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<th>Journal:</th>
<th>Polymer International</th>
</tr>
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<tr>
<td>Manuscript ID:</td>
<td>PI-08-0061</td>
</tr>
<tr>
<td>Wiley - Manuscript type:</td>
<td>Original Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>13-Feb-2008</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Srebrenkoska, Vineta; Eurokompozit, R&amp;D</td>
</tr>
<tr>
<td>Key Words:</td>
<td>eco-composites, polypropylene, kenaf fibers, rice hulls</td>
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RECYCLING OF POLYPROPYLENE BASED ECO-COMPOSITES

Vineta Srebrenkoska*1, Gordana Bogoeva Gaceva2, Maurizio Avella3, Maria Emanuela Ericco3 and Gennaro Gentile3

1Eurokompozit 11Oktomvri, a company for production of special purpose products, Aleksandar Makedonski 2/42, MK-7500 Prilep, Republic of Macedonia
2Faculty of Technology and Metallurgy, Sts. Cyril & Methodius University, MK-1000 Skopje, Republic of Macedonia
3Institute of Chemistry and Technology on Polymers – ICTP-CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Napoli, Italy

email: Vineta Srebrenkoska (rd@eurokompozit.com.mk)

*Correspondence to Vineta Srebrenkoska, Eurokompozit 11Oktomvri, a company for production of special purpose products, Aleksandar Makedonski 2/42, MK-7500 Prilep, Republic of Macedonia

ABSTRACT

BACKGROUND: Renewable resources and recyclable thermoplastic polymers provide attractive eco-friendly quality as well as environmental sustainability to the resulting natural fiber reinforced composites. The properties of polypropylene (PP) based composites reinforced with rice hulls or kenaf fibers were investigated with respect to
their recyclability. Maleic anhydride grafted PP was used as a coupling agent (CA) to improve the compatibility and adhesion between fibers and matrix. The composites containing 30 wt % reinforcement were manufactured by melt mixing and their mechanical and thermal properties were determined. The composites were then granulated into granules used for production of new samples by compression molding.

RESULTS: It was found that the flexural strength and thermal stability of recycled composites is similar to the initial ones. The composites based on kenaf fibers have shown better properties after recycling than those based on rice hulls.

CONCLUSION: The obtained results for flexural strength and modulus of PP-based composites produced from the recycled samples with kenaf fibers or rice hulls as reinforcement are comparable to conventional formaldehyde wood medium density fiberboards. The recycled composites exhibit good characteristics for using as construction materials for housing systems.

Keywords: Eco-composites, polypropylene, rice hulls, kenaf fibers, compression molding

INTRODUCTION

The growing environmental awareness and new rules and regulations are forcing the industries to seek more ecologically friendly materials for their products. In recent years, the development of biocomposites from biodegradable polymers and natural fibers have attracted great interests, because they could allow complete degradation in soil or by composting process and do not emit any toxic or noxious components\(^1,2\). Many
investigations have been made on the potential of natural fibers as reinforcements for so-called eco-composites and in several cases the results have shown that they exhibit good stiffness and promising properties\textsuperscript{1-8}. The main drawback of natural fibers is their hydrophilic nature, which decreases the compatibility with hydrophobic polymeric matrix. Therefore, different kinds of coupling agents have been used for improving interfacial properties between the polymer matrices and natural fibers in order to enhance the physical and mechanical properties of the final products.

Due to their hollow and cellular nature, natural fibers perform as acoustic and thermal insulators, and exhibit reduced bulk density. Depending of their performance, when they are included in the polymer matrix, lignocellulosic fibers can be classified into three categories: (1) wood flour particulates, which increase the tensile and flexural modulus of the composites, (2) fibers of higher aspect ratio that contribute to improving the composites modulus and strength when suitable additives are used to regulate the stress transfer between the matrix and the fibers, and (3) long natural fibers with the highest efficiency amongst the lignocellulosic reinforcements. The most efficient natural fibers have been considered those that have a high cellulose content coupled with a low microfibril angle, resulting in high filament mechanical properties.

