

Polypropylene-based Eco-composites Filled with Agricultural Rice Hulls Waste

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In this work the properties of rice-hull-filled polypropylene (PP) composites were investigated with the purpose of enhancing adhesion between the polymer and the filler through the addition of $w = 5\%$ PP-grafted-MA (CA). Composites containing $w = 20$ and 30% rice hulls (RH), as well as composites with a certain amount of PP matrix substituted with a coupling agent, were prepared by extrusion and compression moulding. The composites' mechanical properties were investigated through tensile and fracture tests at low and high strain rate, using the concept of linear elastic fracture mechanics. Introduction of rice hulls in the PP matrix resulted in a decreased stress at peak, together with increase of composites tensile modulus ($E_{PP} = 1013$ MPa, $E_{PP/RH} (\zeta = 0.70:0.30) = 1690$ MPa) and modulus in flexure. Introduction of $w = 5\%$ PP-g-MA caused 6% and 12% improvement in the composite tensile strength, respectively for the PP composites with $w = 20$ and 30% rice hulls. Modulus in flexure for the composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$) reached $E_f = 1646$ MPa, which was an improvement of 52% when compared to pure polypropylene. K_c and G_c values were determined for PP and PP-based composites. Thermal stability of PP was slightly improved by adding rice hulls.

Key words:

PP, rice hulls, composite, mechanical properties, thermal stability

Introduction

Growing environmental awareness together with restrictive environmental policies have resulted in a significantly increased interest for materials reinforced with natural fibres/fillers that would be eco-friendly and cost-effective. Environmental regulations and criteria for cleaner and safer environment are increasing the pressure on manufacturers of materials and end-products to consider the environmental impact of their products at all stages of their life cycle. For these reasons, some industries were forced to seek out new eco-materials capable of substituting traditional glass or carbon fibre reinforced composites. Renewable agricultural waste materials with recyclable thermoplastic polymers provide an attractive eco-friendly quality as well as sustainability to the resulting natural fibre/filler reinforced composites. Advantages of natural fibres/fillers over traditional ones are: low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to processing equipment), enhanced energy recovery, CO₂ neutral when burned, biodegradability. Because of

their hollow and cellular nature, natural fibres perform as acoustic and thermal insulators, and exhibit reduced bulk density.^{1,2} As an oil-based product PP could not be classified as a biodegradable polymer, but by introducing thermo-sensitive catalysts to increase its degradability, PP takes an important place in eco-composite materials.³ Amongst eco-compatible polymer composites, special attention has been given to polypropylene composites due to their added advantage of recyclability.⁴ Mohanty *et al.* have demonstrated that the PP composites reinforced with natural fibres have the potential to replace glass/PP composites.⁵ It has been also reported that PP can be effectively modified by maleic anhydride, which provides polar interactions and covalently links PP to the hydroxyl groups of the cellulose material.⁶

Yang *et al.* have studied the possibility of using lignocellulosic rice husk flour as reinforcing filler in polyolefin composites.⁷ They have designed rice husk flour/polypropylene composites with four levels of filler loading ($w = 10, 20, 30$ and 40%). The results of the tensile test performed at six levels of temperatures and various crosshead speeds revealed that tensile strength of the composites slightly decreased as the filler loading increased. The tensile modulus improved with increasing the filler content. Notched and unnotched Izod impact strengths

