CHARACTERIZATION OF GRAIN BY-PRODUCTS AND PROPERTIES OF ITS BIODEGRADE COMPOSITES

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ABSTRACT

Natural fibres as well as by-products from renewable resources are guiding the development of next generation materials, products and processes which are dominating petroleum based products with concerning resources, price and sustainability. In this research work different types of grain by-products such as wheat husk and rye husk have been characterized. Particle size distribution, particle shape, bulk density, thermal behaviour water absorption and solubility properties have been investigated and properties have been compared with standard engineering material softwood fibre.

PP-composite materials were prepared through compounding process with high speed hot-cool melt mixer with 50 wt% load of grain by-products. To characterize the composites materials, mechanical properties and morphology were studied. Coupling agent (MAH-PP) has been used to increase the better interaction between grain by-products and polymer matrix. The grain by-product -polymer matrix adhesion and interaction of the composites was studied by scanning electron microscope. The emitted odour concentrations of different modified and non modified grain by-product composites have also been measured.

The properties of grain by-products reinforced PP composites which are comparable to the wood fibre- PP composites. The tensile, flexural and charpy impact strength of wheat husk reinforced composites were found better than those of wood fibre composite. The addition of coupling agent (MAH-PP) in all grain by-products composites increased almost all mechanical properties 30 to 50% except modulus properties.

1. INTRODUCTION

Natural / bio fiber composites (Bio-Composites) are emerging as a viable alternative to synthetic fiber reinforced composites especially in automotive, packaging and building product applications In recent years, a special concern has been manifested towards “green chemistry” [1]. 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 compounds are compatible with the environment and could provide the sources for specialty chemicals [2].

Wheat (*Triticum aestivum* subsp. *spelta*) 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;[3] and for fermentation to make beer [4] 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 by-product, which is about 20% of wheat product, through food processing from wheat. Small extents of wheat husk use as cattle food and fuel [5].

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, some whiskies, some vodkas, and animal fodder. Non food part of rye husk is agro waste which is 20 % of rye [6, 7].

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 lignocellulosic by-product is ecofriendly, 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. The waste products from the food chain wheat husk and rye husk fillers have been taken as reinforcement of polypropylene composites.

Panthapulakkal et al. [8, 9] reported flexural, tensile and impact properties of wheat straw, corncob and cornstalk reinforced polypropylene and polyethylene composites. Wheat straw showed better mechanical properties compared to corncob and cornstalk as well as due to addition of compatibiliser, all types of fibre composites showed lower water absorption property.

Yang et al. [10, 11] reported tensile and impact properties of non modified and modified rice husk reinforced polypropylene composites. Modified rice husk composites showed 20% improved mechanical properties.

Dai et al. [12] investigated effect of blend ability; feed volume, blend speeds, wetting times and water content of rice husk / PVA composites. Process conditions and parameters have been optimized for specific wet blending process.

There are some scientists investigated different kinds of lignocellulosic waste products reinforced different kind of thermoset and thermoplastic polymer composites but till now wheat husk and rye husk reinforcement thermoplastic composites have not been investigated in injection moulding process through hot-cool mixer. Those of bio by-products could be great important through industrial processing and potential utilization in value added products.

Wood fibre is most common natural fibre and relative low price [13]. During the last decade wood fibre reinforcement has gain remarkable attention as an engineering material such as automobile industries, household utilities, constructions and packaging industries but the wood fibre price increased 25% to 30% compare to last year price[14].

The objective of this research work was to prepare grain by-product reinforced polypropylene composite materials through filler characterization, compare to wood fibre composites and utilization for different industrial applications.

2. EXPERIMENTS

2.1 Materials

Polymeric matrix

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/cm^3.

Wheat husk and Rye husk

Wheat husk and Rye husk were collected from IGV institute, Germany.

Soft wood

Soft wood fibres, commercial name is WEHO 500, were supplied by Jelu-Werk Ludwigsmühle, Rosenberg, Germany. The particles colour is light yellow [14].

Coupling agent

A commercially available maleic anhydride-polypropylene copolymer (Licomont AR 504 FG) with acid number (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 gm/cm^3. It accounted for 5% of the weight percentage of fillers.

2.2 Processing

Mixer-injection moulding

Grain by-products with PP were mixed by high speed cascade mixer (Henschel heat-cooling mixer system, type HM40-KM120). Fillers were dried at 80°C in an air circulating oven for 24 hours (moisture content <1%) before mixing. Then cold agglomerate granules were dried again (80°C, 24 hours) before the sample preparation by injection moulding process. Test samples were prepared from dried agglomerate by injection moulding process at temperature zone 150°C-180°C, mould temperature of 60°C and under an injection pressure 20 kN/mm². The same procedure was preserved for all cases.