Amongst eco-compatible polymer composites, special attention has been given to polypropylene composites, due to their added advantage of recyclability\textsuperscript{9}. As an oil-based product, PP could not be classified as a biodegradable polymer, but by introducing thermo-sensitive catalysts to increase the degradability, PP takes an important place in eco-composite materials. For example, Mohanty et al. have demonstrated that the NF reinforced PP composites have potential to replace glass-PP composites\textsuperscript{10}. It has also
been reported that PP can be effectively modified by maleic anhydride, providing polar
interactions and covalent links of PP to the hydroxyl groups of the cellulose fiber\textsuperscript{11}. Significant research efforts have been also spent on eco composites based on recyclable
polymer with natural fibers. Currently, the widely favored PP is used for great number of
recyclable eco-composites. Visteon and Technilin developed their own flax/PP material
R-Flax\textsuperscript{\textregistered}, based on a low cost fiber. Tech-Wood International from the Netherlands
announced its Tech-Wood\textsuperscript{\textregistered} eco-composite, aimed for construction elements\textsuperscript{12}. Tech-
Wood\textsuperscript{\textregistered} eco-composite material contains 70\% pine-wood fibers and 30\% compatibilized PP.

Yang et al. have studied the possibility of using lignocellulosic rice-husk flour (RHF) as reinforcing filler (10-40 wt \%) in polyolefine composites\textsuperscript{13}. The results of
tensile test have shown that tensile strength of the composites slightly decreased as the
filler load increased. Applying the method used in the wood-based panel industry,
composite insulation boards were produced with rice hulls\textsuperscript{14}. Composite boards with
specific gravity of 0,8 and rice hulls content of 10 wt\% have slightly better bending
modulus than wood particle board (as a control board), however they show no differences
from the control boards at a 20 wt\% rice hulls. Toro et al. (2005)\textsuperscript{15} have studied the
compatibilizing effect of polypropylene grafted with monomethyl itaconate in PP/rice-
husk composites. It was shown that tensile modulus and water arpsorption of the
composite were improved by adding compatibilizer.

The purpose of this study was to investigate the recycling ability of PP based
composites with rice hulls or kenaf fibers. The fibers were compounded with matrix and
coupling agent by reactive blending, and the compounds were compression molded. The
composites were then kneaded repeatedly two times by melt mixing, followed by
compression molding of new samples, and their properties were compared to those of the
initial composites, produced by the same processing conditions.

This work is a part of ECO-PCCM project 16, in which eco-composites based on
PLA, PHBV and PP reinforced with different natural fibers were investigated aimed for
construction panels and elements for eco-houses 16,17.

EXPERIMENTAL

Materials

Maleated polypropylene (PP) KA 805, produced by Montell, Italy, was used as a
matrix, while the agricultural waste rice hulls was kindly supplied by Rice Institute from
Kocani, R.Macedonia and kenaf fibers, average length 5.1mm and average diameter
21µm, were kindly supplied by Kenaf Eco Fibers Italia S.p.A. (Guastall-Italy). In order to
promote the matrix/fiber compatibilization, different amount of maleic anhydride (MA)
grafted PP has been added during the reactive blending. The kenaf fibers (K) and the rice
hulls (RH) were vacuum-dried for 24h to adjust the moisture content to 1-2 wt% before
they were mixed to produce composites.
Compounding of composite materials

The preparation of the composites has been performed by melt mixing, in a Brabender-like apparatus (Haake Rheocord, New Jersey, USA). During the blending the coupling agent MAPP has been added. First, the polymer and coupling agent were mixed and then the fillers/fibers have been added. The filler/fiber content in all composites was 30 wt%. The kneading temperature was 185°C, and the mixing proceeded 10 minutes with progressively increasing the mixing speed up to 64 rpm. The obtained composites were cut into pellets to perform the sheets for further characterization. In order to investigate recyclability of the systems and possibility of their reuse for the production of a new composite material with appropriate mechanical and thermal properties, the obtained composites were granulated, used for the production of new composite samples. The preparation has been performed under the same conditions as applied for the starting composites. The recycling process was carried out repeatedly twice and thus different composites have been prepared, as shown in table 1.