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were lowered by adding rice husk flour. The composite became brittle at higher crosshead speed, and showed plastic deformation at higher test temperatures. Kim *et al.* analysed the thermal degradation and thermal stability of rice husk-flour-filled polyolefin composites.⁸ They discovered that as the rice-husk flour content increased, the thermal stability of the composites decreased and the ash content increased as a logical consequence of lower thermal stability of the rice husk flour. In order to enhance the performance of rice-husk-filled polyolefins, Panthapulakkai *et al.*⁹ studied the effect of coupling agents on rice-husk-filled polyolefin extruded profiles. They analyzed four different coupling agents based on ethylene-acrylic ester-maleic anhydride terpolymers, and ethylene-acrylic ester-glycidyl methacrylate terpolymers. The results showed that these coupling agents significantly improved the tensile and flexural strength of the composites. The extent of the coupling effect depended on the nature of the interface formed. Incorporation of coupling agents enhanced the resistance to thermal deformation and the water absorption properties of the composite, whereas it reduced the extrusion rate. Toro *et al.*¹⁰ studied the compatibilizing effect of polypropylene grafted with monomethyl itaconate (PP-g-MMI) in PP/rice-husk composites. It was shown that in the presence of PP-g-MMI as compatibilizer, the tensile modulus and water absorption of the composite were improved. Mohd Ishak *et al.* studied the effect of the filler volume fraction on the tensile behaviour of injection-moulded rice-husk-filled polypropylene composites.¹¹ Incorporation of rice husk into the PP matrix led to a significant improvement in the tensile modulus and a moderate improvement in the tensile strength. Elongation at break and energy at break, on the other hand, decreased drastically with the incorporation of the filler. Premalal *et al.*¹² compounded rice husk filler with polypropylene in a Bradender plasticorder internal mixer at 180 °C and 50 rpm in order to obtain composites that contain $w = 0\text{--}60\%$ of filler at 15 % intervals. In terms of the composite's mechanical properties, Young's modulus and flexural modulus increased, whereas yield strength and elongation at break decreased with the increase in filler loading. Prachayawarakorn and Yaembunying found that tensile, flexural and impact properties as well as percent water absorption of the rice-husk-filled polypropylene dropped only slightly upon the recycling process.¹³ Applying the method used in the wood-based panel industry, composite insulation boards were produced with rice straw.¹⁴ Composite boards with specific gravity of 0.8 possess a slightly better bending modulus than wood particle board (as a control board) with a rice straw content of $w = 10\%$, and show no differ-

ences from control boards with a $w = 20\%$ rice straw level.

The objective of the present work was to find an adequate use for agricultural rice hulls waste as a cheap, widely available, biodegradable eco-filler for PP. Particular attention was given to the improvement of interfacial adhesion using a coupling agent prepared through chemical modification of the matrix. Experiments were performed in order to determine the mechanical properties, morphology and thermal stability of the prepared rice hulls/PP composites.

This work was developed in the frame of FP6-INCO-WBC program supported by the EU (ECO-PCCM, INCO-CT-2004-509185). PLA, PHBV and PP based eco-composites, reinforced with different natural fibres/fillers are aimed for eco-houses construction panels and different elements. Some of our previous results on eco-composite materials have been published elsewhere.^{15–18}

Experimental

Polypropylene used as a matrix in the composites is a product of Montell, whilst the waste rice hulls (RH) used as filler were kindly supplied by the Rice Institute of Kočani, R. Macedonia. Maleated polypropylene with 5 % grafted maleic anhydride (PP-g-MA), a Questrow KA 805 product by Montell, was used as a coupling agent (CA).

Composites with $w = 20$ and 30 % rice hulls loading, as well as corresponding ones where part of the PP matrix was replaced with PP-g-MA, PP/RH/CA ($\xi = 0.75:0.20:0.05$) and PP/RH/CA ($\xi = 0.65:0.30:0.05$), were prepared by extrusion in HAAKE Rheocord at $T = 175\text{ °C}$ using a defined combination of mixing time and screws rotation speed (3 min with 8 rpm, 4 min with 16 rpm and 3 min with 32 rpm). Prior to extrusion, the ingredients were mixed and then added to the extruder heated to predefined temperature. Concerning the composites prepared with CA, a mixture of pure and modified PP was initially prepared during 3 min with 8 rpm, and then the rice hulls were added. Before the extrusion, the rice hulls were vacuum-dried for 24 h. Composite plates with $\delta = 1$ and 3 mm thickness, necessary for purchasing test samples, were prepared by compression molding in CARVER press at $T = 180\text{ °C}$ and $p = 50\text{--}150$ bar.

