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Biocomposites Based on Poly (Lactic Acid) and Their Recyclability

Vineta Srebrenkoska[1]* and Gordana Bogoeva Gaceva[2]
[1]Faculty of Technology, Goce Delčev University, "Krste Misirkov" Štip, Republic of Macedonia
[2]Faculty of Technology and Metallurgy, St.Cyril & Methodius University, MK-1000 Skopje, Republic of Macedonia

Abstract: Biodegradable poly (lactic acid) (PLA) based biocomposites reinforced with rice hulls were prepared by compression molding and their properties were compared to those of commonly used thermoplastic based-polymer, polypropylene (PP) containing the same reinforcements.

Rice hulls from rice processing plants represent renewable sources that could be utilized for production of new class of eco-materials. In this study, rice-hulls-filled poly (lactic acid) (PLA) biocomposites were prepared through addition of 5 wt. % PLA-grafted-MA (CA) for enhancement of adhesion between polymer matrix and natural filler. The composites containing 30% wt. rice hulls (RH) were prepared and the possibility of recycling and reuse of these biocomposites were investigated. For all biocomposites, the mechanical and thermal properties were analyzed and compared to those of commonly used thermoplastic based-polymer, polypropylene (PP) containing the same reinforcement. Thermal stability of neat biocomposites and of the new composites produced from recycled ones was practically unchanged. Utilization of the mixture obtained after the thermal-mechanical recycling of the whole biocomposite has resulted into composite with slightly increased flexural modulus and decreased flexural strength.

The obtained results have shown that rice-hull-filled poly(lactic acid) biocomposites could be recycled and utilized for production of new eco-materials with acceptable thermal and mechanical properties. Namely, the results for flexural strength and modulus of the recycled biocomposite samples are comparable to those of conventional formaldehyde wood medium density fiberboards used as construction elements for indoor applications.

Keywords: biocomposites, natural fiber-reinforced composites, poly(lactic acid), polypropylene, rice hulls, kenaf fibers, compression moulding.

Introduction

Recently the use of renewable resources for the production of polymer-based materials has attracted a growing attention, both in academia and industry, as a result of the increasing demand of environmental friendly materials [1]. The development of eco-composites (based on recyclable thermoplastics) as well as biocomposites (based on biodegradable polymers) and natural fibers as reinforcement has accelerated rapidly, primarily due to improvements in process technology and economic factors. These materials could allow complete degradation in soil or by composting process and do not emit any toxic or noxious component [1, 2]. Many investigations have been made on the potential use of different natural fibers as reinforcements for eco-composites (composite material with environmental and ecological advantages over conventional composites) and the results have shown that they exhibit good stiffness and promising properties [1, 2, 3, 4, 5, 6, 7, 8]. Natural fibers from renewable sources represent environmentally friendly alternative to conventional reinforcing fibers (glass, carbon, kevlar). Advantages of natural fibers over traditional ones are low cost, high toughness, low density, good specific strength properties, reduced tool wear (nonabrasive to

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*   *Correspondence to Vineta Srebrenkoska, Faculty of Technology, Goce Delčev University, "Krste Misirkov" b.b.* P. O. Box *201, 2000 Štip, Republic of Macedonia, phone: +389 32 550 000, fax: +389 32 390 700*
e-mail: Vineta Srebrenkoska (vineta.srebrenkoska@ugd.edu.mk)

processing equipment), enhanced energy recovery, CO_2 neutral when burned, biodegradability. The main drawback of natural fibers is their hydrophilic nature, that prevents their compatibility with hydrophobic polymers used as matrices for the production of composite materials, and therefore, different kinds of coupling agents have been used for improving interfacial adhesion between polymer matrices and natural fibers in order to enhance the physical and mechanical properties of the final products [9].

Depending on their performance, when they are included in polymer matrices, lignocellulosic fibers can be classified into three categories: wood flour particulates, which increase the tensile and flexural modulus of the composites, fibers (higher aspect ratio), that contribute to the improvement of the composite modulus and strength when suitable additives are used to optimize the stress transfer between the matrix and the fibers, and long natural fibers, with the highest efficiency among the lignocellulosic reinforcements. The most efficient natural fibers have been considered those showing high cellulose content coupled with a low microfibril angle, resulting in the best composite mechanical properties [10, 11].

