The effect of coupling agent on the mechanical properties of injection molded polypropylene/wheat straw composites

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Abstract: The objective of this work is to evaluate the effect of maleic anhydride-grafted polypropylene (MAPP) as coupling agent in polypropylene (PP)-based composites filled with ground wheat straw (WS) particles. The WS and the MAPP content in the composites was 10 wt% and 2 wt%, respectively. The samples were fabricated through melt compounding using a twin-screw extruder and then formed into dumbbell-shaped specimens by injection molding. The mechanical properties of neat PP and the composites with and without coupling were evaluated based on tensile and flexural tests and dynamic mechanical analyses (DMA). The experimental results showed that incorporating WS into the PP reduces its tensile strength by ~3 MPa, while improving its Young’s modulus by 0.14 GPa. The addition of MAPP compensated for the loss in tensile strength without affecting the modulus. Similar observations were made during the flexural tests as well, in which case, however, there was no loss revealed in the strength in the presence of WS due to the different types of load. The results of DMA analyses indicated an improved stiffness of WS-containing samples throughout the whole analyzed temperature range of 20-120 °C as a consequence of reduced chain mobility of PP caused by the stiff straw particles.

Keywords: polypropylene; composites; natural fibers; wheat straw; mechanical properties; injection molding

I. INTRODUCTION

Natural fiber-reinforced thermoplastics gained more and more interest throughout the last several years, mostly due to the increasingly strict environmental regulations and the demand for sustainable lightweight plastic products. As a result, the importance of composites containing vegetable-based additives grew significantly in many fields, including the packaging, building, and automotive industries [1-3].

Polypropylene (PP) is one of the most versatile commodity plastics, which is produced in large quantities. The foremost reason for PP attracting major industrial and scientific interest lately is the wide variety of properties that can be achieved by combining it with other polymers or different fillers [4, 5]. Such property-tailoring actions enable the fabrication of highly ductile PP-based polymer blends with superior toughness [6, 7], and reinforced composites for engineering applications [8] at the same time. Within the last several years, numerous scientific studies were devoted to the development of PP-based polymer composites filled with various natural fibers [9, 10].

A specific type of natural fiber-filled composites is the group where polymers are filled with fibers generated as by-products during agricultural and forest industrial activities [11-14]. The foremost advantages of such lignocellulosic fillers are their low density, non-abrasive characteristics, high stiffness, low cost and, most importantly that they come from an annually renewable resource, while also being biodegradable [15]. Wheat straw (WS) is such an agricultural residue that is generated in vast amounts during the harvesting of wheat worldwide. In many countries, agricultural residues such as WS are still being gotten rid of through open-air burning,
which poses a considerable threat to the air quality, and through that to public health as well [16].

Incorporating lignocellulosic residues, like wheat straw into polymeric matrices, comes with a major challenge of forming a proper interfacial adhesion between the two components, else, the straw particles might act as stress concentration sites, leading to an early failure, when the polymer is exposed to a critical mechanical load. The generally poor interfacial compatibility between PP and natural fillers is due to the large polarity difference [17].

To date, a number of techniques have been introduced in order to improve the surface compatibility between plastics and natural fillers to produce high-performance composites. These techniques include physical methods (steam cooking, plasma treatment, etc.) and chemical pretreatments (alkaline treatment, mercerization, acetylation, etc.) as well [18]. Another potential way to promote the adhesive forces acting between the natural fibers and the polymer matrix is the use of coupling agents. For inert polymers, such as PP, the most commonly used coupling agents are the acid-modified versions of the base polymer [19]. In the case of PP it is the maleic anhydride-grafted polypropylene (MAPP), which is often used for natural filler-containing composites based on PP matrix. MAPP has been successfully used to improve the mechanical properties of polymer composites with PP matrix and various natural fillers, including jute [20], bamboo [21], wood [22], coconut fiber [23], banana fiber [24], and hemp [25].

In this present study, the effect of MAPP has been evaluated regarding the mechanical properties of ground WS particles-filled PP composites, where the test objects were prepared through injection molding. The quasi-static mechanical properties of the prepared samples were investigated by means of tensile and flexural tests, and the temperature-dependent mechanical properties were measured through dynamic mechanical analysis.