2.3 Measurements

Thermal property

The thermal gravimetric analysis (TGA) is a analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. The thermal gravimetric analysis of different grain by-products were conducted by thermal gravimetric analyser (TGA Q500), supplied by TA Instrument. 20 mg sample of each has been taken for analysis. The samples were heated up; steady stately 20 K / min from 25°C to 850°C in nitrogen medium. To get perfection analysis has been done two times for each sample.

Bulk density

Bulk density values were obtained using gravimetric method in g/cm^3 [15]. A known inner volume of glass cylinder was taken which is directly connected to the precious balance for measurement. The glass cylinder is equipped with two automatic sensors which control the cylinder full or empty. Grain by-product samples were dried at 80°C for 48 hours before measurement. The dry sample mass was taken while glass cylinder was full. The bulk density was calculated by dividing the dry mass M of each sample by the known volume of glass cylinder.

Water adsorption and solubility properties

Grains by-products were evaluated for water absorption and water solubility properties.
The water-absorption index equalled the weight of gel obtained per gram of dry sample in a modification of the method described by *Kite* et al. [16] for measuring swelling of material. A 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 3000XG for 10 min. The supernatant liquor was poured carefully into a tared evaporating dish. The remaining gel was weighed and the water-absorption index 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 just described was expressed as percentage of dry solids in the 2.5 g sample.

Mechanical properties

Tensile and flexural tests were performed at a test speed of 5 mm/min according to EN ISO 527 and EN ISO 178 for different grain by-products-PP composites with and without coupling agent on a Zwick UPM 1446 machine. Charpy impact test was carried out using 10 notched samples according to EN ISO 179. In each case a standard deviation < 15% (drop weight) was used to calculate the charpy impact strength. All tests were performed at room temperature (23°C) and at a relative humidity of 50%.

Scanning electron microscope

The morphology of the grain by-products reinforced PP composites with and without MAH-PP were investigated using scanning electron microscope (SEM) , MV2300, CamSan Electron Optics, fractured surfaces of flexural test samples were fractured in liquid nitrogen and studied with SEM after being sputter coated with gold.
Particle geometry has also been investigated by SEM. A little amount of adhesive took on small metal plate and smoothening surface by needle. Then fibres were distributed on metal surface carefully and investigated fibre geometry.

Odour measurement

The most important method to evaluate odour is olfactometry. It uses the human nose as a sensor. In the principal of olfactometry, the sample gas (odour sample) is diluted with neutral air at defined ratio (1gm/ 1 litre). This dilution is represented to the panel lists as smell sample. The panel lists are offered several dilution steps. The odour concentration of the examined sample is the dilution factor at the detection threshold and it expressed as multiples of one odour unit per cubic meter (OU/m^3) at the standard conditions. The odour level (L_{od}) is observed to describe the intensity of a sensation as a function of the logarithm of the amount of the stimulating quantity. The reference quantity of the odorant concentration at the threshold is 1 OU/m^3. The equation can express as

$$L_{od} = 10.\log (C_{od,cs}/ C_{od}) \text{ in } dB_{od}$$

The odour measurements were performed with olfactometer T07 (ECOMA) as followed by standard method VDI 3881. The samples were stored for 30 minutes at 60 ^{o}C in all cases.

3. RESULTS AND DISCUSSION

3.1 Grain by-product characterizations

Fillers 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 same amount of smaller particles expose more effective surface area than the bigger particles if the particle has same shape. Figure 1 shows particle size and shape of wheat husk, rye husk and soft wood. There are different types of fibre shape observed in figure1. Most of the particles are round and angular shape and small amount of particles are long shape. Particle size distribution was shown in figure 2. It was observed that 60 to 65 % of all fibres were distributed in the range of 50 to 200µ but distribution is not same.
The feature of thermal analysis result of different grain by-products showed in figure3. The table 1 is pointed out decomposition temperature, moisture content, organic content and residues of wheat husk and rye husk. Organic content indicated the total amount of cellulose, hemicellulose, lignin, starch, protein and others. Residues indicated total amount of inorganic content (Si, Mg, P, K, and Ca).

