ON ENGINEERING OF PROPERTIES OF WOOD-POLYPROPYLENE COMPOSITE

Abstract: New materials based on wood have the advantage in the sense that their properties can be engineered so as to correspond to user demands. The properties which can be engineered are those relating both to their utilisation and machining, in particular - the tensile strength, elongation at break, modulus of elasticity and impact resistance. The research at the Faculty of Forestry and “Hipol” Chemical Industry related to the new type of wood-polypropylene composite. The content of wood filler was varied in the range between 40% and 70% mass contents of beech wood flour. After the highest tensile strength at 50% of filler content was determined, the effect of the wood filler origin was also examined at this content value. Therefore, wood flour of beech, poplar, acetylated pine and the waste MDF was used. The influence of the composition of the wood filler (beech combined with MDF, poplar and acetylated pine) in comparison with pure polypropylene matrix was also examined, as well as the effect of the type of coupling agent. Hopefully, the results obtained in this study might serve as the initial data for production of easily machined high-strength composites.

Key words: wood plastic composites, polypropylene, wood filler, coupling agents, acetylation
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There has recently been a dramatic increase of interest in using biomass such as wood or agricultural fibres as replacements for glass to reinforce thermoplastic composites, because the wood material offers several advantages over inorganic fillers, such as its low price, biodegradability, renewability, recycle-ability, low density, etc. (Bolton, 1994). Because of those advantages, the use of natural fibres as fillers for plastic has been rapidly expanding. Over 50% growth in the use of natural fibres in the plastic industry is forecast for 2000-2005 (Stark, Rowlands, 2003).

As has been often pointed out, one of serious disadvantages of using wood fillers such as wood flour (WF) as reinforcement for polyolefinic matrix like polypropylene (PP) is that the composites usually have a significantly reduced impact and tensile strength (Bolton, 1994). It is due to poor adhesion between the hydrophilic wood filler and hydrophobic thermoplastic. This problem can be overcome by the modification of filler/matrix interface by suitable coupling agents coating on the surface of wood particles, polymer or both by compounding, blending, soaking, spraying, or other methods (Lu et al., 2000). A number of investigations on isocyanates, silanes, anhydrides and anhydride-modified polymers such as maleated polypropylene (MAPP) as coupling agents were performed (Lu et al., 2000, Điporović et al., 2003). Review of wood - plastic composites showed that highly hydrophobic matrix improve the water resistance of such composites, but not enough. This is because of hydrophilic wood filler (Takatani et al., 2000).

The properties of these composites can be engineered because they also depend on the size, geometry, aspect ratio \((L/D)\), modulus of elasticity and on the type of filler. The concentration of the filler in composite also is important. Therefore, the mechanical properties of the composites are major criteria for determining their application. With the increased penetration of wood fibre - plastic based materials at the market for a wide range of products, there will be increased need for secondary machining processes of such materials.

In this study the influence of different contents of wood flour (WF) on mechanical properties of wood/polypropylene (W/PP) composites was investigated. The effect of the
wood filler origin as well as composition of the wood filler blend (beech combined with MDF, poplar and pine) in comparison with polypropylene was also examined. In addition, the influence of concentration of commercial coupling agents like silane (A-1100) and MAPP on mechanical properties of W/PP composites has been evaluated. Besides, the effect of acetylated wood filler for potential exterior use of W/PP composites were investigated too.

2. EXPERIMENTAL

Materials - The following materials were used for production of wood-polypropylene composites:

- POLYPROPYLENE (PP) powder, MFR 3 g/10 min; density 0.905 g cm$^{-3}$; stress at break 24 MPa; elongation 570%; elasticity modulus 1260 MPa; IZOD impact resistance (notched) 33.5 J m$^{-1}$. Produced by HIPOL, Odžaci;
- ADDITIVES: Neutralizer - Ca stearate (HICI Chemical); Initiator - organic peroxide TRIGONOX 7.5P (AKZO Chemie), 7.5% peroxide carrier on PP powder; Antioxidants - IRGANOX RA1010, IRGANOX PS802, ULTRANOX 626 (CIBA);
- COUPLING AGENTS: Maleic anhydride (MAPP) - NOURYMIX MA 915 - 50% MA carried on PP powder (AKZO Chemie), Silane (A-1100)- 3-aminopropyliethoxysilane (bruto formula C$_9$H$_{23}$NO$_3$Si), SIGMA Aldrich;
- ACETYLATION AGENT: Acetic anhydride (Pro Analyti, produced by “Zorka” Šabac);
- WOOD FILLER: dried wood flour of beech (Fagus moesiaca), pine (Pinus nigra), poplar (Populus cv. robusta) and of waste from cutting of (MDF) boards - the blend of particle size distribution (DIN 1171): 8% on 14 mesh, 26% on 20 mesh, 27% on 24 mesh, 36% on 40 mesh and 3% passed through 40 mesh. Average aspect ratios of wood flour particles were 5.7, 6.7, 5.5 and 4.4 for beech, poplar, pine and MDF wastes, respectively.

