

Топлотна карактеризација композита на бази поли (млечне киселине)

Thermal characterization of the composites based on poly(lactic acid)

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Izvod

U ovoj studiji, kompoziti na bazi poli(mlečne kiseline) (PLA) i pirinačne ljuske su pripremljeni sa dodatkom 5% tež. PLA-kalemljene-MA (CA), za poboljšanje adhezije između polimernih matrica i prirodnih punila. Kompoziti koji sadrže 30% tež. pirinačne ljuske (RH) pripremljeni su kompresionim presovanjem. Termička svojstva kompozita su analizirana u odnosu na kompozita na bazi najčešće korišten termoplastični polimer polipropilen (PP), koji sadrži istu armaturu. Toplotna stabilnost kompozita na bazi PLA matrica je nešto niža u odnosu na kompozita na bazi PP. Uvođenje CA poboljšava termička stabilnost kompozita na bazi PLA, kao rezultat poboljšane međupovršinske adhezije. SEM analize pokazuju da u svim kompozita interakcije između matrice i RH su veoma dobre, šta je dobiveno kao rezultat visokih međupovršinskih adhezije. PLA matrica je efikasan materijal za proizvodnju kompozita sa prirodnih vlakana sa visokim svojstva toplotnu stabilnost. Dobijeni rezultati su pokazali da kompoziti na bazi poli(mlečne kiseline) i pirinačne ljuske mogu se iskoristiti za proizvodnju nova eko-materijala sa prihvatljiva termička svojstva i za proizvodnju eko-kompozita. Kompozita na bazi PP i kompozita na bazi PLA su odgovarajuće za proizvodnju sa korišćenjem kompresione tehnike i oba kompozita su pogodna za primena kao građevinskog materijala.

Abstract

In this study, rice-hulls-filled poly (lactic acid) (PLA) composites 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 by compression molding. For the composites, the thermal properties were analyzed and compared to those of commonly used thermoplastic based-polymer, polypropylene (PP) containing the same reinforcement. Thermal stability of composites based on PLA matrix is slightly lower as compared to the PP ones. Introduction of CA improved the thermal stability of PLA based composites, as a result of enhanced interfacial adhesion. SEM analyses show that in all composites the interaction between matrix and RH are very good, resulting in high interfacial adhesion. The PLA matrix is effective material for production of the natural fiber composites with high thermal stability properties. The obtained results have shown that rice-hull-filled poly(lactic acid) composites could be utilized for production of new eco-materials with acceptable thermal properties and they can be successfully used for production of eco-composites. Moreover, the PP-based composites and PLA- based composites are appropriate for processing by compression molding and both composites are suitable for applications as construction materials.

Introduction

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 [1-8]. The development of wholly biodegradable polymers and polymeric materials can play a fundamental role in helping to solve the waste disposal problems [9,10]. 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 to 2 years, compared to other petroleum plastics needing very longer periods [5, 6, 7]. The mechanical properties of PLA have been extensively studied as a biomaterial in the medicine, but only recently it has been used as a polymer matrix in eco-composites [8], although its applications is still limited by its relatively high price when compared with some other biodegradable polymers. Although PP could not be classified as a biodegradable polymer, this thermoplastic polymer takes an important place in amongst eco-composites [11] primarily due to its recyclability, low cost and good price/performance ratio. The purpose of this study was to investigate the thermal behavior of the materials based on biodegradable PLA matrix.

Experimental

Poly(lactic acid) used as a matrix in the composites was supplied by Biomer (Krailling-Germany), whilst the waste rice hulls (RH) used as a filler were kindly supplied by the Rice Institute of Kočani, R. Macedonia. Sigma-Aldrich reagent products (Steinheim-Germany), maleic anhydride (MA) and dibenzoylperoxide (DBPO) were used as received.

PLA-g-MA used as a coupling agent (CA), was prepared through reactive mixing in a Brabender-like apparatus of 48.5 g PLA (previously mixed for 5 minutes at 170 °C), and mixture of 1.5 g MA and 0.75 g DBPO. The reactive mixing was performed at 180 °C for 5 minutes, increasing progressively the mixing speed up to 32 rpm. Finally, the obtained material was dried under vacuum at 100°C in order to remove unreacted maleic anhydride. More details concerning the synthesis and characteristics of CA are presented earlier in [12].

Composites with 30 wt.% rice hulls loading, as well as corresponding ones where part of the PLA matrix was replaced with a CA, PLA/RH/CA (65/30/5wt.%), were prepared by extrusion in HAAKE Rheocord (New Jersey, USA) at T=175 °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 afterward added to the extruder heated on predefined temperature. Concerning the composites prepared with coupling agent, a mixture of pure and modified PLA was initially prepared during 3 min with 8 rpm, and afterward the rice hulls were added.

Before the extrusion, the milled rice hulls agricultural waste were vacuum-dried during 24 h. The codes of the samples obtained are shown in Table 1.