II. MATERIALS AND METHODS

1. Materials

An injection molding grade PP (Tippen H145F), kindly supplied by MOL Petrochemicals (Tiszaujváros, Hungary) was used as a polymer matrix (density = 0.9 g/cm³; MFI = 29 g/10 mins – measured at 216 kg and 230 °C). Chopped WS fibers were provided by Miko-Stroh (Borota, Hungary). The wheat straw fibers were washed in distilled water, dried, and sieved prior to blending them with PP. Particles were collected from sieves between 125 µm and 250 µm gaps. Optical microscopic image of the wheat straw can be seen in Fig. 1. The bulk density of wheat straw particles is reported to be in a wide range, mostly depending on its porosity, which, on the other hand, is greatly affected by the particle size [26]. The density of the straw particles used in this current study were determined to be ~1.49 g/cm³. The coupling agent was a maleic anhydride-grafted polypropylene (MAPP) under the brand Polybond 3002, which was obtained from Crompton Company (Middlebury, Connecticut, USA). It has an MFI of 7 g/10 mins at 230 °C and 2.16 kg load.

2. Sample preparation

All the components (PP pellets, MAPP, and WS particles) were dried in a Faithful drying chamber (Model WGLL-125BE, Huanghua, Cangzhou, China) at 80 °C for 6 hours prior to the processing. Melt compounding was performed on a Labtech twin-screw extruder (Model LTE 20-44, Samut Prakarn, Thailand). Melt compounding was performed with a barrel temperature profile of 160, 160, 165, 165, 170, 170, 170, 175, 175, 180, and 180 °C from feeder to die. The rotational speed of the screws was 40 rpm, while starve feeding was applied by gradually pouring premixed dry batches of 30 g into the extruder. The extruded strings were cooled down in a water tank and pelletized subsequently. The designations, the compositions and the density (determined according to Archimedes’ principle) of the fabricated samples are listed in Table 1. The measured density values confirmed that the resulting ratios of the components

![Figure 1. Optical microscopic image of the wheat straw used as a natural filler](image)

Table 1. Designation and composition of the prepared composite samples and their density

<table>
<thead>
<tr>
<th>Designation</th>
<th>PP [wt%]</th>
<th>WS [wt%]</th>
<th>MAPP [wt%]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>0.90</td>
</tr>
<tr>
<td>PP_WS</td>
<td>90</td>
<td>10</td>
<td>-</td>
<td>0.93</td>
</tr>
<tr>
<td>PP_WS_C</td>
<td>88</td>
<td>10</td>
<td>2</td>
<td>0.93</td>
</tr>
</tbody>
</table>
equal the theoretical values with little to no porosity being present in the samples. The composite pellets were dried once more prior to further processing with the same parameters as before the melt compounding.

The prepared composites were formed into dumbbell-shaped specimens according to the standard ISO 3167 as per injection molding, which was performed using an Arburg Allrounder machine (Model 420C, Lossburg, Germany) with a screw diameter of 35 mm. The heating zones of the injection unit were set to 170, 180, 190, 200, and 210 °C from the feeder to the nozzle. The mold was tempered to 25 °C. The injection rate was 30 cm³/sec, while the injection pressure was 1000 bar. A holding pressure profile of 750-650-250 bar was used for a total of 10 sec.

3. Characterization

The tensile and flexural mechanical properties of the PP/WS composites were determined using an Instron universal testing machine (Model 5582, Norwood, Massachusetts, USA). The tensile tests were performed according to the ISO 527 standard at a crosshead speed of 25 mm/min and with a gripped length of 100 mm. For the three-point bending tests the ISO 178 standard was followed, using rectangular specimens of 80 × 10 × 4 mm³, and the span length was set to 64 mm.

Dynamic mechanical analyses (DMA) were carried out in order to analyze the temperature-dependent mechanical properties of the prepared samples. For this purpose, a TA Instruments DMA machine (Model Q800, New Castle, Delaware, USA) equipped with a dual cantilever grip was applied. A heating rate of 3 °C/min was used in the temperature range of 20-120 °C. The amplitude was set to 0.02% deformation, while the frequency was 1 Hz. The specimens were rectangular bars with a length of 55 mm and a cross-section of 10 × 4 mm².