Prepared composites were characterized by tensile, flexural and impact tests. Tensile tests were conducted according to ASTM D 638-99, using an Instron Machine (model 4505) at a crosshead speed of 10 mm min^{-1} and room temperature. Three-point-bending sharply notched specimens were used to perform fracture tests at room temperature, at low

and high strain rate. Same mechanical tester Instron 4505 was used for the low strain rate measurements on parallelepiped samples ($60 \times 6 \times 3$ mm). Flexural elastic modulus measurements were performed with the same apparatus and the same testing conditions as above, using unnotched specimens. The high strain rate tests were realized on parallelepiped samples ($60 \times 10 \times 3$ mm), using Ceast 6545 equipped with a DAS 4000 and Hammer M197, at an impact speed of 0.99 m s^{-1} . The fracture data were analysed according to the concept of linear elastic fracture mechanics.¹⁹ The critical stress intensity factor, K_{Ic} , was calculated using the equation: $K_{Ic} = \sigma Y \sqrt{a}$, where σ is the nominal stress at the onset of crack propagation, a is the initial crack length, and Y is a calibration factor depending upon the specimen geometry. For three-point-bending specimens, Y is given by Brown and Srawley.²⁰ For the determination of critical strain energy release rate, G_c , following equation was used: $G_c = U (\delta b \Phi)^{-1}$, where U is the fracture energy, δ and b are the thickness and the width of the specimen, respectively, and Φ is a calibration factor which depends on the length of the notch and the size of the sample. Values for Φ were taken from Plati and Williams.²¹ Each value obtained represents the average of five tested samples.

Morphology of composites fracture surfaces were analysed using a JEOL SEM. Previously, vacuum Au/Pd alloy deposition on the samples was carried out in a Polaron Sputtering apparatus.

Thermal stability of the prepared composites was examined using a Perkin Elmer Pyris Diamond TG/DTA. Samples were heated from $T = 40$ to $800 \text{ }^\circ\text{C}$ with $20 \text{ }^\circ\text{C min}^{-1}$ heating rate in a nitrogen atmosphere.

Results and discussion

Results from the tensile tests performed on PP and PP-based composites are presented in Table 1. Loading $w = 20 \%$ rice hulls in the PP matrix causes a 35 % drop in the stress at peak and significant decrease in the strain at break, compared to the corresponding values for pure PP. By further increase in the amount of filler ($w = 30 \%$ rice hulls) even lower stress at peak values were detected. The decrease of tensile strength is related to the increase of fragility of the composites, as it is clearly seen by the decrease of elongation at break. The reason for this outcome is that by increasing the rice hulls content we increase the interfacial area between the filler and the matrix. Bearing in mind the rice hulls hydrophilic and polypropylene matrix hydrophobic character, we can say that composites strength decreases because of a lack of adequate interfacial bonding. Because of the weak PP/RH interface, introduction of rice hulls in the polymer matrix causes weak spots in the structure, where cracking can easily progress. Also, for irregular shape reinforcements, the strength of the composites decreases due to the inability of the reinforcement to support stress transfer from the polymer matrix.⁷ In contrary to the strength of examined composites, the increased rice hulls content resulted in a higher tensile modulus ($E_{PP} = 1013 \text{ MPa}$, $E_{PP/RH} (\zeta = 0.80:0.20) = 1548 \text{ MPa}$, $E_{PP/RH} (\zeta = 0.70:0.30) = 1690 \text{ MPa}$). This behaviour of rice-hulls-filled PP composites is in accordance with the literature data ascribed to similar systems.^{7,11,12}

Introduction of $w = 5 \%$ PP-g-MA, as a coupling agent in the composites formulation, caused a 6 % and 12 % improvement in the strength of PP

Table 1 – Mechanical properties of PP-based eco-composites (tensile and flexural test)

Sample ID	Tensile test			Flexural test	
	stress at peak, σ/MPa	strain at break, %	Young's modulus, E/MPa	stress at peak, σ/MPa	modulus in flexure, E_f/MPa
PP	33.3	621.1	1013	51.5	1081
PP/RH ($\zeta = 0.80:0.20$)	21.5 (−35.4 %)*	4.0	1548 (+52.8 %)*	41.4 (−19.6 %)*	1342 (+24.1 %)*
PP/RH ($\zeta = 0.70:0.30$)	18.6 (−44.1 %)	3.5	1690 (+66.8 %)	31.4 (−39.1 %)	1451 (+34.2 %)
PP/RH/CA ($\zeta = 0.75:0.20:0.05$)	23.6 (−29.1 %)	3.7	1574 (+55.4 %)	36.7 (−28.7 %)	1389 (+28.5 %)
PP/RH/CA ($\zeta = 0.65:0.30:0.05$)	22.7 (−31.8 %)	3.8	1779 (+75.6 %)	41.6 (−19.2 %)	1646 (+52.3 %)