Table 1. Codes of composite samples produced by compression molding

Codes	Description	Matrix (wt%)		Fiber/Filler		Coupling agent (CA)	
		Type	Content (wt%)	Type	Content (wt%)	Type	Content (wt%)
PLA/RH	Neat	PLA	70	/	/	/	/
PLA/RH/CA	Neat	PLA	65	Rice Hulls	30	MAPLA	5
PP/RH/CA	Neat	PLA	65			MAPP	

The samples for mechanical testing were fabricated by compression moulding in CARVER press. The pellets obtained after melt mixing of starting materials were put in moulding frame with desired dimensions and compression moulded at T= 175 °C for 10 minutes, with

progressively increasing pressure from 50 to 150 bar. Finally, the press was cooled using a cold water flow. Sheets with thickness of about 5 mm were obtained.

The thermal stability of composites was analyzed using a Perkin Elmer Pyris Diamond Thermogravimetric 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 (25mL/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

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 2. As can be seen, rice hulls undergo two-step weight loss process: below 110 °C weight loss resulted from the evaporation of absorbed moisture and in the temperature range between 170 and 500 °C - from the degradation of rice hulls three major constituents. The lignocellulosic materials are chemically active and decompose thermo-chemically between 150 and 500 °C: hemicellulose mainly between 150 and 350 °C, cellulose between 275 and 350 °C, and lignin between 250 and 500 °C [13]. 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 products properties [14,15]. PLA gradually losses 10% of its weight till 350 °C, and afterward suffers almost complete weight loss in a temperature interval from 350 °C till 400 °C. PLA based composite PLA/RH/CA (65/30/5wt.%) lose 10% of its weight till 300 °C, followed by ongoing 75% weight loss till 360-365 °C, after that, weight loss continues with slower degradation rate. It should be noted that at temperature of 600 °C rice hulls exhibit high residual weight of 39,7%. These findings are in accordance with the finding of Lee et al. [16] that thermal stability of PLA/bamboo fibre composites is lower than thermal stability of neat PLA matrix.

From the derivative thermogravimetric curves for neat PLA, rice hulls and their composite PLA/RH these results were obtained: maximum weight loss rate for PLA (3,37 %/°C) is reached at 362,9 °C, and for rice hulls weight loss rate is uppermost (0,72 %/°C) at 342,1 °C. Composite PLA/RH/CA (65/30/5wt.%) exhibits maximum weight loss rate of 1,93 %/°C at 343,2 °C, a temperature almost 20 °C lower than the corresponding one for neat PLA, proving again the previous finding of composites insignificantly lower thermal stability.

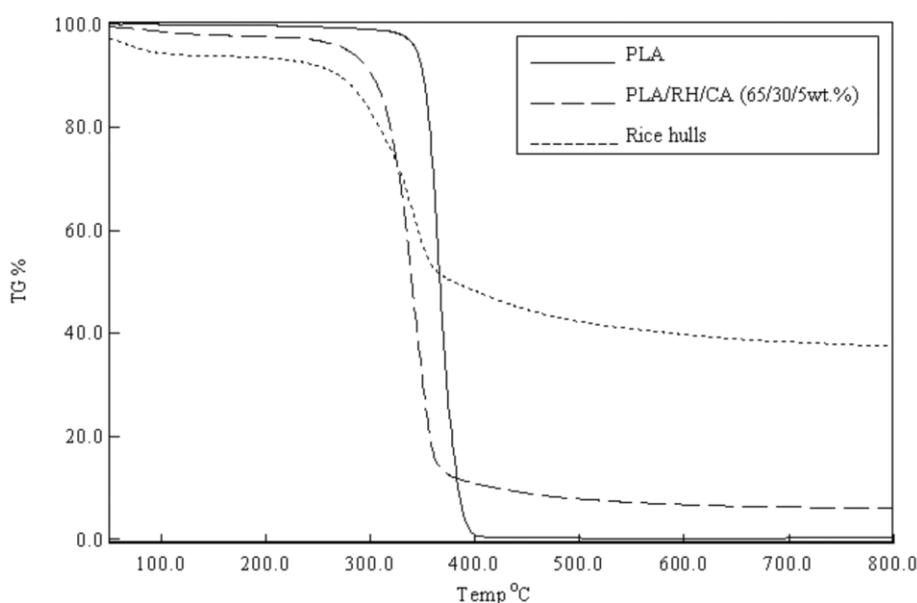


Figure 1a. Thermogravimetric curves of PLA, rice hulls and PLA/RH/CA (65/30/5wt.%) biocomposites: weight loss (%) versus temperature

Table 2. 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

Thermogravimetric (TGA) curve and derivate thermogram (DTG) for PP/RH/CA composite is shown in fig.2. As it can be observed, thermal degradation of PP/RH/CA composite shows single stage process; maximum weight loss rates were observed at 424,5°C for PP/RH/CA. A small shoulder can be noticed at approximately 350°C corresponding to the beginning of the thermal degradation of rice hulls. Notwithstanding the degradation process occurs in a single step, it can be considered the overlapping of the degradation phenomena associated to the different composite components. Thermal stability of the PP-based composites is slightly higher as compared to the PLA ones.