Acetylation treatments - Oven-dried charges of WF of pine were placed in reactor. Acetic anhydride was added, and acetylation of particles was ensured by boiling in acetic anhydride under reflux during one hour. The anhydride to particle ratio in reactor was 2:1. After prescribed reaction time, the particles were washed with distilled water and oven-dried at 103±2°C. The acetyl group content was determined by Freundenberg-Harder method and acetyl content of 21.3% was found.

Preparation of composites - In the first step, the dry mixtures of ingredients in the following quantities (by mass of composites) were used:

- Matrix (60%, 50%, 40%, 30%) - PP powder stabilized with additives: 1.34% TRIGONOX 7.5P (corresponds to 0.10% pure organic peroxide) + 0.05% Ca stearate + 0.15% IRGANOX RA1010 + 0.25% IRGANOX PS802 + 0.15% ULTRANOX 626 - by mass of matrix;
Milanka Điporović, Jovan Miljković, Eva Dingova

– Filler (40%, 50%, 60%, 40%)- wood flour (WF);
– Coupling agent MAPP (0 % and 3.4%) or silane (A-1100) (0%, 4% and 6%).

Conditions of test specimen preparation - In the second step dry mixtures were melt-mixed in intensive mixer “RHEOMIX 600” under following conditions:
– Temperature 210°C;
– Time/rotation frequency 7 min/70 rpm.

The samples for mechanical tests were prepared by press molding under the following conditions:

<table>
<thead>
<tr>
<th>Press molding process</th>
<th>Cooling process</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Temperature 230°C</td>
<td>• Temperature decreasing up to 20°C</td>
</tr>
<tr>
<td>• Time heating up 4-5 min</td>
<td>• Time 7 min</td>
</tr>
<tr>
<td>press molding 3-4 min</td>
<td>• Specific pressure 3.1 MPa</td>
</tr>
<tr>
<td>• Specific pressure 3.1 MPa</td>
<td></td>
</tr>
</tbody>
</table>

Mechanical tests: Tensile properties were measured by INSTRON 4204 testing equipment according to ASTM D 638 standard method, using speed of 50 mm·min⁻¹ for testing tensile strength and elongation, and 5 mm·min⁻¹ for testing modulus of elasticity. The elongation testing was carried by extension-meter. Notched IZOD impact resistance was tested according to ASTM D 256 standard by ZWICK 5101 testing pendulum. Mechanical properties were presented as the statistical averages of 6-12 measurements. The coefficients of variation were for tensile strength about 10.2%, for elongation about 33.8%, for modulus of elasticity about 15.4% and for impact resistance (Izod-notched) about 8.2%. The high variation coefficient is the consequence of the material heterogeneity. The number of measurement does not decrease this coefficient significantly.

3. RESULTS AND DISCUSSION

3.1. The Influence of the coupling agent type and peroxide concentration

The results of examination of the quality improvement of the PP composites filled with 50% of the beech wood flour, with different type of coupling agent and peroxide concentration, are presented in Tab. 1. On the basis of previous research, silane (A-1100) and MAPP were chosen in the quantities of 4% and 3.4%, respectively, as the optimum quantity in the composite (Điporović et al., 2003). As the initiator for bonding of coupling agent both with PP matrix and lignocellulosic filler, commercial peroxide compatible with PP polymer (TRIGONOX 7.5P) has been chosen.