Table1: Thermal analysis of grain by-products results

Fibre name	Decomposition temperature (°C)	Moisture content (%)	Organic content (%)	Residues (%)
Wheat husk	215	6	79	10
Rye husk	190	12	76	12

The bulk density, water absorption and solubility index of grain by-products showed in table 2. It was observed that the bulk density found to be better for soft wood fibre than wheat and rye husk. It means that the same weight of soft wood fibre needs lower storage and transportation space which provide low cost handling. Soft wood fibre also showed better water absorption and solubility index properties.

Table 2: Bulk density, water absorption and solubility index of grain by-products

Fibre name	Bulk density (kg/m3)	Water absorption index (g Gel/ g DS)	Water solubility index (%)
Wheat husk	650	4.5	3.3
Rye husk	600	5.2	11.6
Soft wood	750	4.2	2.8

3.2 Composites characterizations

Mechanical properties

The comparison of flexural properties of different grain by-products reinforced polypropylene composites are illustrated in the figure 4 to 5.

The flexural strength property displays in figure 4. It is observed that wheat husk polypropylene composites shown about 70% better flexural strength property than wood fibre composites. Due to addition of MAH-PP flexural strength improved 15% to 30% for every grain by-products composites which because of ester linkage formation via MAH-PP between cellulose filler and polypropylene molecule. It is point out that fillers not only contents cellulose but also a variety of different chemical composition which can interfere or enhance adhesion for instance aldehyde and kiton are volatile, active and may enhance the adhesion [17].

The flexural elongation of break of different fillers composites are presented in Figure 5. It is observed that rye husk polypropylene composites showed markedly better elongation at break compare to other fibres composites. The elongation property reduced significantly due to addition of MAH-PP for every cases which because of increase of toughness.

Figure 6 and 7 present tensile properties of different grain by-products composites together with wood fibre composites. Wood fibre polypropylene composites shown better tensile modulus (figure 6) properties in both cases of with and without MAH-PP. MAH-PP has an effect, increase 10% to 25% for every case, on tensile modulus.

Tensile strength property present in figure 7. Wheat husk composites show little bit better tensile property than soft wood polypropylene composites and rye husk composites show lower tensile strength. Tensile strength find to be better for wheat husk composites with MAH-PP. MAH-PP has significant effect, tensile properties 25% to 35% increase observed for every filler composites.

Charpy impact strength of grain by-products composites showed in figure 8. It is observed that wheat husk reinforced composites show relative better charpy impact strength property than others composites. It is also observed that charpy impact strength property remain unchanged due to addition of MAH-PP.

The scanning electron microscope (SEM) of different grain by-products reinforced polypropylene composites are shown in figure 9 and 10 with and without MAH-PP. Figure (a) of each case indicates non modified fibre composites and (b) indicates modified fibre composites. It represents filler and polymer matrix adhesion, fracture or pull out, debonding and micro cracks regarding with different grain by- products composites. It observed that the adhesion between filler and matrix is strong but fibre pullouts, debondings and also micro cracks which may cause by local internal stress observed for every case. It is also note that typical lamellar structures of polypropylene disappear for all cases [18]. It is also observed that relatively less fibre pullout, debonding and micro crack observed with MAH-PP.

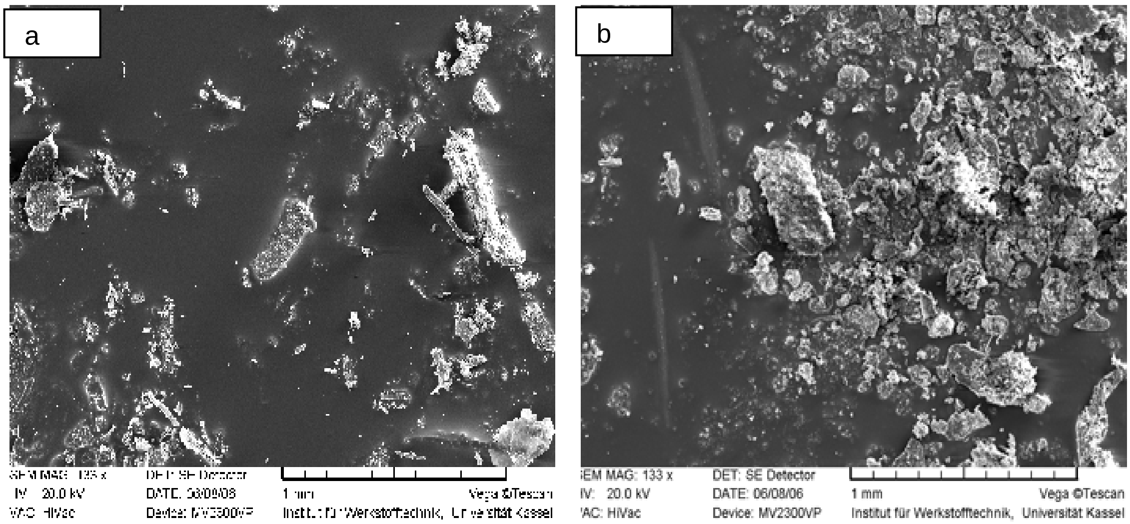
Figure11 shows the odour concentration after processing has been released by different grain by-products composites together with wood fibre composites. The releases of odour concentration depend on volatile organic content of fibre and thermal degradation during the process. It is observed that wood fibre composites emitted remarkable less odour concentration than others organic fillers composites.