Compression molding

The samples for mechanical testing were fabricated by compression molding. The pellets obtained after recycling of starting composite systems, were put in molding frame with desired dimensions and have been molded by thermo-compression at $T= 185^\circ$C for 10 minutes, with increasing pressure up to 10 000 pounds. After expiring of the heating
time, the press was cooled by circulating cold water. From all composites the plates with
thickness 3 mm were produced.

**Methods**

The obtained composites have been characterized by flexural tests, thermogravimetry (TGA) and scanning electron microscopy (SEM). The flexural testing was performed according to ASTM D 638-99 standard on a Universal Instron Machine (Model 4301) using unnotched samples. The tests were performed at crosshead speed of 2mm/min, span 48 mm, at room temperature. Each result obtained represents the average of six samples. Morphology of the cryogenically fractured surfaces of composites was analyzed using a JEOL SEM (vacuum Au/Pd alloy deposition of the samples in a Polaron Sputtering apparatus was performed previously). The thermal stability of the samples was measured using a Perkin Elmer Pyris Diamond Thermogravimetric/Different Thermal Analyzer in a nitrogen atmosphere. About 10 mg of each sample was heated from 50 °C to 600 °C at a heating rate of 20°C/min under nitrogen flow (25ml/min).

**RESULTS AND DISCUSSION**

The flexural properties of the recycled composites are shown in Table 2. There are differences between flexural strength of the composites reinforced with rice hulls and kenaf, and generally, the PP/kenaf composites have better mechanical properties. As can be seen, the flexural strength for initial and recycled composites is very similar.
modulus of recycled PP/kenaf composites are higher than for initial ones, however, the
values for rice hulls composites are not changed after recycling.

Sanadi et al.\textsuperscript{18} have studied the possibility of using highly filled agro-based fiber
thermoplastic composites for furniture, automotive and building applications, by using
melt blending technology. The maleated polypropylene was used as a coupling agent
and kenaf fibers as reinforcement. The composites were compression molded and
therefore the fibers were randomly oriented. The obtained flexural strength and flexural
modulus (75 MPa and 6.4 GPa) of the composites were very high and they are superior
to most types of wood particle, low and medium density fiberboards. Comparison of
flexural properties of commercially available formaldehyde-based wood composites\textsuperscript{18}
and 30\% filled kenaf-PP and rice hulls-PP composites investigated in this paper is given
in Table 3. Obviously, the composites investigated in our paper have flexural properties
comparable to conventional formaldehyde-based fiberboards (Table 3).

Fig. 1 shows the properties of the composites and the effect recycling on the
property retention. The flexural strength for PP/RH recycled composites are decreased
for about 10\% after recycling, although the flexural modulus are practically unchanged.
For PP/K composites the flexural strengths are slightly decreased (about 5\%) after the
second recycling, but the flexural modulus are increased for about 20\%.

Serizawa et al.\textsuperscript{19} have studied the recycling properties of PLA/kenaf composite.
The physical properties and molecular weight of PLA were held close to 90\% of that of
the initial PLA/kenaf composites. The reason for the found decrease in the physical
properties was ascribed to the decline in the molecular weight of PLA and the kenaf
fiber’s length caused by repeated kneading.
The mechanical properties of PP/kenaf and PP/RH composites can probably be kept unchanged by the adjustment of the ratio of the initial composite components and the amount of added recycled PP/kenaf and PP/RH composite, which is a subject of our further research.