*percentage changes of the corresponding property, compared to the value for pure PP

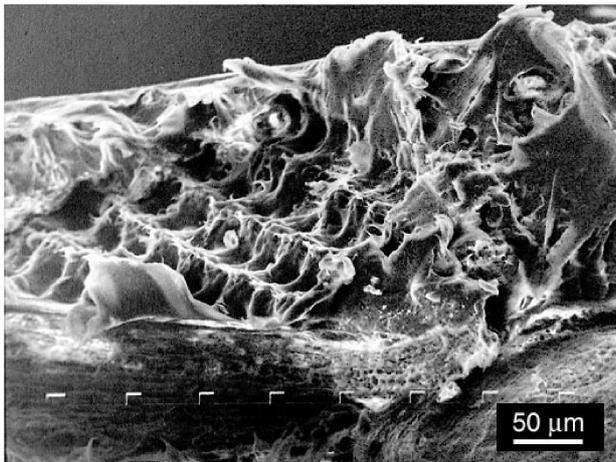
composites with $w = 20$ and 30 % rice hulls content, obviously as a result of enhanced adhesion. Young's modulus of PP composite with $w = 20$ % rice hulls was slightly improved by the presence of a coupling agent, while the same amount of added maleated polypropylene improved the tensile modulus of PP composite with $w = 30$ % rice hulls from $E_{PP/RH} (\zeta = 0.70:0.30) = 1690$ MPa to $E_{PP/RH/CA} (\zeta = 0.65:0.30:0.05) = 1779$ MPa. SEM analysis was carried out on fractured samples PP/RH ($\zeta = 0.80:0.20$) and PP/RH/CA ($\zeta = 0.75:0.20:0.05$), as presented in Fig. 1. The micrographs confirm the interface adhesion enhancement between the filler and the matrix in the presence of PP-g-MA, evident from the present rice hulls pulling out phenomena.

The results from the composites behaviour during flexural test are also presented in Table 1. Similar to the results of the tensile test, the introduction of rice hulls into the PP matrix produced a drop in the stress at peak of around 20 % for composite with $w = 20$ % rice hulls, and 39 % for composite with $w = 30$ % rice hulls, and an increase in their

modulus in flexure, reaching 1342 MPa and 1451 MPa respectively for polypropylene composite PP/RH ($\zeta = 0.80:0.20$) and PP/RH ($\zeta = 0.70:0.30$). Introduction of a coupling agent into the composite with $w = 30$ % rice hulls resulted in improved strength ($\sigma_{PP/RH} (\zeta = 0.70:0.30) = 31.4$ MPa, $\sigma_{PP/RH/CA} (\zeta = 0.65:0.30:0.05) = 41.6$ MPa), while the flexural modulus of the composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$) reached 1646 MPa, which is 52 % higher compared to pure polypropylene ($E_f = 1081$ MPa). However, introduction of a coupling agent caused only a minor change in the modulus in flexure for PP/RH composites with mass fraction $w = 20$ % filler.

The values of toughness parameters: critical stress intensity factor, K_{Ic} , and critical strain energy release rate, G_{Ic} , are presented in Table 2. As can be seen, K_{Ic} is equal for PP and PP composites with $w = 30$ % rice hulls: PP/RH ($\zeta = 0.70:0.30$) and PP/RH/CA ($\zeta = 0.65:0.30:0.05$). Composites G_{Ic} value is slightly increased when compared to the pure matrix. Higher K_{Ic} is exhibited by PP composites with $w = 20$ % rice hulls, with an insignificant change while substituting part of the composite matrix with a coupling agent. It has been observed that the maleated compatibilizer mainly influences the crack initiation stage rather than the crack propagation process, however further investigation is needed to clarify the mechanism of failure of the composites.