4. CONCLUSIONS

This study inspected comparison of mechanical properties of different grain by-products and wood fibre composites as well as the addition of coupling agent effect on microstructure and mechanical properties.

The following conclusion could be drawn:

- Wheat husk and wood fibre composites shown more or less same tensile strength property.
- Wheat husk composites show about 70% better flexural strength property than wood fibre composites.
- Wheat husk and rye husk composites show better; about three to five folds improve flexural and tensile elongation at break, than wood fibre composites.
- Wood fibre composites show better modulus property.
- Bulk density, water absorption and solubility index of grain by-product is comparable to soft wood fibre.



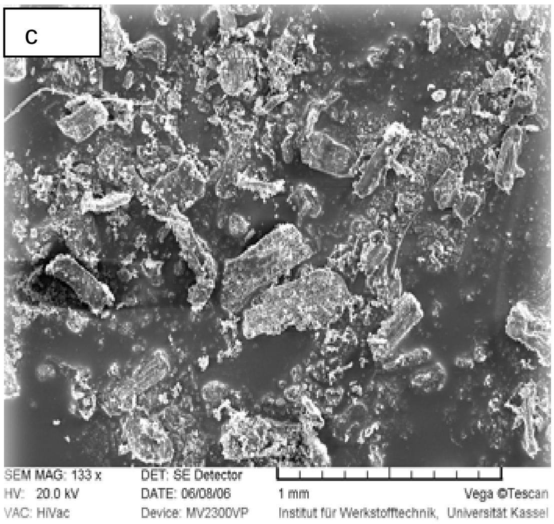


Figure1: SEM microgram of fibre geometry a) wheat husk, b) rye husk and c) soft wood.