In Tab. 1, it can be seen that both of the chosen coupling agents increased TS at break of the composites by about 66-80%, indicating that they improved the adhesion at the filler/matrix surface. The silane (A-1100) agent in this combination is somewhat more efficient as the coupling agent, since it produces higher TS and considerably higher E and impact resistance.
Table 1. The influence of coupling agent type and concentration of peroxide on properties of PP composites filled with 50% beech wood flour

<table>
<thead>
<tr>
<th>Type of coupling agent</th>
<th>Silane (A-1100)</th>
<th>MAPP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coupling agent addition</td>
<td>%</td>
<td>4</td>
</tr>
<tr>
<td>Concentration of peroxide</td>
<td>%</td>
<td>0.1</td>
</tr>
<tr>
<td>Tensile strength (TS)</td>
<td>MPa</td>
<td>15.7</td>
</tr>
<tr>
<td>Elongation (E)</td>
<td>%</td>
<td>0.81</td>
</tr>
<tr>
<td>Modulus of elasticity (MOE)</td>
<td>MPa</td>
<td>/</td>
</tr>
<tr>
<td>Impact resistant (Izod-notched)</td>
<td>J/m²</td>
<td>/</td>
</tr>
</tbody>
</table>

*By mass of composite (у односу на масу композита), a at break (при кидању)

The efficiency of this agent in improving the adhesion of the wood filler and the matrix is based upon its chemical reactivity (Mal das et al., 1989). It is considered that, in presence of absorbed moisture, the alkoxy groups (OR) of the silanes form silanols:

\[
R-(CH_2)_n-Si(OR')_3 + H_2O \rightarrow R-(CH_2)_n-Si(OH)_3 + OR'.
\]  

(1)

Formed silanol’s –OH groups as a (OR’) groups, build a number of hydrogen bonds with –OH groups of the cellulosic filler-polymer. Functional silanol’s (R) groups in this case amino –NH₂ groups can adhere to the PP with weak Van der Waals force. It is suggested that –NH₂ groups of this silane can, in presence of peroxide, yield amino radicals (‘NH'), which might connect with radicals of polymer matrix by following reaction (Điporović et al., 2003):

\[
\sim \sim PP+‘NH-(CH_2)_n-Si(OR')_3+OH–Wood–COOH\sim \sim PP–NH-(CH_2)_n-Si(OR')_3 OH–Wood–COOH.
\]  

(2)

In addition, the present –NH₂ groups can also establish the hydrogen bonds with the –OH groups of cellulose, lignin and carboxyl groups of hemicelluloses as well as with the other –NH₂ (OR’) groups, or even –OH groups of silanol, forming so-called cage structure in which matrix polymer chains can also be rapted, giving a special effect of coupling in the filler-matrix system. Only subsequent reaction of the functional active group (R) with polymer through thermally induced cross-linking in the presence of reactive substance could produce a molecular bridge between the polymer and filler and lead to an increase in mechanical properties (Albano, 2001).
From the application aspect MAPP is more favourable, since it is already grafted anhydride (MA) with PP in powder form, which addition during compounding step in known quantity is very easy. However, despite the optimum concentration of 1.7%, MA produces composite of lower impact resistance and lower elongation. The increased composite brittleness presumably originates from higher degradation of PP in the presence of MA and peroxide than in the presence of peroxide itself (Hog t, 1988).

The higher concentrations of peroxide (more than the usual 0.05%) had been chosen in this paper, since the filler contents were higher too (Điporović et al., 2003). From the Tab. 1 it can be noticed that peroxide concentration increases from 0.1% to 0.2 %, influencing decrease of TS for about 18%, while the E decreased by about 27%. This is presumably the consequence of degradation of PP in the presence of higher quantity of peroxide. On the basis of above research results, silane (A-1100) was chosen as the coupling agent for further experiment at the peroxide concentration of 0.1%.

3.2. The Influence of Concentration of Silane (A-1100) as the Coupling Agent

For the quality of composite, it is of particular importance to establish the optimum quantity of coupling agent. The optimum quantity of silane was determined on the base of higher content of filler (70%) applied in this study. It is well know that incompatibility of the wood filler and PP matrix grows with increasing contents of filler (Điporović et al., 2003).

![Figure 1. The influence of concentration silane (A-1100) as a coupling agent on tensile strength (TS) and elongation (E) of PP composites filled with 70% beech wood flour](image)

Слика 1. Утицај концентрације силана (А-1100) као куплујућег агенса на затезну чврстоћу (ТС) и елонгацију (Е) РП композита испуњених са 70% буковог дрвног брашна
This is why the filler quantity of 70% was tested here. The results of the influence of concentration of silane as the coupling agent are shown in Fig. 1.