On the other hand, the development of wholly biodegradable polymers and polymeric materials can play a fundamental role in helping to solve waste disposal problems [12]. Among biodegradable plastics, poly (lactic acid) (PLA), produced on a large scale from fermentation of corn starch to lactic acid and subsequent chemical polymerization, exhibit excellent mechanical properties, good heat resistance coupled with moldability, and recyclability. This polymer is characterized by its transparency, humidity and oil resistance. Pure PLA can degrade to carbon dioxide, water and methane in the environment over a period of several months up to 2 years, compared to other petroleum plastics needing longer periods [3, 4, 6]. The mechanical properties of PLA have been extensively studied as a biomaterial in medicine, but only recently it has been used as a polymer matrix in eco-composites [7], although its application is still limited by its relatively high price when compared to some other biodegradable polymers. Kenaf fibers have been already tested as natural reinforcement for polyolefines, but there is an even growing interest on the preparation of biocomposites [13, 14]. Xia et al. [9] investigated the use of PLA resin reinforced with kenaf fibers for the interior parts of its Prins hybrid car. In 2002 Cargill-Dow LLC started up a commercial polylactide plant, with the aim of production of PLA fibers for textiles and nonwovens, PLA film packaging applications, and rigid thermoformed PLA containers (http://www.cargilldow.com (accessed 2005).

Although PP could not be classified as a biodegradable polymer, this thermoplastic polymer takes an important place among eco-composites [11] primarily due to its recyclability, low cost and good price/performance ratio. Mohanty et al. has demonstrated that the natural fiber reinforced PP composites have potential to replace glass fiber-PP composites [10]. It has also been reported that PP can be effectively modified by maleic anhydride, providing polar interactions and covalent bonds between the matrix and the hydroxyl groups of cellulose fibers [15]. Visteon and Technilin developed flax/PP materials, R-Flax® based on low cost fibers. Tech-Wood International from the Netherlands announced Tech-Wood® eco-composite, suitable for construction elements [16]. Tech-Wood® eco-composite material contains 70% pine-wood fibers and 30% compatibilized PP.

In our previous study [17, 18, 19], compatibilization strategy was developed for both PLA and PP-based composites, and utilization of reinforcements from renewable sources for eco-composites has been investigated [20].

The purpose of this study was to investigate the recycling ability of the materials based on biodegradable PLA. PP-based composites were produced and their properties have been parallel determined, in order to compare their recycling behaviour and overall characteristics with those of PLA-based biocomposites. The rice hulls fillers were compounded with polymer matrix and coupling agent by melt mixing and then the obtained compounds were compression moulded. Also, the biocomposites were further granulated

and blended twice by melt mixing, followed by compression moulding of new samples. Finally, the influence of the recycling process on the properties of composites was evaluated through the mechanical and thermal characterization of the composites.

This work is a follow up of the successfully finished ECO-PCCM project [21], in which eco-composites based on PLA, PHBV and PP were prepared and investigated in order to obtain new eco-friendly construction panels and elements for eco-houses [17, 19].

Materials and methods

Materials

PLA, produced by Biomer, Krailling – Germany and isostatic PP, Moplen X30S, kindly supplied by Basell Polyolefins (Ferrara, Italy), were used as matrices for bio- and eco-composites. Rice hulls from agricultural waste were kindly supplied by Rice Institute from Kocani, Macedonia. Before mixing, rice hulls (RH) were vacuum-dried for 24h to adjust their moisture content to 1-2 wt%. Maleic anhydride-grafted PLA (MAPLA) and maleic anhydride-grafted PP (MAPP), KA 805 (Basell Polyolefins Ferrara, Italy), were used as coupling agents (CA) and they have been added to PLA and PP during the reactive blending.

Compounding of composite materials

The preparation of the composite compounds has been preformed by melt mixing, in a Haake Rheocord 9000 batch mixer (New Jersey, USA). First, the polymer and coupling agent were mixed for 3 min at 185°C and 175°C, respectively for PP and PLA based composites; then 30 wt% of fillers (rice hulls, RH)/fibers (kenaf, K) were added and the mixing proceeded for further 10 min at the same temperature. The mixing speed was progressively increased during the mixing, up to 64 rpm (3 min with a mixing speed of 8 rpm, then 4 min at 38 rpm and finally 3 min at 64 rpm). Then the obtained composites were cut into granules and reprocessed under the same preparation conditions (recycling process). This recycling process was carried out twice.

The codes of the samples obtained are shown in Table 1.