(a)



(b)

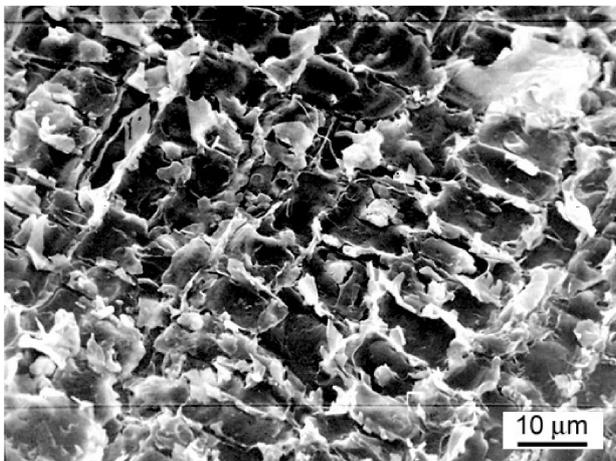


Fig. 1 – SEM micrographs of the fracture surface for composites: (a) without coupling agent, PP/RH ($\zeta = 0.80:0.20$) and (b) with $w = 5$ % coupling agent, PP/RH/CA ($\zeta = 0.75:0.20:0.05$)

Table 2 – Toughness parameters for PP-based eco-composites (impact test)

Sample ID	Impact test	
	$K_{Ic}/\text{MN m}^{-3/2}$	$G_{Ic}/\text{kJ mm}^{-2}$
PP	1.90	3.03
PP/RH ($\zeta = 0.80:0.20$)	2.08	4.00
PP/RH ($\zeta = 0.70:0.30$)	1.90	3.78
PP/RH/CA ($\zeta = 0.75:0.20:0.05$)	2.05	3.17
PP/RH/CA ($\zeta = 0.65:0.30:0.05$)	1.90	3.11

Thermogravimetric curves of PP, rice hulls and their composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$) are given in Fig. 2, and corresponding thermal analyses results in Tables 3 and 4. As can be seen, rice hulls go through a two-step mass-loss process: below 110 °C mass loss resulted from the evaporation of absorbed moisture, and in the temperature range between $T = 170$ and 500 °C – from the degradation of rice hulls three major constituents (45 % amid $T = 200$ and 400 °C). The lignocellulosic materials are chemically active and decompose thermochemically between $T = 150$ and 500 °C: hemicellulose mainly between $T = 150$ and 350 °C, cellulose be-

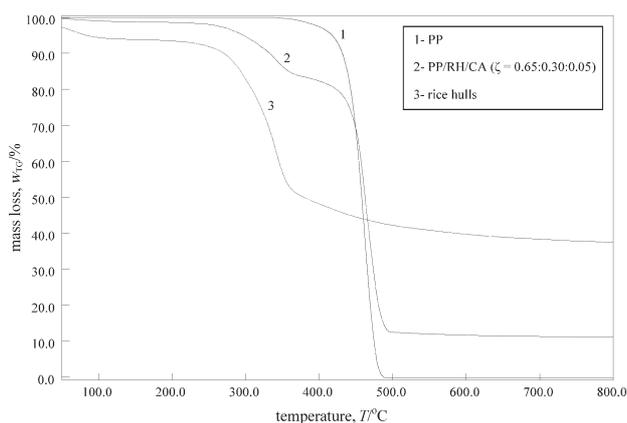


Fig. 2 – Thermogravimetric curves of PP, rice hulls and PP/RH/CA ($\zeta = 0.65:0.30:0.05$): mass loss ($w_{TG}/\%$) vs. temperature ($T/^\circ\text{C}$)

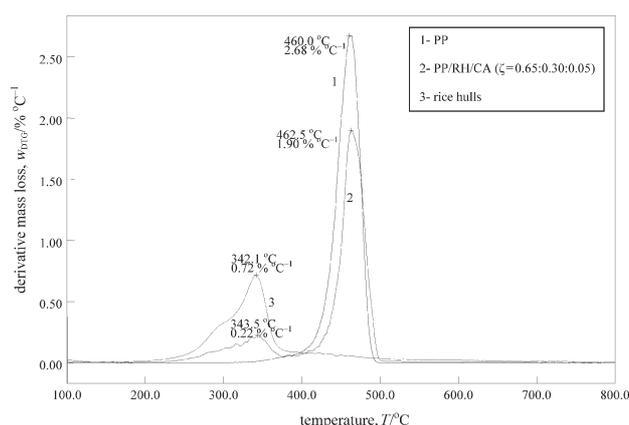


Fig. 3 – Derivative thermogravimetric curves of PP, rice hulls and PP/RH/CA ($\zeta = 0.65:0.30:0.05$): derivative mass loss ($w_{DTG}/\% \text{ } ^\circ\text{C}^{-1}$) vs. temperature ($T/^\circ\text{C}$)

