Oxford: Oxford University Press; 1990.

[36] Cherian BM, Pothan LA, Nguyen-Chung T, Menning G, Kottaisamy M, Thomas S. A novel method for the synthesis of cellulose nanofibril whiskers from banana fibres and characterisation. *Agric Food Chem* 2008;56:5617–27.

[37] Stuart B. Biological applications of infrared spectroscopy. West Sussex (UK): John Wiley & Sons; 1997.

[38] Sun XF, Xu F, Sun RC, Fowler P, Baird MS. Characteristics of degraded cellulose obtained from stream exploded wheat straw. *Carbohydr Res* 2005;340:97–106.