Table 1. Codes of composite samples produced by compression molding using neat or recycled polymer as a matrix, and produced from wholly recycled composites

Codes	Description	Matrix (wt%)		Fiber/Filler		Coupling agent	
		Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PLA/RH	Neat	PLA	70	Rice hulls	30	/	/
PLA/RH/CA	Neat						
PLA/RH/CA (x1)	Composite recycled once						
PLA/RH/CA (x2)	Composite recycled twice	PLA	65	Rice hulls	30	MAPLA	5
PP/RH	Neat	PP	70	Rice hulls	30	/	/
PP/RH/CA	Neat						
PP/RH/CA (x1)	Composite recycled once				30		
PP/RH/CA (x2)	Composite recycled twice	PP	65	Rice hulls		MAPP	5

Compression moulding

The samples for mechanical testing were fabricated by compression moulding. The pellets obtained after melt mixing of starting materials were put in a moulding frame with desired dimensions and compression moulded at T= 175^{0}C for PLA based composites and T= 185^{0}C for PP based composites, both for 10 minutes, with a progressive increase of pressure from 50 to 150 bar. Finally, the press was cooled using a cold water flow. Sheets with a thickness of about 5 mm were obtained.

Methods

Mechanical and thermal properties of the composites such as impact resistance (Charpy impact test according ASTM D 256), compression strength (ASTM D 695), flexural strength and the modulus (ASTM D 790) were determined. For all mechanical tests, the universal testing machines (Schenk and Frank, Germany) were used. The thermal stability of composites was analyzed using a Perkin Elmer Pyris Diamond Thermo gravimetrical Analyzer (TGA). About 10 mg of each sample was heated from 50°C to 600°C at heating rate of 20°C/min under nitrogen flow rate (25 ml/min). Morphological analysis was performed by using a JEOL scanning electron microscope (SEM), on cryogenically fractured surfaces of composite samples. Before the observation, the specimens were metallized with a gold/palladium coating in a Polaron Sputtering.

Results and discussion

Mechanical analysis

In our previous studies we investigated the properties of a new class of biodegradable PLA-based composites reinforced with kenaf fibers produced with or without compatibilizing agent [12]. Also, the ef-

fects of compatibilization on the performance of PHBV-based biocomposites were evaluated [18, 22]. The main goal of this work was the preparation and characterization of PLA-based biocomposites reinforced with rice hulls, with particular attention to possibility of their reuse. For this purpose

PLA biocomposites and PP eco-composites were first prepared by a proper in situ reactive compatibilization, a strategy inducing a strong interfacial fiber/polymer adhesion and thus resulting in improvement of the mechanical properties [23].

The coupling agents used for compatibilization are constituted from PP and PLA segments (the same as the polymer matrices) and by MA groups grafted onto PP and PLA segments, which become reactive with respect to hydroxyl groups present on the reinforcement surface. In this way, physical and/or chemical interactions between hydroxyl and maleic anhydride groups, generated during the mixing, are responsible for *in situ* formed grafted species that can act as effective compatibilizer for the PP and PLA/ natural filler reinforcement composites [24, 25].

Our task was to examine the recycling behaviour of the biocomposite itself by the analysis of the properties of re-processed composites produced from the recycled ones. In order to evaluate the response of composites to the recycling process in terms of mechanical properties, the obtained materials were successively reprocessed as reported in the experimental session. Table 2 shows the summary of the flexural properties for neat and recycled rice hulls-based composites. Incorporation of rice hulls into PLA matrix produced an increase in the flexural modulus, reaching 3,0 GPa for composite PLA/RH (70/30wt.%), and a drop in the stress at a peak of around 57%. However, the presence of a coupling agent in PLA/RH composites doubled the stress at the peak in flexure value. Composite PLA/RH/CA (65/30/5wt.%) exhibited stress at the peak in flexure of almost 29 MPa, which is close to the value displayed by pure PLA. Modulus in flexure increased in the presence of coupling agent. The extent of the modulus improvement is correlated to the filler/matrix interfacial adhesion, thus justifying the highest modulus value obtained in the presence of reactive coupling agent. Flexural strength of PLA/RH/CA (65/30/5wt.%) recycled composites decreases for about 50% after recycling, although the flexural modulus is practically unchanged. As reported in literature, the recycling process of polymer/fiber composites frequently induces a decrease in the physical properties of composites. The extent of this decrease is strictly correlated to the decline in the molecular weight of the polymer matrix and to the deterioration of fibers/fillers in terms of length caused by repeated kneading [26].