tween $T = 275$ and 350 °C, and lignin between $T = 250$ and 500 °C.⁸ Polypropylene suffers complete degradation between $T = 335$ and 488 °C. Thermogravimetric curve of PP/rice-hulls-based composite exhibits two-step degradation: between $T = 218$ and 373 °C, originating mostly from the rice hulls constituents, and the second up to $T = 507$ °C, originating from both the PP matrix and the rice hulls constituents. Above temperature of $T = 450$ °C, composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$) shows better thermal stability than pure PP, i.e. at 475 °C mass loss of pure PP is 91.1 %, and for PP/RH/CA ($\zeta = 0.65:0.30:0.05$) it is 73 %.

As can be seen from the derivative thermograms given in Fig. 3 and results in Table 4, maximum mass loss for PP (2.68 % $^\circ\text{C}^{-1}$) is reached at 460 °C, and rice hulls mass loss is uppermost (0.72 % $^\circ\text{C}^{-1}$) at 342.1 °C. Derivative thermogravimetric curve of composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$) shows two peaks: the first at temperature of 343.5 °C (mass loss of 0.22 % $^\circ\text{C}^{-1}$), and the second at temperature of 462.5 °C (mass loss of 1.90 % $^\circ\text{C}^{-1}$). Both temperatures of maximum mass loss correspond to the temperatures of maximum mass loss already seen in neat composite

Table 3 – Thermal stability of PP, rice hulls and composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$)

$T/^\circ\text{C}$	mass loss, w/%		
	rice hulls	PP/RH/CA ($\zeta = 0.65:0.30:0.05$)	neat PP
50	2.7	0.4	0
100	5.6	1.0	0
280	11.6	3.4	0
310	20.7	6.6	0
340	35.9	11.4	0.1
370	49.1	16.1	0.8
400	51.8	17.7	2.6
430	54.2	21.4	9.4
460	56.1	44.4	55.2
490	57.4	86.3	100
800	62.6	88.8	100

Table 4 – Thermal analysis results: temperature of initial decomposition (T_i), temperature of maximum decomposition rate (T_{max}), mass loss for steps of degradation (w/%) and residual mass at 800 °C for neat PP, rice hulls and composite PP/RH/CA ($\zeta = 0.65:0.30:0.05$)

Sample ID	TGA/DTG test (in nitrogen)						
	$T_i/^\circ\text{C}$		$T_{max}/^\circ\text{C}$		mass loss, w/%		residual mass at 800 °C, w/%
	I step	II step	I step	II step	I step	II step	
PP	335.3	/	460.0	/	100	/	0
rice hulls	171.1	/	342.1	/	45.5	/	37.4
PP/RH/CA ($\zeta = 0.65:0.30:0.05$)	217.8	373.0	343.5	462.5	14.7	71.4	11.2

constituents, but with minor displacement toward higher temperatures.

It is interesting to point out that PP/RH/CA composites can be recycled several times, and, as a result of homogenisation taking place during extrusion process as well as increased l/d ratio of the filler, the mechanical properties of recycled products are improved.²²

Conclusion

Results from the examination of PP/rice hulls eco-composites mechanical properties revealed that rice hulls could be used rather as a biodegradable, eco-friendly filler to minimize environmental pollution and the price of the final product than as a reinforcement of the PP matrix. The stiffness of the composites increased with the content of rice hulls, while the strength decreased. The decrease of tensile strength is related to the increase of fragility of the composite, as it is clearly seen by the decrease of strain at break. Introduction of $w = 5\%$ maleated polypropylene improves the strength of PP-based composites with $w = 30\%$ rice hulls, but the level of improvement is still beneath the exhibited by pure PP. Considering the toughness, better results were displayed by the composite with $w = 20\%$ loaded rice hulls. Thermal stability of PP/rice hulls eco-composites was insignificantly higher when compared to neat PP, as determined by TG analysis. Our further analysis involves investigation of the influence of RH dimensions on overall PP/RH/CA composite properties.