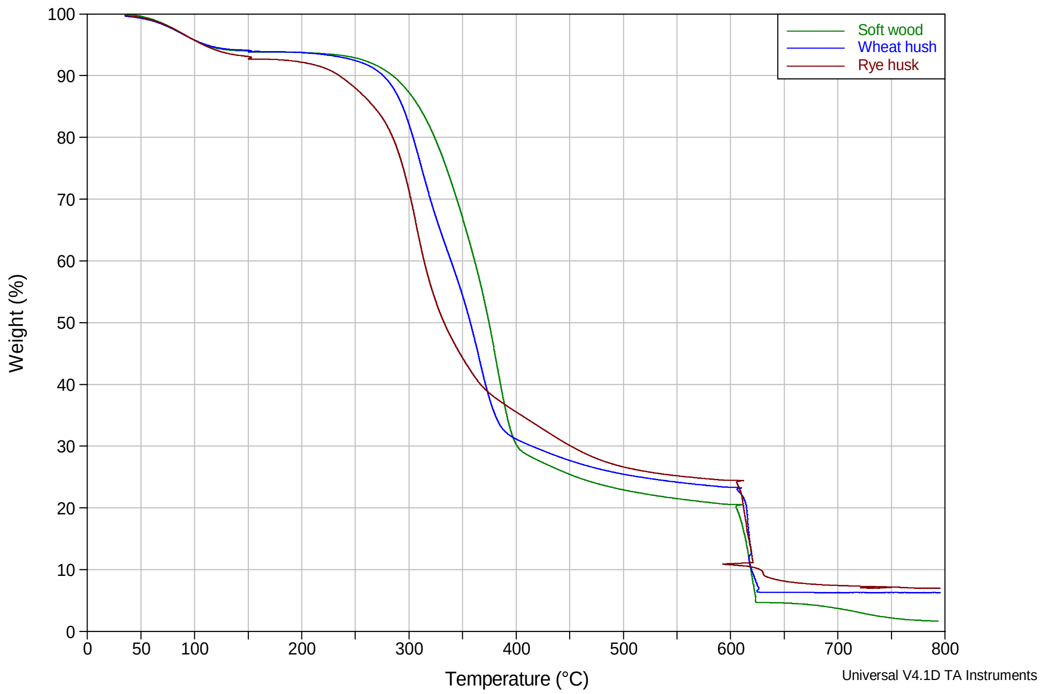


Figure2: TGA analysis of wheat husk, rye husk and soft wood

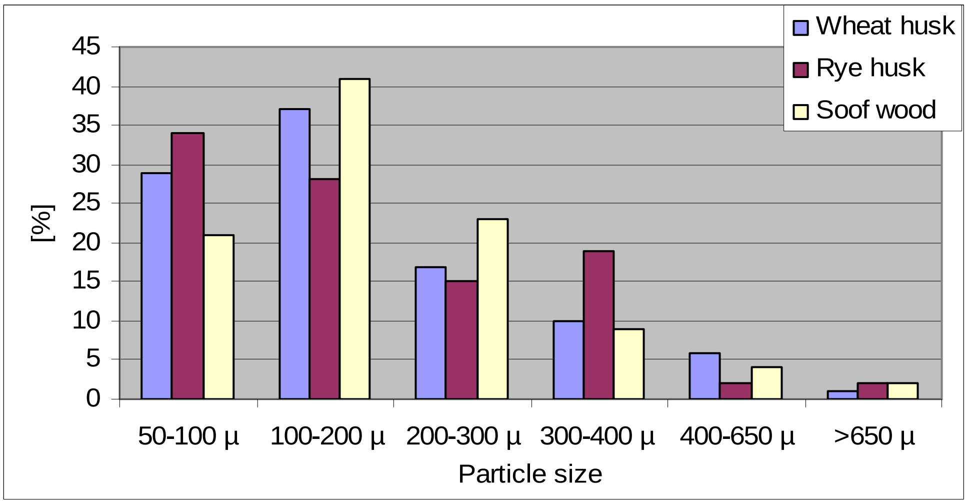


Figure3: Particle size distributions of wheat husk, rye husk and soft wood

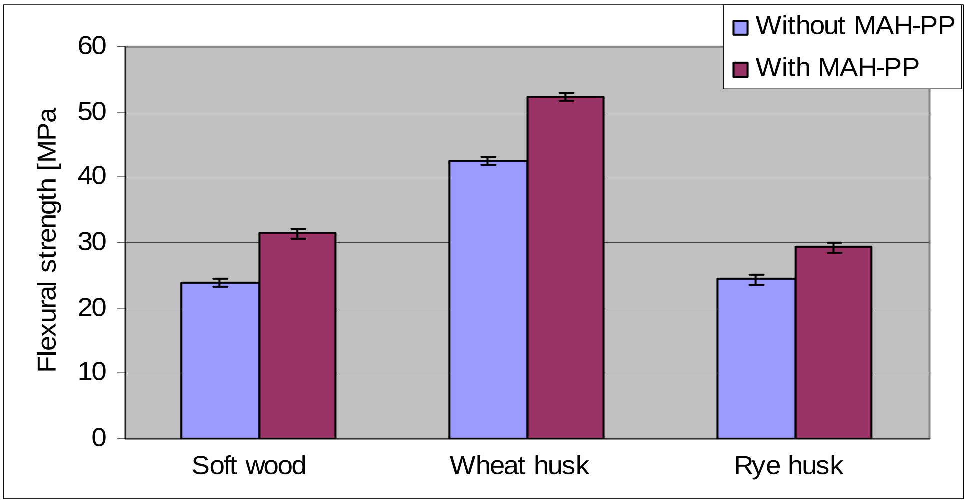


Figure4: Flexural strength of different fillers PP composites with and without MAH-PP.