Table 2. Flexural properties of neat and recycled PLA - based biocomposites

Sample	Stress at peak, MPa	Modulus, GPa
PLA	32,0 ± 2,8	2,4 ± 0,14
PLA/RH (70/30wt.%)	13,9 ± 3,4 (-56,6 %)[a]	3,0 ± 0,21 (+25,0 %)[a]
PLA / RH /CA (65/30/5wt.%)	28,8 ± 6,6 (-3,5 %)[a]	3,2 ± 0,18 (+33,3 %)[a]
PLA/RH /CA (x1) (65/30/5wt.%)	12.1 ± 4,8 (- 58,0 %)[b]	3,24 ± 0,38 (+1,25 %)[b]
PLA/RH /CA (x2) (65/30/5wt.%)	10,7 ± 2,5 (- 62,8 %)[b]	3,32 ± 0,18 (+ 3,75 %)[b]

[a] In brackets are the percentage changes of the corresponding property, compared to the value for neat PLA
[b] In brackets are the percentage changes of the corresponding property, compared to the value for neat composite PLA/RH/CA

Within the framework of this investigation, the recycling behaviour and overall characteristics of PLA-based biocomposites were also compared to composites based on commonly used thermoplastic polymer, polypropylene (PP) containing the same reinforcement. For that aim, PP-based composites were produced and their recycling behaviour and overall properties have been determined. Although PP could not be classified as a biodegradable polymer, this thermoplastic polymer takes an important place among eco-composites [11] primarily due to its recyclability, low cost and good price/performance ratio. Mohanty et al. has reported that PP can be effectively modified by maleic anhydride, providing polar interactions and covalent bonds between the matrix and the hydroxyl groups of cellulose fibers [10].The obtained values for PP-based composites for flexural strength and modulus are similar with those of neat PP (Table 3). The recycling processes for these composites induce a slight decrease of the flexural strength after the second recycling (about 5%) and an increase of the flexural modulus (about 20%). As expected, the PLA-based biocomposites have lower mechanical properties than the PP - based ones, but significant deterioration of flexural properties is seen in recycled PLA based biocomposites. Nevertheless it is well known that polyolefins are less sensitive to the reprocessing than other polymers such as polyesters. Therefore, unless recycling processes can induce beta-scission in the polymer matrix, the possible molecular weight decrease due to the reprocessing does not seem to significantly affect the mechanical properties of the PP based composites reinforced with rice hulls. Concerning PLA-based biocomposites, our further investigations are directed towards the possibilities of improving their stability during re-processing cycle, which will be a subject of our future publication.

Table 3. Flexural properties of neat and recycled PP - based composites

Sample	Stress at peak, MPa	Modulus, GPa
PP	51,5 ± 5,5	1,1 ± 0,12
PP/RH (70/30wt.%)	31,6 ± 2,4	0.9 ± 0,31
PP /RH /CA (65/30/5wt.%)	42,6 ± 3,4	1,9 ± 0,08
PP/RH /CA (x1) (65/30/5wt.%)	44,8 ± 3,0	1,88 ± 0,16
PP/RH /CA (x2) (65/30/5wt.%)	38,5 ± 7,2	1,91 ± 0,06

Oksman et al. [6] has studied the recycling properties of the PLA/kenaf composite. The physical properties and molecular weight were held close to 90% of that of the initial PLA/kenaf composites. The physical properties of the PLA/kenaf composite probably can be kept constant by the adjustment of the ratio of the initial PLA/kenaf composite and the recycled one. Sanadi et al. [27] has studied the possibility of using highly filled agro-based fiber thermoplastic composites for furniture, automotive and building applications. They have shown that the performances of thermoplastic based composites are better than most of wood particle, low and medium density fiberboards. For our systems, a comparison of flexural properties of commercially available formaldehyde-based wood composites [27] and 30% filled PP/rice hulls and PLA/ rice hulls composites produced by compression molding is given in Table 4.

The investigated composites show flexural properties comparable to conventional formaldehyde-based fiberboards [27]. Moreover, these parameters remain similar to those of formaldehyde-based wood composites also after the recycling processes.