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List of symbols

a	– initial crack length, mm
b	– width, mm
E	– tensile modulus, MPa
G_c	– critical strain energy release rate, KJ mm ⁻²
K_c	– critical stress intensity factor, MN m ^{-3/2}
Y	– calibration factor (related to K_c)
U	– fracture energy, J
w	– mass fraction, %
p	– pressure, bar
δ	– thickness, mm
ζ	– mass ratio, $w_{PP}:w_{RH}:w_{AC}$
T	– temperature, °C
σ	– nominal stress at the onset of crack propagation, MPa
Φ	– calibration factor (related to G_c)

Abbreviations

CA	– coupling agent
DAS	– data acquisition system
DTG	– derivative thermogravimetry
PHBV	– poly(hydroxybutyrate-co-valerate)
PLA	– poly(lactic acid)
PP	– polypropylene
PP-g-MA	– polypropylene grafted with maleic anhydride
PP-g-MMI	– polypropylene grafted with monomethyl itaconate
RH	– rice hulls
TG	– thermogravimetry

References

1. Khan, M. A., Hassan, M. M., Brown, T. K., *Compos. A* **36** (2005) 71.
2. Lee, S. G., Choi, S.-S., Park, W. H., Cho, D., *Macromol. Symp.* **197** (2003) 89.
3. Bogoeva-Gaceva, G., Avella, M., Malinconico, M., Buzarovska, A., Grozdanov, A., Gentile, G., Errico, M. E., *Polym. Compos.* **28** (2007) 98.
4. Yang, H.-S., Kim, D.-J., Lee, J.-K., Kim, H.-J., Jeon, J.-Y., Kang, C.-W., *Bioresour. Technol.* **95** (2004) 61.
5. Mohanty, A. K., Drzal, L. T., Misra, M., *J. Adhes. Sci. Technol.* **16** (2002) 999.
6. Keener, T. J., Stuart, R. K., Brown, T. K., *Compos. A* **35** (2004) 357.
7. Yang, H.-S., Kim, H.-J., Son, J., Park, H.-J., Lee, B.-J., Hwang, T.-S., *Compos. Struct.* **63** (2004) 305.
8. Kim, H.-S., Yang, H.-S., Kim, H.-J., Park, H.-J., *J. Therm. Anal. Calorim.* **76** (2004) 395.
9. Panthapulakkai, S., Sain, M., Law, S., *Polym. Int.* **54** (2005) 137.
10. Toro, P., Quijada, R., Murillo, O., Yazdani-Pedram, M., *Polym. Int.* **54** (2005) 730.
11. Mohd Ishak, Z. A., Yow, B. N., Ng, B. L., Khalil, H. P. S. A., Rozman, H. D., *J. Appl. Polym. Sci.* **81** (2001) 742.
12. Premalal, Hattotuwa, G. B., Ismail, H., Baharin, A., *Polym. Test.* **21** (2002) 833.
13. Prachayawarakorn, J., Yaembunying, N., *J. Sci. Technol.* **27** (2005) 343.
14. Yang, H.-S., Kim, D.-J., Kim, H.-J., *Bioresour. Technol.* **86** (2003) 117.
15. Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., *J. Appl. Polym. Sci.* **102** (2006) 804.
16. Grozdanov, A., Buzarovska, A., Bogoeva-Gaceva, G., Avella, M., Errico, M. E., Gentile, G., *Polym. Eng. Sci.* **47** (2007) 745.
17. Avella, M., Bogoeva-Gaceva, G., Buzarovska, A., Errico, M. E., Gentile, G., Grozdanov, A., *J. Appl. Polym. Sci.* **104** (2007) 3194.
18. Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., Gentile, G., Errico, M. E., *J. Mater. Sci.* **42** (2007) 6501.
19. Williams, J. G., *Fracture Mechanics of Polymers*, John Wiley and Sons, New York, 1984.
20. Brown, W. F., Srawley, J., *ASTM Spec. Tech. Publ.* **410** (1966) 13.
21. Plati, E., Williams, J. G., *Polym. Eng. Sci.* **15** (1975) 470.
22. <http://intm.bg.ac.yu/eco-pccm>