The overall results for the mechanical properties of eco-composites based on PP reinforced with kenaf fibers or rice hulls, obtained in the framework of ECO-PCCM project, are presented in Fig 2. The increased rice hulls content in the composites not containing CA has resulted in higher flexural modulus (E_{PP/RH(80/20)} =1342 MPa, E_{PP/RH(70/30)} =1451 MPa), however, flexural strength was reduced for about 20%. Obviously, at higher rice hulls content, the interfacial area between the filler and the polymer also increased, which reduced the interfacial bonding between the rice hulls (hydrophilic) and polypropylene (hydrophobic matrix). For irregular shape reinforcements, the strength of the composites decreases due to the reinforcement to support stress transfer from the polymer matrix\(^\text{20}\). Mechanical behavior of the composites has been improved by using compatibilizing agent and by increasing its amount (Fig.2).

Since the industrial manufacturing of the composites proceeds mainly in nonisothermal regime, analysis of the crystallization parameters and crystallization behavior of the polypropylene / rice hulls composites is especially important from a practical point of view. For composites based on semicrystalline polymers, the crystallinity is an important factor that determines the stiffness and fracture behavior of the matrix\(^\text{21}\). The crystallinity depends upon processing parameters, e.g. T_c, cooling rate, nucleation density and annealing time\(^\text{22}\). It should be mentioned, that, as it was found
earlier by DSC analysis, the addition of rice hulls or kenaf fibers to polypropylene, has resulted in an increased crystallization temperature and accelerated crystallization process due to the “nucleating” effect of the filler\textsuperscript{22}. This could advantageously affect the processing of the composites.

Characteristic dynamic-mechanical data of polypropylene and PP/RH composites are shown in Fig. 3. According the obtained results for the ratio of loss and storage modulus (\(\tan \delta = E''/E'\)), PP/RH composites exhibit higher mechanical properties compared to neat polypropylene in range of -50 to 50 °C (at 25°C \(E'_\text{PP} = 3.53\text{GPa}\;
\end{equation}
\(E'_{\text{PP/RH (80/20 wt%)} = 5.37\text{GPa}; E'_{\text{PP/RH (70/30 wt%)} = 4.51\text{GPa}; E''_{\text{PP}} = 0.08\text{GPa}; E''_{\text{PP/RH (80/20 wt%) = 0.18\text{GPa}; E''_{\text{PP/RH (70/30 wt%) = 0.12\text{GPa}}}, while they decreased by increasing the temperature above 50 °C\textsuperscript{23}.

The thermogravimetric (TGA) curves and derivate thermograms (DTG) for PP/RH/CA, PP/RH/CA(x1), PP/RH/CA(x2) and PP/K/CA, PP/K/CA(x1), PP/K/CA(x2) composites are shown in fig 4 and fig 5. Thermal degradation of initial rice hulls-PP composite and recycled rice hulls-PP composites showed a single stage process and occurred at 424,5 °C, 424,9 °C and 402,1°C, respectively, and the curves have the same appearance. A small shoulder can be noticed approximately at 350°C corresponded to thermal degradation of rice hulls. The lignocellulosic materials are chemically active and decompose thermochemically between 150 °C and 500 °C: hemicellulose, mainly between 150 and 350 °C, cellulose between 275 and 350°C, and lignin between 250 and 500 °C (Kim et al., 2004)[20]. The residue at about 550 °C corresponded to the amount of silica (approximately 10%) in the rice hulls, which is determined previously by TGA[23]. Ash in the rice hulls (12%) is mainly composed of silica (~96%), and the
amount and distribution of silica in the rice hulls is likely to be an important factor in
determining the properties of the composite products (Kim et al., 2004)[20]. The mass
loss step of the polypropylene matrix occurs slowly under 430 °C, but after 430 °C this
process occurs rapidly and is completed at 560 °C 23.

In the case of kenaf-PP composites two-stage loss of mass was observed but the
curves have similar behavior. Thermal degradation occurred at 452.8 °C, 434.9 °C and
433.1 °C respectively. The first stage in the temperature range from 350 °C to 400 °C is
characteristic of low molecular weight components, such as hemicelluloses and cellulose
which is corresponded to thermal degradation of kenaf 24.