Table 4. Comparison of flexural properties of commercially available formaldehyde-based wood composites (Sanadi, et al.,2001) and compatibilized PP/Rice hulls and PLA/Rice hulls biocomposites produced by compression molding

| Sample	Flexural strength range (MPa)		Flexural modulus range (GPa)	
	low	high	low	high
High-density fiberboards [28] (commercial)	38	69	4.48	7.58
Medium-density fiberboards [28] (commercial)	13.1	41.4	2.24	4.83
PP/RH	42.6 (3.4)[a]		1.94 (0,08)[a]	
PLA/RH	28.8 (3.1)[a]		3.0 (0.09)[a]	

[a] Standard deviations are in brackets for the PP/rice hull and PLA/rice hull biocomposites

Since the industrial manufacturing of the composites proceeds mainly in nonisothermal regime, analysis of the crystallization parameters and crystallization behavior of the polypropylene based composites is especially important from a practical point of view. Generally, for composites based on semicrystalline polymers, the crystallinity is an important factor that determines the stiffness and fracture behavior of the matrix [22]. The crystallinity depends upon processing parameters, e.g. T_c, cooling rate, nucleation density and annealing time [18, 19]. It should be mentioned, that, in our previous paper it was reported that the addition of rice hulls or kenaf fibers to polylactic acid and polypropylene resulted in an increased crystallization temperature and accelerated crystallization process due to the "nucleating" effect of the filler [26]. This behavior could advantageously affect the industrial processing of the composites.

Thermal stability of PLA-biocomposites and their behaviour after recycling

Thermal stability of biocomposites produced from neat and recycled matrix, as well as from wholly recycled composite, was analyzed by TGA/DTG, and the results were compared to those obtained for PP-based eco-composites.

Results from the thermogravimetric analyse of PLA, rice hulls and the biocomposite PLA/RH/CA (65/30/5wt.%) are presented in figure 1(a) and table 5.
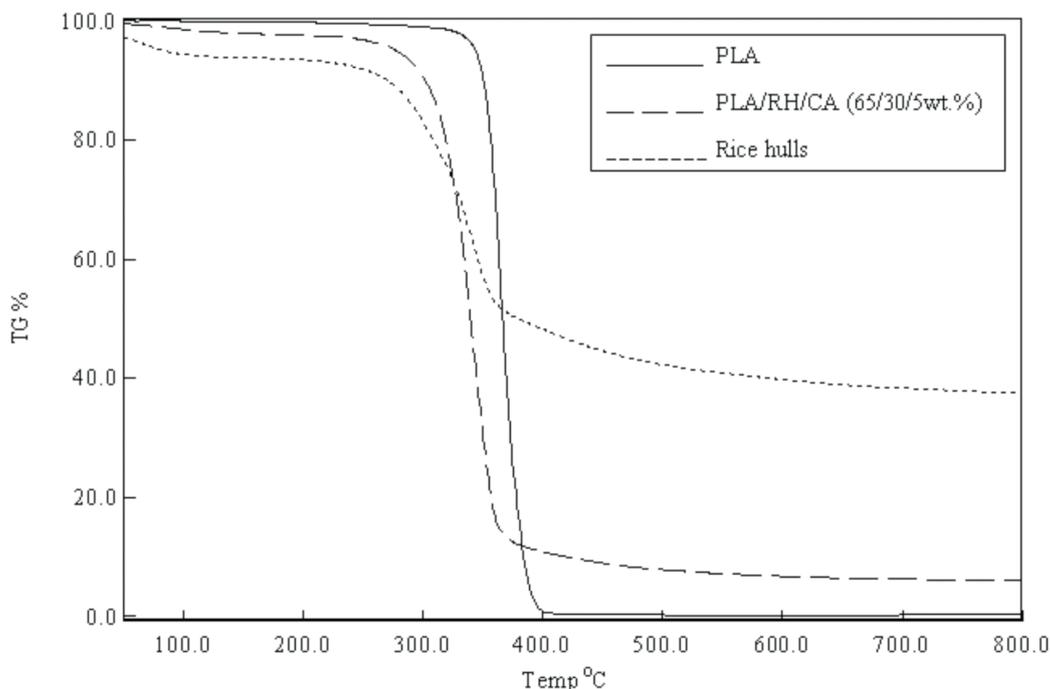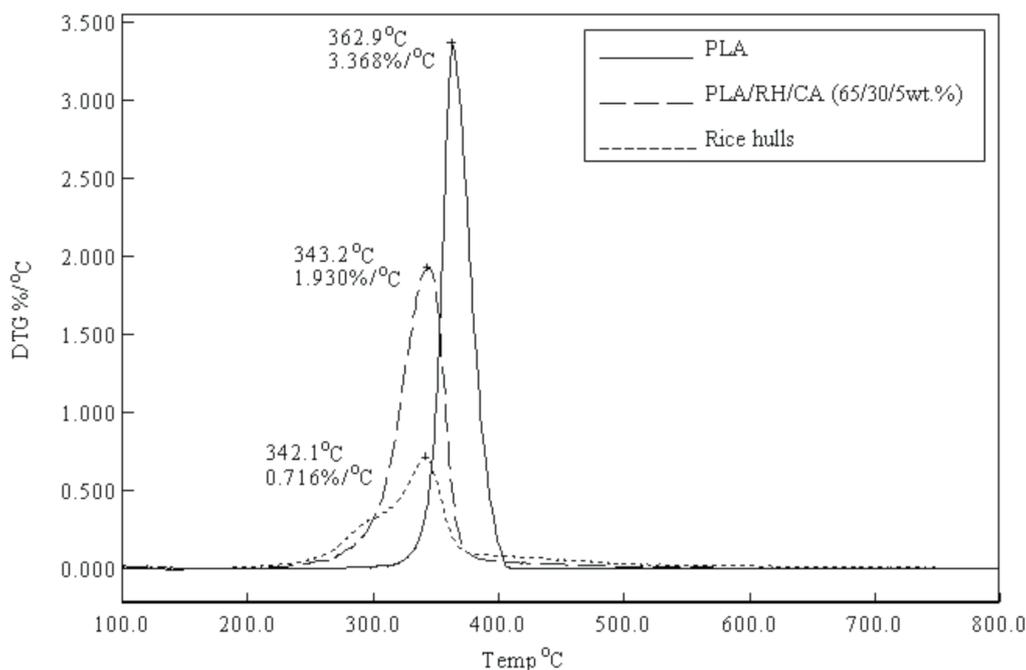
Figure 1a. Thermogravimetric curves of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) biocomposites: weight loss (%) versus temperature