III. RESULTS AND DISCUSSION

1. Tensile mechanical properties

Typical tensile stress-strain curves of PP and its WS-filled composites are displayed in Fig. 2, while the corresponding tensile properties (i.e. tensile strength, Young’s modulus, and elongation) are collected in Table 2. The incorporation of 10 wt% of WS resulted in a slight loss of strength, compared to neat PP (27.6 MPa vs. 30.7 MPa), which is ascribed to the poor stress transfer efficiency between the PP matrix and the straw particles. This can be attributed to the difference in polarity between the components. While straw fibers are greatly hydrophilic, PP is a hydrophobic material. The addition of 2 wt% MAPP as a coupling agent successfully compensated part of the loss in strength caused by the straw fibers, which refers to its efficiency in improving the interfacial interactions between PP and the straw. This is in good agreement with scientific studies dealing with similar topics [27, 28].

It is clear that the Young’s modulus of unfilled PP (1.61 GPa) was greatly enhanced by the addition of WS. A relative improvement of 8-9% was achieved for both PP_WS (1.75 GPa) and PP_WS_C (1.74 GPa) samples. The explanation for the composites with and without coupling agent exhibiting very similar modulus values can be explained by the fact, that the quality of adhesion does not play a crucial role at low levels of mechanical loads, in which stage the Young’s modulus is determined. Similar findings were also reported in the literature dealing with PP/WS composites containing straw particles of various size and concentration [29]. Interestingly, Ashori et al. [30] found increasing modulus values in the presence of 2 wt% maleated PP coupling agent,

![Figure 2. Typical stress-strain curves recorded during the tensile tests](image)

<table>
<thead>
<tr>
<th></th>
<th>PP</th>
<th>PP_WS</th>
<th>PP_WS_C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength [MPa]</td>
<td>30.7 ± 0.3</td>
<td>27.6 ± 0.6</td>
<td>28.1 ± 0.1</td>
</tr>
<tr>
<td>Young’s modulus [GPa]</td>
<td>1.61 ± 0.02</td>
<td>1.75 ± 0.03</td>
<td>1.74 ± 0.03</td>
</tr>
<tr>
<td>Elongation at yield [%]</td>
<td>7.37 ± 0.16</td>
<td>5.47 ± 0.03</td>
<td>6.12 ± 0.14</td>
</tr>
<tr>
<td>Elongation at break [%]</td>
<td>8.99 ± 1.21</td>
<td>6.79 ± 0.69</td>
<td>9.46 ± 1.10</td>
</tr>
</tbody>
</table>
which indicates that the characteristics (i.e., molecular weight) of the given MAPP might also influence the resulting stiffness of the PP/WS composites.

Considering the elongation at break of the samples, the neat PP broke rather early (8.99%) even before showing a necking phenomenon, which is, however, in most cases not typical for this polymer. The lack of necking can be ascribed to the low molecular weight of the specific PP grade used in this study and the relatively high crosshead speed during the tensile tests. Introducing the WS resulted in a drop in deformability, reducing the elongation at break to 6.79%. In this regard, the sample containing MAPP as a compatibilizer proved to be superior (9.46%) compared to the previous ones. This supports the assumption that the maleated PP coupling agent promotes the interfacial adhesion between the components, making the composites able to endure higher levels of deformation.

2. Flexural mechanical properties

Comparative stress-strain curves recorded during the 3-point bending tests are shown in Fig. 3, while Table 3 summarizes the flexural mechanical property values of the prepared samples. Even though the ISO 178 standard does not consider the flexural strength of polymeric materials when the deflection exceeds the conventional limit, currently, both the flexural strength at conventional deflection and the flexural strength values have been collected to describe the mechanical behavior of the fabricated samples.

The flexural modulus of both WS-containing samples outperformed the unfilled PP (1.66 GPa), as a consequence of stiff straw particles being present in the polymer. Similarly to the tensile tests’ results, there is little to no difference agent in the modulus values determined through the 3-point bending tests, regardless of the presence of the coupling. Both the

### Table 3. Flexural mechanical properties of PP and its WS-filled composites with and without coupling agent

<table>
<thead>
<tr>
<th></th>
<th>PP</th>
<th>PP_WS</th>
<th>PP_WS_C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flex. stress at conv. defl. [MPa]</td>
<td>41.8 ± 0.5</td>
<td>42.9 ± 0.5</td>
<td>43.9 ± 0.3</td>
</tr>
<tr>
<td>Flexural strength [MPa]</td>
<td>49.8 ± 0.4</td>
<td>48.7 ± 0.6</td>
<td>50.5 ± 0.2</td>
</tr>
<tr>
<td>Flexural modulus [GPa]</td>
<td>1.66 ± 0.02</td>
<td>1.89 ± 0.03</td>
<td>1.89 ± 0.03</td>
</tr>
</tbody>
</table>

PP_WS and the PP_WS_C composites showed a flexural modulus of 1.89 GPa, which refers to the lack of significance of the coupling agent considering the stiffness.