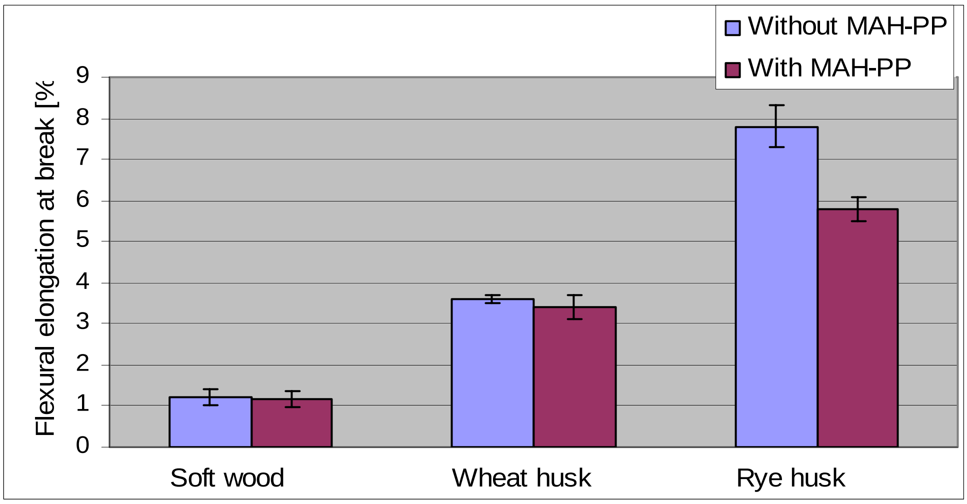


Figure5: Flexural elongation at break of different fillers PP composites with and without MAH-PP.

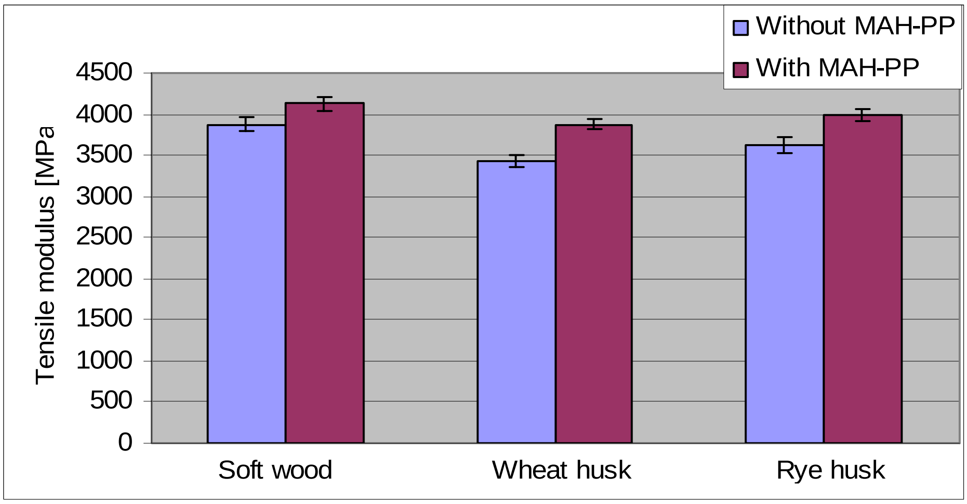


Figure6: Tensile modulus of different fillers PP composites with and without MAH-PP.

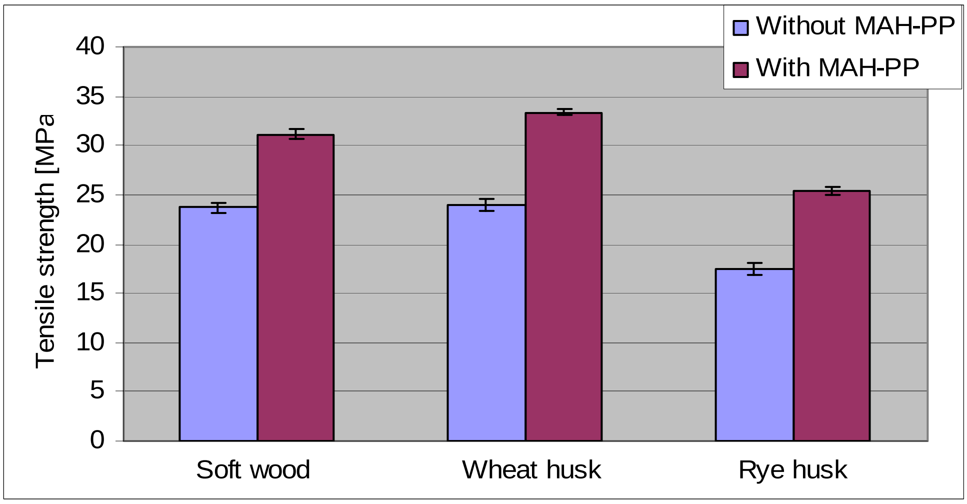


Figure7: Tensile strength of different fillers PP composites with and without MAH-PP.

Figure8: Charpy impact strength of different fillers PP composites with and without MAH-PP.