The recycling process has slightly affected the thermal degradation temperatures
(see Table 4): the recycled PP/RH composites showed a lower degradation temperature
for about 20 °C, which may be attributed to the decrease of molecular weight of PP by
kneading process. Slightly higher degradation temperatures of PP/kenaf composites may
be attributed to better interfacial adhesion, improved as a result of recycling process. It
can be generally said that the increase of molecular weight by cross-linking reaction
between matrix and fibers, or molecular chain–extension of the matrix itself, could
increase the thermal degradation temperature 25-27.

Fig. 6 shows SEM micrographs of the fractured samples of the initial and recycled
composites. In PP/RH composites, a number of holes have been seen in the polymer
matrix region. The clean rice hulls surface indicate that the adhesion between the rice
hulls filler and polymer matrix is weak. Although some holes can be observed in PP
phase of PP/kenaf composites, it can be clearly seen that kenaf fibers are coated with
polymer. Addition of CA into PP has obviously enhanced the interfacial bonding between matrix and kenaf fibers, resulting in higher interfacial adhesion.

CONCLUSION

Based on the results obtained on the effect of recycling of the PP - rice hulls and PP - kenaf composites, on the mechanical properties, thermal stability and morphology of the composites, the following conclusions can be drawn: the flexural properties of the recycled composites are very close to those of the initial ones. In particular, composites with kenaf fibers containing appropriate amount of coupling agent have shown higher mechanical properties after recycling. Thermal stability of the recycled composites is not changed significantly. SEM analyses have revealed that in all PP/kenaf composites better effect of enhancing polymer/fiber interactions is achieved. PP composites, especially those reinforced with kenaf fibers, represent a good potential for utilization after recycling. The obtained results for composite’s flexural strength and modulus produced from the recycled samples, both with kenaf fibers or rice hulls, are comparable to conventional formaldehyde wood medium density fiberboards.

Acknowledgments

This work was supported by the grant of EU FP6-INCO-WBC program (INCO-CT-2004-509185)
References


16. ECO-PCCM, FP6-INCO-CT-2004-509185


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Figure 5. TGA and DTG curves of PP/K/CA, PP/K/CA (x1) and PP/K/CA (x2)

Figure 6. SEM micrographs of interface between matrix and fibers in: PP/RH/CA composite (A), PP/RH/CA (x1) composite (B), PP/RH/CA (x2) composite (C), PP/K/CA composite (D), PP/K/CA (x1) composite (E) and PP/K/CA (x2) composite (F)
### TABLE 1

Assignation of the composites produced from recycled systems

<table>
<thead>
<tr>
<th>Composites</th>
<th>Matrix</th>
<th>Fiber/Filler</th>
</tr>
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<tbody>
<tr>
<td>PP/RH/CA*</td>
<td>PP</td>
<td>Rice Hulls</td>
</tr>
<tr>
<td>PP/RH/CA (x1) recycled one time</td>
<td>PP</td>
<td>Rice Hulls</td>
</tr>
<tr>
<td>PP/RH/CA (x2) recycled two times</td>
<td>PP</td>
<td>Rice Hulls</td>
</tr>
<tr>
<td>PP/K/CA</td>
<td>PP</td>
<td>Kenaf fibers</td>
</tr>
<tr>
<td>PP/K/CA (x1) recycled one time</td>
<td>PP</td>
<td>Kenaf fibers</td>
</tr>
<tr>
<td>PP/K/CA (x2) recycled two times</td>
<td>PP</td>
<td>Kenaf fibers</td>
</tr>
</tbody>
</table>