The results in Fig. 1 show that TS and E of composites initially increase up to the concentration of 4% of silane, and then decrease with its further increase of concentration. Thus, concentration of 4% of silane in the composite is optimum. This concentration was used in the further experiments.

3.3. The Influence of Wood Flour Contents

The results of measurements of the tensile properties of PP composites produced with the varying contents of the wood flour particles of beech and with 4% silane (A-1100) added to composite mass are presented in Fig. 2.

From Fig. 2 it can be noticed that TS improves with the increase of wood particles contents up to 50%, and thereafter decreases. The highest TS values were reached by the composites with the contents of 50% of WF, while the 60% WF content causes rapid decrease of TS to a value even lower than the original matrix strength. The values of TS of composites with 60% and 70% of WF contents are similar to each other, indicating saturation of the composite by the filler. The same effect was noticed with the concentration of 50% of wood filler in the PP composite (Takase, Shiraiishi, 1989). In general, the decrease of the TS with increasing wood filler contents in the composite (in this case higher
than 50%) is the consequence of incompatibility of the wood filler and PP matrix. Ever
decreasing quantity of the matrix polymer in the composites with high wood filler contents
requires careful adjustment of the composite production parameters. For these reasons, the
temperature of 210°C has been chosen for softening and mixing of components, in order
to make them more plastic and ready to flow. In such way mixing and homogenisation of
matrix and filler is more successful.

From Fig. 2 a dramatic decrease of E of composites is also noticed already with
the wood filler content of 40%, with a trend of a mild decrease with further filler increase.
This decrease results from the higher presence of stiff wood particles, contrary to original
PP matrix, which has high elongations.

3.4. The Influence of the Origin of Wood Filler

The influence of the origin of the wood filler upon the mechanical properties of PP
composites with 50% content of different fillers (beech, poplar, acetylated pine and MDF
waste) with addition of 4% of silane, are shown in Tab. 2.

<table>
<thead>
<tr>
<th>Type of wood flour</th>
<th>TS* (MPa)</th>
<th>E* (%)</th>
<th>MOE (MPa)</th>
<th>Izod - notched (J/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beech / Буква</td>
<td>28.53</td>
<td>1.28</td>
<td>3200</td>
<td>37.3</td>
</tr>
<tr>
<td>Poplar / Топола</td>
<td>28.93</td>
<td>0.41</td>
<td>4255</td>
<td>37.05</td>
</tr>
<tr>
<td>MDF waste / Отпадак од MDF плоче</td>
<td>34.84</td>
<td>1.08</td>
<td>3528</td>
<td>33.59</td>
</tr>
<tr>
<td>Acet. Pine / Ацетиловани бор</td>
<td>19.74</td>
<td>0.24</td>
<td>3570</td>
<td>35.16</td>
</tr>
<tr>
<td>PP matrix / Полипропиленска матрица</td>
<td>24.00</td>
<td>12.92</td>
<td>1237</td>
<td>33.57</td>
</tr>
</tbody>
</table>

* at break / при кидању

In Tab. 2 it can be noticed that all the types of wood particles except the acetylated
WF of pine reinforced the matrix polymer, since they produced considerably higher TS
of PP composites with respect to the matrix. This reinforcement (about 28%) is the con-
sequence of the influence of silane as a coupling agent, which enabled bonding of the
wood filler and PP at their interface. WF from the MDF waste produced the maximum
value of TS of PP composites, exceeding by far that of WF of beech and poplar. This ef-
fect is a consequence of the fibrous form of wood particles (Fig. 3, a and b), which were
homogenised better in the matrix (Fig. 3, c and d) and therefore, due to higher contact
surface of the fibrous particles, can achieve better adhesion with the matrix supported by
coupling agents.
However, acetylated pine particles produced the composites of lower TS even than that of the matrix. It has also been expected, since the acetylated particles are more hydrophobic and chemically inert, and hence unable to form bonds with the matrix polymer in presence of the coupling agent. Because of their hydrophobicity they are more compatible with the matrix PP polymer, mostly reflected in the improvement of the impact resistance, shown in Tab. 2. Considerably higher impact resistance (by about 10.5%) of PP composites was produced by the WF particles of beech and poplar, not only compared with the matrix, but also in comparison with the other particles, due to the presence of the coupling agent. WF particles from the waste MDF boards, due to their lower impact resistance, produced composites of resistance similar to the matrix polymer.