Table 5. Thermal stability of PLA, rice hulls and biocomposite PLA/RH/CA (65/30/5wt.%)

T (ºC)	Weight loss (%)		
	Rice hulls	**PLA/RH/CA (65/30/5wt.%)**	**neat PLA**
50	2,7	0,5	0
100	5,6	1,4	0
150	8	3,2	0,5
290	14	6,9	0,9
310	20,6	13,7	1,2
330	29,7	33,5	2,1
350	43	69,8	9,5
370	49,1	86,9	61,3
390	51	88,7	95,7
410	52,6	89,7	99,6
600	60,3	93,3	100

As evident, rice hulls undergo two-step weight loss process: below 110ºC weight loss resulted from the evaporation of absorbed moisture and in the temperature range between 170 and 500ºC - from the degradation of rice hulls three major constituents. The lignocellulosic materials are chemically active and they are thermo-chemically decomposed between 150 and 500ºC: hemicellulose mainly between 150 and 350ºC, cellulose between 275 and 350ºC, and lignin between 250 and 500ºC [28]. Ash in the rice husk (12%) is mainly composed of silica (~96%), and the amount and distribution of silica in the rice husk is likely to be an important factor in determining the composite product properties [28, 29]. PLA gradually loses 10%

of its weight till 350ºC, and afterward suffers almost complete weight loss in a temperature interval from 350ºC till 400ºC. PLA based composite PLA/RH/CA (65/30/5wt.%) loses 10% of its weight till 300ºC, followed by ongoing 75% weight loss till 360-365ºC, after that, weight loss continues with slower degradation rate. It should be noted that at the temperature of 600ºC rice hulls exhibit high residual weight of 39,7%. These findings are in accordance with the finding of Lee et al. [30], that thermal stability of PLA/bamboo fibre composites is lower than thermal stability of neat PLA matrix.

Figure 1b. Derivative thermogravimetric curves of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) biocomposites: derivative weight loss (% / ºC) versus temperature

Derivative thermogravimetric curves for neat PLA, rice hulls and their composite PLA/RH are presented in figure 1 (b). Maximum weight loss rate for PLA (3,37%/ºC) is reached at 362,9ºC, and for rice hulls weight loss rate is uppermost (0,72 %/ºC) at 342,1ºC. Composite PLA/RH/CA (65/30/5wt.%) exhibits maximum weight loss rate of 1,93 %/ºC at 343,2ºC, a temperature almost 20ºC lower than the corresponding one for neat PLA, proving again the previous finding of composites' insignificantly lower thermal stability.