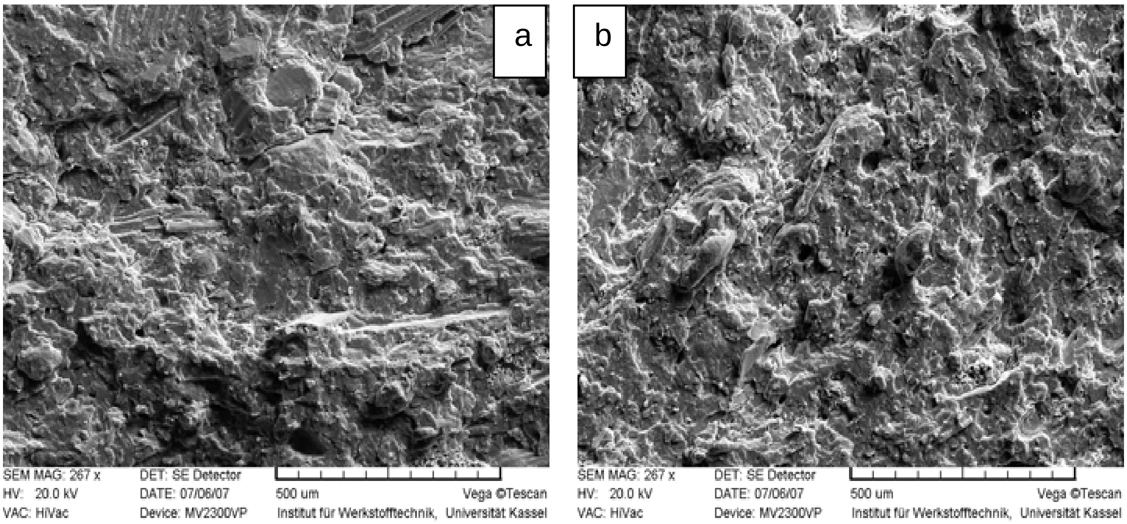


Figure9: SEM micrographs of wheat husk- PP composites; a) without MAH-PP, b) with MAH-PP

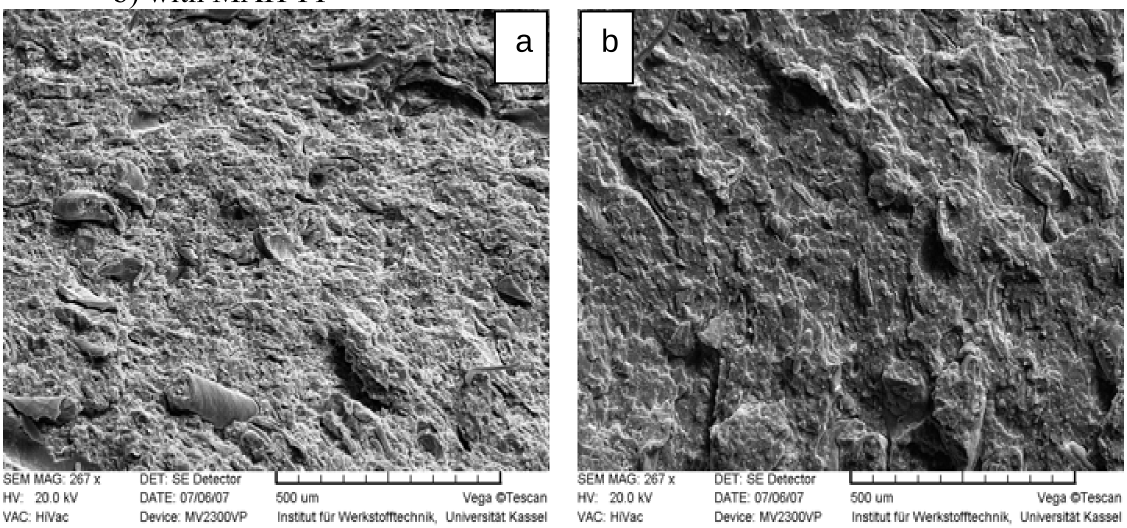


Figure10: SEM micrographs of rye husk- PP composites; a) without MAH-PP, b) with MAH-PP