In Tab. 2 it can be noticed that the MOE values of PP composites are by far higher (by about 160-225%) in comparison with the values of the original matrix, while E in tension is lower. This has been expected as a consequence of the addition of wood particles, which are considerably more rigid than the PP matrix. The maximum MOE value has been produced by the poplar particles because of the higher aspect ratio as well as the influence of the lower density (490 kg m⁻³) of this species. In other words, with the same mass, the number of particles of lower-density wood species is higher. For that reason, the beech particles probably produced lower MOE of the composites, while the composites with poplar and pine had considerably lower tensile E. In view of the potential application of these composites, the addition of any wood particles reduces the large deformation of PP composites to an acceptable measure. This is favourable since the wood particles break the continuity of the PP matrix chains.

3.5. The Influence of Wood Filler Blend

It is known in practice that the waste from the primary and final wood processing represents a blend of the used domestic wood species. Therefore, the aim in this paper was to investigate the influences of the most probable blends of the species and waste upon the properties of WF/PP composites, as well as at to estimate in what range the composite properties vary with the addition of the acetylated particles. Such chemical modification
has been suggested, since large utilisation is foreseen of this material for exterior use (Djiporovic et al.). With respect that the beech is most represented species in our wood industry, beech WF in the quantity of 70% has been mixed with 30% of wood particles of poplar, Austrian pine and MDF waste. The blend content in the composite was 50%. The results of determinations of properties of such composites are shown in Fig. 4.

The results at Fig. 4 show that PP composites produced with the blend of wood particles of beech and poplar as well as of beech and waste MDF boards are stronger and tougher than the matrix polymer, since their TS and impact resistance are considerably higher because of the positive influence of the silane (A-1100) as a coupling agent. The presence of the poplar particles in the blend improved MOE of the PP composites and reduced tensile E due to the mentioned effect of lower density.

However, in the blend of beech and waste MDF particles the effect of the beech particles dominated with respect to all studied PP composite properties, since in their values they are very similar to those composites produced with WF of beech only (Tab. 2). The participation of acetylated particles of pine in the blend with WF of beech, due to their chemical inertia deteriorated the TS and impact resistance of PP composites in comparison with the composites based on beech WF only. In addition, its presence influenced tensile E to reduce, and, on the other hand, upon improving MOE of composites, probably due to the mentioned effect of the lower density (490 $kg\cdot m^{-3}$) of pine.

3. CONCLUSIONS

Based on the results of the mechanical properties of WF/PP composites, it can be stated that:
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1. The optimum concentration of silane (A-1100) as a coupling agent in tested composites is 4%, when added simultaneously to the filler and matrix in presence of 0.1% of peroxide;
2. The optimum content of WF particles in PP composites was found to be 50%. This high wood filler content is very favourable from the viewpoint of the composite price;
3. Wood flour in the form of MDF waste produces stronger and more brittle PP composites, while WF of poplar is more favourable for production of strong and tough composites, which is very significant from the viewpoint of machining and application of composites;
4. The properties of PP composites can be adjusted by mixing different wood species for filler blend;
5. Acetylated pine particles (20% wt. gain of acetyl) were not found as reinforcing fillers, but their combination with untreated wood particles can lead to better tensile strength. This will be (together with dimensional stability) objective of further research.

REFERENCES

Миланка Đипоровић, Јован Милјковић, Ева Дингова


**ПОДЕШАВАЊЕ СВОЈСТАВА ДРВО-ПОЛИПРОПИЛЕНСКИХ КОМПОЗИТА**

**Резиме**

Резултати механичких својстава композита на бази дрвног брашна и полипропилена добијени у овом раду, указују да је оптимална концентрација куплујућег агенса на бази силана A-1100 4% у присуству пероксида 0,1%. Са друге стране, оптимална концентрација дрвног пуниоца је била 50%, што је повољно са становишта цене композита.

Дрвно брашно од MDF плоча даје јаче и кртије PP композите, а дрвно брашно од тонаре је погодније за чврсте и жилаве композите. Ово је значајно за обрадивост и примену ових композита. Својства PP композита се тако могу подешавати блендирањем пуниоца из различитих извора.

Мешањем ацетилованог и неацетилованог пуниоца могуће је побољшати затезну чврстоћу композита, што ће, уз димензионалну стабилност, бити предмет неких наредних истраживања.