We investigated thermal behavior of the composites produced from wholly recycled ones, in terms of their sustainability values. Thermal degradation of once and twice recycled PLA/RH/CA (65/30/5wt.%) biocomposites proceeds in a single step, and occurrs at 323,8⁰C (PLA/RH/CA x1) and 319,5⁰C (PLA/RH/CA x2), respectively, and the TG-curves have the same behavior. The recycled composites have shown a lower degradation temperature (less than 20ºC), exhibiting a decrease of the degradation temperature (for about 20ºC) after the second recycling.

Table 6. Thermal stability of bio- and eco-composites
produced from recycled matrices and recycled composites,
as determined by TGA at residual weight of 90% (Td_{90}), 50% (Td_{50}), and 10% (Td_{10})

Sample	Td_{90} (ºC)	Td_{50} (ºC)	Td_{10} (ºC)
PLA/RH/CA (65/30/5wt.%)	308,2	341,3	534,2
PLA/RH/CA (x1) (65/30/5wt.%)	294,4	323,8	517,3
PLA/RH/CA (x2) (65/30/5wt.%)	289,1	319,5	501,1
PP/RH/CA (65/30/5wt.%)	344,43	411,21	452,17
PP/RH/CA (x1) (65/30/5wt.%)	336,7	409,9	471,0
PP/RH/CA (x2) (65/30/5wt.%)	322,6	389,0	455,3

The results obtained from thermal analysis have shown that biocomposites based on PLA and rice hulls as reinforcement could be reused by recycling and re-forming, and this process is more convenient than the recycling and re-use of the matrix itself.

Conclusion

On the basis of the results obtained for the mechanical properties and thermal behavior of PLA-based biocomposites produced from: neat and from wholly recycled composite, the following conclusions can be drawn: the rice hulls representing agricultural waste derived from rice-production could be used as a biodegradable eco-friendly filler, rather to minimize environmental pollution and cost of the final product than as a reinforcement of PLA matrix. Introduction of 5 wt.% PLA-g-MA improved the strength of PLA based composites with 30 wt.% rice hulls, which is a result of enhanced interfacial adhesion. The flexural properties of wholly recycled biocomposites are very close to those of the neat ones. Thermal stability of the biocomposites produced by re-processing from wholly recycled composites is not significantly affected by the first recycling process. Therefore, it could be recommended as a procedure for further utilization of these materials after their life time. The biodegradable PLA based biocomposites represent a good potential for utilization after recycling. The obtained results for flexural strength and modulus of the recycled biocomposite samples are comparable to those of conventional formaldehyde wood medium density fiber-boards used as construction elements for indoor applications.

Our further analyses are concerned with investigation of the possibilities of improving their stability during the re-processing cycle.

Acknowledgements

References

[1]   Chen Y., Chiparus L.S., Negulescu I., Parikh D.V., Calamari T.A. (2005). Natural Fibers for Automotive Nonwoven composites. J. of Ind. Text. 35, 47-61.

[2]   Mieck K.P., Nechwatal A., Knobeldorf C. (1994). Potential applications of natural fibres in composite materials. Melliand Textilber-ichte. 11, 228-330.

[3]   Heijenrath R. Peijs T. (1996). Natural-fibre-mat-reinforced thermoplastic composites based on flax fibers and polypropylene. Advanced Composites Letters. 5(3), 81-5.

[4]   Oksman K. (2000). Mechanical properties of natural fibre mat reinforced thermoplastics. Appl. Comp. Mat. 7, 403-14.

[5]   Oksman K. (2001). High quality flax fibre composites manufactured by the resin transfer moulding process. Journal of Reinforced Plastics and Composites. 20(7), 621-37.

[6]   Oksman K., Skrifvars M., Selin J.F. (2003). Natural fibers as reinforcement in polylactic acid (PLA) composites. Composites Science and Technology. 63, 1317-24.

[7]   Serizawa S., Inoue K., Iji M. (2006). Kenaf-fiber-reinforced poly(lactic acid) used for electronic products. Journal of Applied Polymer Science. 100, 618-24.

[8]   Seung-Hwan Lee, Siqun Wang (2006). Biodegradable polymers/bamboo fiber biocomposite with bio-based coupling agent. Composites: Part A. 37, 80-91.

[9]   Xia Z., Curtin W.A., Okabe T. (2002). Compos. Sci. Technol. 62, 1279-91.

[10]   Mohanty A.K., Drzal L.T., Misra M. J. (2002). Adhes. Sci. Technol. 16, 999-1023.