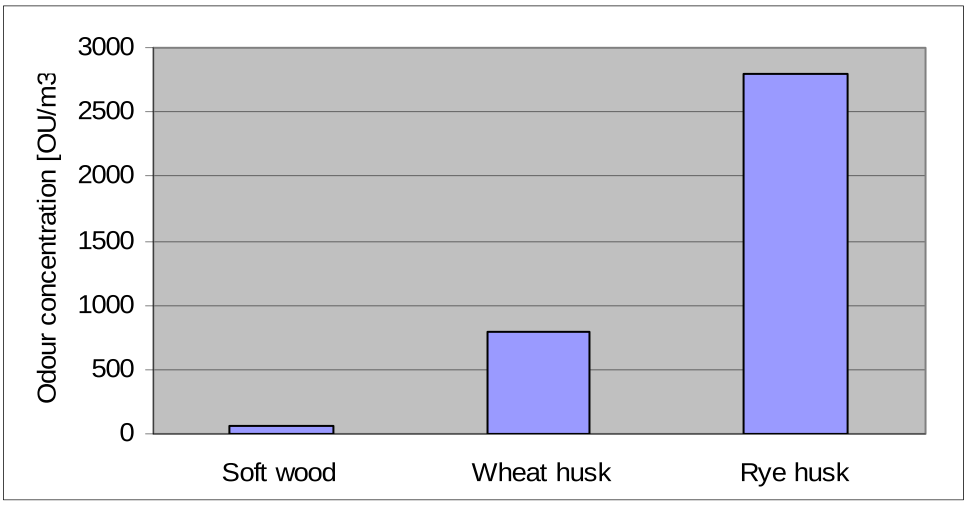


Figure11: Emitted odour concentration of different fillers PP composites

REFERENCES

1- Mohanty, A. K., Misra, M., and Drzal., L. T. "Sustainable biocomposites from renewable resources: opportunities and challenges in the green materials world," J. Poly. and Environment, 2002;10, 19-26.
2- Bălaş, A., and Popa, V. I., "The influence of natural aromatic compounds on the development of Lycopersicon Esculentum plantlets," BioRes.2007; 2(3), 363-370.
3- Cauvain, S.P. Cauvain P. C., Bread Making. CRC Press,2003; p. 540.
4- Palmer, J.J., How to Brew. Defenestrative Pub Co., 2001; p. 233.
5- Smith, A. E., Handbook of Weed Management Systems, Marcel Dekker, 1995; p. 411.
6- Daniel Z., Maria H., Domestication of plants in the Old World, third edition, Oxford: University Press, 2000; p. 75.
7- Duke, J.A. Handbook of Edible Weeds, CRC Press, Boca Raton, FL;1992.
8- Panthapulakkal, S., Sain, M., Injection molded wheat straw and corn stem filled polypropylene composites,J. Polym Environ., 2006;14, p.265-272.
9- Panthapulakkal, S., Sain, M., Agro-residue reinforced high-density polyethylene composites: Fiber characterization and analysis of composite properties, Composites: Part A, 2007; 38, p.1445–1454.
10- Yang, H.S., Kim, J.K., Son, J., Park, H.,J., Lee, B.,J., Hwang, T.,S., Rice husk flour filled polypropylene composites; mechanical and morphological study, Composite Structure, 2004; 63, p.305-312.
11- Yang, H.S., Kim, J.K., Son, J., Park, H.,J., Lee, B.,J., Hwang, T.,S., Effect of compatibilizing agents on rice husk flour filled polypropylene composites, Composite Structure, 2007;77, p.45-55.
12- Dai, W.L., Blendability and processing methodology of an environmental material rice husk/ PVA composites, Materials Letters, 2003; 57, p.3128-3136.
13- Bledzki A. K., Mamun, A.A., Volk, J., Manufacturing of grain by-products reinforced polypropylene composite, Naro.tech Messe und Kongresse für nachwachsende Rohstoffe, 2007; Sept 6-9.
14- Product and price information sheet, JELU WERK, Josef Ehler GmbH & Co. KG, Ludwigsmühle 73494 Rosenberg, Germany; 2007.
15- Blake, G.R., Hartge, K.H., Bulk density analysis, Part I. Physical and Mineralogical methods: Agronomy monograph, 1986; 9, p. 363-375.
16- Kite, F. E., Schoch, T. J., Leach, H. W., "Baker's digestion", Jr. Cereal Sci. Today, 1957; 31, p.42-49.
17- Bledzki, A. K., Mamun, A. A., Faruk, O., Abaca fibre reinforced PP composites: Comparison with jute and flax fibre composites considering fibre contents, Journal of eXPRESS polymer letters, 2007; 1(11), p.755-762.
18- Dobreva, D., Nenkova, S., Vasileva, St., monphology and mechanical properties of polypropylene and wood flour composites, BioRes., 2007;1(2), p.209-219.