* CA = coupling agent

### TABLE 2

The results of flexural test of initial and recycled composites

<table>
<thead>
<tr>
<th></th>
<th>Stress at peak, MPa</th>
<th>Standard deviation</th>
<th>Modulus, GPa</th>
<th>Standard deviation</th>
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<tbody>
<tr>
<td>PP/RH/CA</td>
<td>42.6</td>
<td>3.4</td>
<td>1.941</td>
<td>0.082</td>
</tr>
<tr>
<td>PP/RH/CA (x1)</td>
<td>44.8</td>
<td>3.0</td>
<td>1.884</td>
<td>0.163</td>
</tr>
<tr>
<td>PP/RH/CA (x2)</td>
<td>38.5</td>
<td>7.2</td>
<td>1.910</td>
<td>0.059</td>
</tr>
<tr>
<td>PP/K/CA</td>
<td>51.3</td>
<td>4.8</td>
<td>2.106</td>
<td>0.068</td>
</tr>
<tr>
<td>PP/K/CA (x1)</td>
<td>51.8</td>
<td>9.1</td>
<td>2.531</td>
<td>0.179</td>
</tr>
<tr>
<td>PP/K/CA (x2)</td>
<td>48.7</td>
<td>4.7</td>
<td>2.575</td>
<td>0.080</td>
</tr>
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TABLE 3

Comparison of flexural properties of commercially available formaldehyde-based wood composites\textsuperscript{18} and 30\% filled kenaf-PP and rice hulls–PP composites investigated in this paper

<table>
<thead>
<tr>
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<th>Strength range (MPa)</th>
<th></th>
<th>Modulus range (GPa)</th>
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<tbody>
<tr>
<td></td>
<td>low</td>
<td>high</td>
<td>low</td>
<td>high</td>
</tr>
<tr>
<td>High-density fiberboards\textsuperscript{11} (commercial)</td>
<td>38</td>
<td>69</td>
<td>4,48</td>
<td>7,58</td>
</tr>
<tr>
<td>Medium-density fiberboards\textsuperscript{11} (commercial)</td>
<td>13,1</td>
<td>41,4</td>
<td>2,24</td>
<td>4,83</td>
</tr>
<tr>
<td>30% kenaf - PP</td>
<td>51,3 (4,8)</td>
<td>2,11 (0,068)\textsuperscript{a}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30% rice hulls - PP</td>
<td>42,6 (3,4)</td>
<td>1,94 (0,082)\textsuperscript{a}</td>
<td></td>
<td></td>
</tr>
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</table>

\textsuperscript{a} Standard deviations are in brackets for the kenaf-PP and rice hull-PP composites.

TABLE 4

Weight residual for initial and recycled composites determined by TGA

<table>
<thead>
<tr>
<th></th>
<th>$Td$ [$^\circ$C] (weight residual)</th>
<th>$Td$ [$^\circ$C] (weight residual)</th>
<th>$Td$ [$^\circ$C] (weight residual)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>~ 90 %</td>
<td>~ 50 %</td>
<td>~ 10 %</td>
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<tr>
<td>PP/RH/CA</td>
<td>344,43 (89,74 %)</td>
<td>411,21 (49,74 %)</td>
<td>452,17 (9,74 %)</td>
</tr>
<tr>
<td>PP/RH/CA x1</td>
<td>336,66 (90,91 %)</td>
<td>409,93 (50,91 %)</td>
<td>471,04 (10,91 %)</td>
</tr>
<tr>
<td>PP/RH/CA x2</td>
<td>322,63 (86,99 %)</td>
<td>389,01 (46,99 %)</td>
<td>455,28 (11,99 %)</td>
</tr>
<tr>
<td>PP/K/CA</td>
<td>340,57 (90,94 %)</td>
<td>408,94 (50,94 %)</td>
<td>441,96 (10,94 %)</td>
</tr>
<tr>
<td>PP/K/CA x1</td>
<td>343,10 (91,11 %)</td>
<td>413,71 (51,11 %)</td>
<td>447,01 (11,11 %)</td>
</tr>
<tr>
<td>PP/K/CA x2</td>
<td>344,28 (91,02 %)</td>
<td>414,94 (51,02 %)</td>
<td>448,84 (11,02 %)</td>
</tr>
</tbody>
</table>
Figure 1.

Recycled PP/RS composites

Recycled PP/Kenaf composites

Figure 2.

Recycled PP/Kenaf composites

Property retention, %

Flexural Strength
Flexural Modulus

Flexural modulus [MPa]
Stress at peak [MPa]
Figure 3.
Figure 4.
Figure 5.