Apparently, the flexural stress at conventional deflection values of both WS-containing composites were higher than that of unfilled PP (41.8 MPa). This is, however, partly due to the higher stiffness. Higher stiffness increases the initial slope of the flexural stress-strain curves, making them cross the limit of conventional deflection at higher stress values unless failure occurs earlier than that. On the other hand, the flexural strength of PP_WS (48.7 MPa) was lower than that of neat PP (49.8 MPa) due to the poor stress transfer between the polymer and the filler. Interestingly, the addition of MAPP, in this case, did not only compensate for the loss in strength, but the PP_WS_C composite (50.5 MPa) outperformed even the neat PP in terms of flexural strength. This means that under the bending type of load, the straw particles actually acted as reinforcement in PP, which was enabled by the successful stress transfer in the presence of maleated polypropylene compatibilizer. Similar results, namely enhanced flexural strength values of PP/WS composites in the presence of MAPP were reported by Panthapulakkal et al. [27] as well.

3. Dynamic mechanical properties

Comparison plots of the storage modulus (\(E'\)) and loss factor (\(\tan \delta\)) as a function of temperature were obtained through the DMA measurements. The corresponding curves are presented in Fig. 4. Evidently, the storage modulus of all samples decreases as a function of temperature, which can be attributed to the softening of PP. Compared to neat PP, the WS-containing samples exhibited a different DMA behavior. The \(E'\) curves of WS-filled composites shifted to higher modulus values due to the greater stiffness of straw particles compared to the polymer matrix. The plots of the PP/WS composites with and without MAPP are mostly

![Figure 3. Typical stress-strain curves recorded during the flexural tests](image_url)
overlapping, indicating the fact that the presence of the coupling agent did barely alter the storage modulus of the system in the investigated temperature range. At room temperature (~25 °C), the storage modulus of the samples PP, PP_WS, and PP_WS_C was 1626 MPa, 1779 MPa, and 1775 MPa, respectively. This is in good agreement with both the tensile and flexural tests’ results. The reason for the coupling agent-containing curve being slightly lower is explained in the literature by the formation of a thin and irregular polymer layer around the filler particles, which promotes plastic deformation. Similar trends were observed in the literature by Pan et al. [31] for compatibilized PP/WS composites, where the authors prepared the samples through compression molding.

Regarding the loss factor (tan δ), which is the ratio of loss modulus to storage modulus, the addition of WS particles resulted in lower values in the entire temperature range, referring to a decreased molecular mobility of PP, which is in good accord with the findings registered throughout the tensile and the flexural tests, namely an increased stiffness. Considering the rather stiff nature of the straw particles it seems reasonable that their presence restricted the motion of the polymer chain molecules.

**IV. CONCLUSIONS**

In this research, the effect of maleated polypropylene as a coupling agent was investigated, considering the quasi-static and dynamic mechanical properties of PP/WS composites. The samples were prepared through extrusion followed by injection molding, while the properties were analyzed by means of tensile tests, flexural tests, and DMA measurements. According to the results, the incorporation of WS into the PP matrix leads to enhanced stiffness, however, at cost of deteriorating strength and deformability due to the limited interfacial adhesion between the components. Adding the MAPP coupling agent to the composite system promotes the chemical interactions, thereby improving the strength of PP/WS composites. In the case of tensile tests, the presence of MAPP compensated part of the loss in strength caused by WS, while in the case of flexural tests the strength of the compatibilized samples even exceeded that of neat PPs. The dynamic mechanical analysis revealed that the stiffness enhancement caused by WS is present throughout the entire analyzed temperature range and is not affected by MAPP, while the damping factor of the composites decreased due to the stiff straw particles limiting the molecular mobility of PP.

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**AUTHOR CONTRIBUTIONS**

L. Lendvai: Conceptualization, Methodology, Experiments, Investigation, Theoretical analysis, Funding acquisition, Writing – Original draft preparation

A. Patnaik: Investigation, Theoretical analysis, Writing – Review and editing

**DISCLOSURE STATEMENT**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES


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