[11]   Yang H.S., Kim D.J., Lee J.K., Kim H.J., Jeon J.Y., Kang C.W. (2004)b. Possibility of using waste tire composites reinforced with rice hulls as construction materials. Bioresource Technol. 95, 61-5.

[12]   Avella M., Bogoeva-Gaceva G., Buzarovska A., Errico M.E., Gentile G., Grozdanov A. (2008). Poly (lactic acid)-based biocomposites reinforced with kenaf fibers. J. Appl. Poly. Sci. 108, 3542-51.

[13]   Chen H-L., Porter R.S. (1994). Journal of Applied Polymer Science. 59, 1329-42.

[14]   Karnani R., Krishnan M., Narayan R. (1997). Polymer Engineering and Science. 37, 476-94.

[15]   Keener T.J., Stuart R.K., Brown T.K. (2004). Compos. A. 35, 357-81.

[16]   Netravali A.N., Chabba, S. (2003). Mater. Today. 6(4), 22-39.

[17]   Bogoeva-Gaceva G., Grozdanov A., Buzarovska A. (2005). Eco-friendly polymer composites based on polypropylene and kenaf fib-ers. Proceedings of 3rd International Conference on Eco Composites. Royal Institute of Technology, Stockholm, Sweden, june 20-1.

[18]   Avella M., Bogoeva - Gaceva G., Buzarovska A., Errico M.E., Gentile G., Grozdanov A. (2007). Poly (3 - hydroxybutyrate - co - 3 - hydroxyvalerate) - based biocomposites reinforced with kenaf fibers. J. Appl. Polym. Sci. 104, 3192-200.

[19]   Dimzoski B., Bogoeva-Gaceva G., Gentile G., Avella M., Errico M.E., Srebrenkoska V. (2008). Preparation and characterization of poly(lactic acid)/rice hulls based biodegradable composites. J. Polym. Eng. 28, 369-84.

[20]   Grozdanov A., Bužarovska A., Bogoeva-Gaceva G., Avella M., Errico M.E., Gentile G. (2006). Rice straw as an alternative reinforce-ment in polypropylene composites. Agronomy for Sustainable Development. 26, 251-5.

[21]   ECO-PCCM, FP6-INCO-CT-2004-509185.

[22]   Grozdanov A., Bužarovska A., Bogoeva-Gaceva G., Avella M., Errico M.E., Gentile G. (2007). Nonisothermal crystallization of kenaf fiber/polypropylene composites. Polymer Engineering and Science. 47, 745-9.

[23]   Dimzoski B., Bogoeva-Gaceva G., Gentile G., Avella M., Grozdanov A. (2009). Polypropylene based eco-composites filled with agri-cultural rice hulls waste. Chem. Biochem. Engineering Quarterly. 23 (2), 225-20.

[24]   Bogoeva-Gaceva G., Grozdanov A., Buzarovska A. (2006). Nonisothermal crystallization of maleic anhydride grafted PP: comparison of different kinetic models. Proceedings of 5th International Conference of the Chemical Societes of South-East European countries ICOSECS-5, Ohrid, Macedonia, september 10-4.

[25]   Bogoeva-Gaceva G., Grozdanov A., Dimzoski B. (2007). Analysis of the reaction of modified polypropylene in melt. Proceedings of European Polymer Congress EPF, Portoroz, july 2-6.

[26]   Buzarovska A., Bogoeva-Gaceva G., Grozdanov A., Avella M. (2006). Crystallization behavior of polyhydroxybutyrate in model composites with kenaf fibers. Journal of Applied Polymer Science. 102 (1), 804-9.

[27]   Sanadi A.R., Hunt J.F., Caulfield D.F., Kovacsvologyi G., Destree B. (2001). High fiber-low matrix composites: kenaf fiber/polypropylene. Proceedings of 6th International Conference on Woodfiber-Plastic Composites, Madison, Wisconsin, may 15-6.

[28]   Kim H.S., Yang H.S., Kim H.J., Park H.J. (2004). Thermogravimetric analysis of rice husk flour filled thermoplastic polymer composites. J. Therm. Anal. Calorim. 76, 395-404.

[29]   Sanadi A.R., Caulfield D.F., Jacobson R.E., Rowell R.M. (1995). Renewable agricultural fibers as reinforcing fillers in plastics: Mechanical properties of kenaf fiber-polypropylene composites. Indust. Eng. Chem. Res. 34, 1889-96.

[30]   Lee S.H., Wang S. (2006). Composites Part A. 37, 80-91.