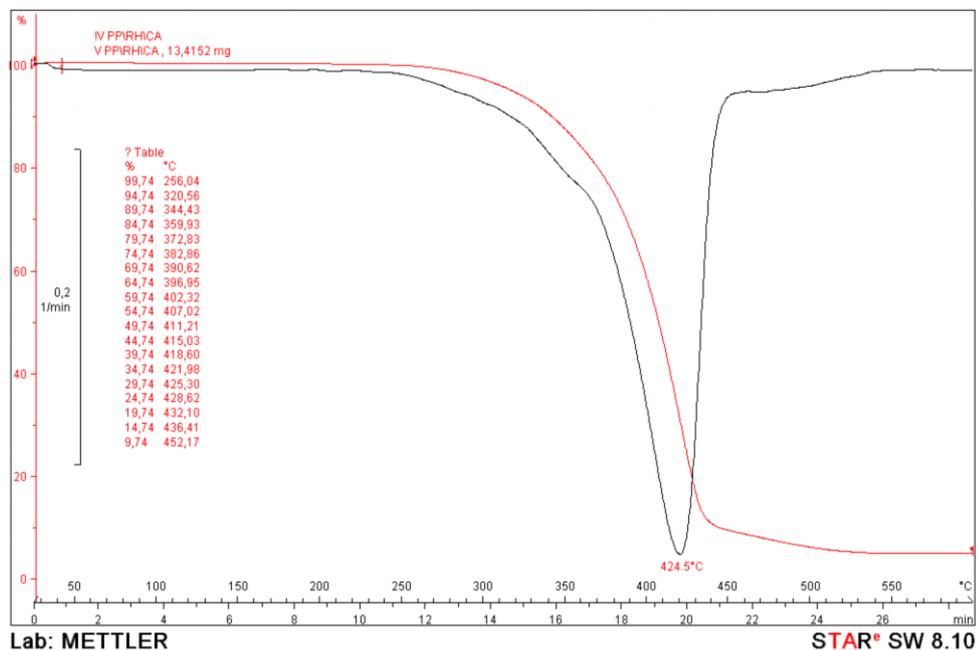


Figure 2. Weight loss and weight loss rate curves of PP/RH/CA

The micrographs of composites containing 30 wt.% rice hulls are presented in Figure 2. In PLA/RH (70/30wt.%) composite, rice hulls appear poorly covered with the PLA matrix thus indicating a poor filler-polymer adhesion. Moreover, more plastic deformation of the PLA matrix in glass state is evident from the present tips resulted from “neck” formation during material stressing (see micrograph a). An enhancement of adhesion level between the rice hulls and the matrix, in PLA/RH/CA (65/30/5wt.%) composite, can be remarked from the well

covered rice hulls with PLA and the absence of “neck” formation indicating that no debonding phenomena occur (micrographs b).

These results make it possible to assess that reactive compatibilization allows a significant improvement of the rice hulls-polymer interfacial adhesion.

As concerns PLA based biocomposites, the cellular structure of rice hulls embedded in the polymer matrix is clearly observed. This finding is in agreement with the results obtained for thermal behavior recorded for PLA based composites.

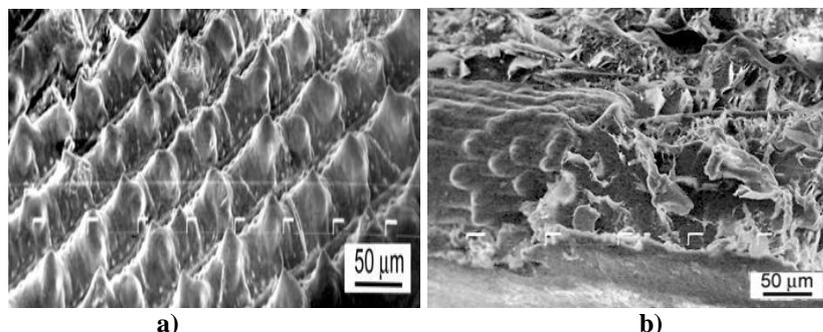


Figure 2: SEM micrographs of the cryogenically fracture surface for composites: a) PLA/RH (70/30wt.%) without coupling agent and b) PLA/RH/CA (65/30/5wt.%) with coupling agent

Conclusion

On the basis of the results obtained for the thermal behavior of PLA-based biocomposites produced, 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 thermal stability of PLA based composites with 30 wt.% rice hulls, as a result of enhanced interfacial adhesion. These features are typical of compatible polymer composites. Morphological analysis carried out by SEM have revealed that the morphology of PLA-composites is not significantly affected by the processing. Considering the thermal properties of the composites produced with PLA matrix is slightly lower as compared to the PP ones. The biodegradable PLA based biocomposites represent a good potential for utilization used as construction elements for indoor applications.

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

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