

PREPARATION AND CHARACTERIZATION OF POLYMER BIOCOMPOSITES BASED ON LINEAR LOW DENSITY POLYETHYLENE AND RICE HUSKS

¹Emi GOVORCIN BAJŠIĆ, ¹Nikolina MRKONJIĆ, ¹Veljko FILIPAN, ¹Igor SUTLOVIĆ,
²Emilija ZDRAVEVA

¹University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia, EU,
egovor@fkit.hr; nmrkonic@fkit.hr; vfilipan@fkit.hr; isutlo@fkit.hr

²University of Zagreb Faculty of Textile Technology, Zagreb, Croatia, EU,
emilija.zdraveva@tff.hr

<https://doi.org/10.37904/nanocon.2019.8450>

Abstract

Ecological concern has recently resulted in a natural sources which are rich in cellulose, cheap and provide good prospective as reinforcements fillers in polymer matrix composites as recyclability and environmental safety. Rice husk is a cellulose-based fibrous material and a waste product of the rice processing industry. Biocomposites made from linear low density polyethylene (LLDPE) and rice husks (RH) in different content (10, 20, 30, 40, 50 wt. %) were prepared by melt compounded in laboratory Brabender mixer. The LLDPE/RH biocomposites were characterized by using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA). The effects of RH content on the thermal properties of the biocomposites have been discussed. The DSC results showed that the addition of the RH and increasing the RH content in biocomposites increased the crystallinity degree of the LLDPE/RH biocomposites at lower filler concentration of RH, i.e. 10 and 20 wt.% due to nucleating ability of RH. The results obtained by DMA analysis show a decrease of glass transition temperature (T_g) of LLDPE when it was blended with RH. In terms of thermal stability it has been found that the addition of RH decreased the thermal stability of the neat LLDPE.

Keywords: Linear low density polyethylene (LLDPE), rice husk (RH), biocomposites, thermal properties, thermal stability

1. INTRODUCTION

Usually biocomposites consist of a biodegradable polymer matrix and biofibers as reinforcement. Since both components are biodegradable, it is expected that the composite will be biodegradable as well. Biopolymers are usually biodegradable but do not possess the required thermal and mechanical properties required for engineering plastics. On the other hand, the best engineering plastics are obtained from synthetic polymers, but they are not biodegradable. The advantages of biofibers over traditional reinforcements such as glass fibers, talc and mica are low price, low density, high toughness, acceptable specific strength, good thermal properties and biodegradability [1]. The main drawback is that they are hydrophilic, thus affecting their compatibility with the hydrophobic polymer during production. Another disadvantage is the low processing temperature required by the fibers due to their possible degradation at higher temperature and volatilization of substances that may affect the properties of the composite. The processing temperature is therefore limited for most of the plant fibers up to 200 °C, although it is possible to use higher temperatures over short periods of time [2]. In the biocomposites the biofibers serve as reinforcements that increase the strength and rigidity of the composite. The reinforced polymer composites have several advantages such as: low price, biodegradability, they are renewable and have no health hazards [3]. The most commonly used types of biopolymers as food packaging materials are natural polymers such as: cellulose, starch, chitosan, and agar derived from carbohydrates, as well as: gelatin, gluten, whey protein and collagen derived from proteins. Agricultural plants are a source of raw materials for the production of natural fibers, independent of oil

derivatives and therefore particularly interesting due to their availability, renewability and acceptability from the point of view of environmental protection. Recent research in the field of polymer materials aims at finding new types of composites, especially those with natural fibers. Rice husks are lignocellulosic materials or agricultural industrial waste obtained as the by-product of the rice processing and is particularly important natural resource. Compared to wooden biocomposites, biocomposites reinforced with rice husks exhibit excellent chemical resistance, good mechanical properties, greater dimensional stability when exposed to moisture and lower cost. Cellulose is a partially crystalline polysaccharide while hemicellulose is a highly crosslinked amorphous polymer. Cellulose has better mechanical properties than most commonly used reinforcements and offers exceptional benefits such as biodegradability and biocompatibility, high strength and low density. To achieve better adhesion of the fibers within the polymer matrix the ash content as well as the fat must be minimal. The fats reduce the interlayer adhesion and as a result, the composite is disintegrated. The hydroxyl groups present in the cellulose of natural fibers reduce the interfacial interactions thus the composite is more hydrophilic. Lignocellulose natural fibers are biodegradable because organisms recognize a hydrocarbon polymer, mainly hemicellulose in the cell wall and have specific enzymes capable of converting it into digestive units [4]. The main focus of this paper is the fabrication of biocomposites containing fine minced rice husks (RH) in a linear low density polyethylene (LLDPE), thus to produce biodegradable polymeric material reinforced with waste or rice husks, as an alternative low cost LLDPE filler. After the preparation of the biocomposites, the influence of the rice husks contents (of 10, 20, 30, 40 and 50 wt%) on the thermal properties of LLDPE/RH biocomposites was investigated.

2. EXPERIMENTAL

2.1. Materials

The biocomposites on the base of the linear low density polyethylene (LLDPE) LLDPE-EFDA 7047, with a MFR of 1.0 g/10 min at 190 °C and density of 0.918 g/cm³ was supplied from Equate Petrochemical Company, Kuwait. The rice husks (RH) were obtained from Kocani, Macedonia, and the rice cultivar was 'Sant Andrea' (*Oryza sativa* L. 'Sant Andrea'), Italy.

2.2. Preparation of LDPE/RH biocomposites and films

Biocomposites were prepared by mixing of LLDPE and RH in the Brabender mixer at the temperature of 170 °C for 5 min. The content of RH was 10, 20, 30, 40 and 50 wt. %. Before mixing with LLDPE the RH were dried for 24 h at 105 °C to remove any residual water. The LLDPE/RH films were pressed in a hydraulic press Fontune, Holland (SRB 140, EC 320x320NB) at the temperature of 160 °C and a pressure of 25 kPa for 5 min.

2.3. Characterization

Thermal transitions and related heat fusion of the neat LLDPE and LLDPE/RH biocomposites were studied using a differential scanning calorimeter DSC Mettler Toledo 822e. Dynamic measurements were performed in the temperature range from -100 to 150 °C with rate of 10 °C/min, in two heating/cooling cycles and inert atmosphere of nitrogen.

Dynamic mechanical measurements are performed with a TA Instruments model DMA 983 Analyzer. The measurements are conducted over temperature range of -100 °C to 150 °C at a constant frequency of 1 Hz with amplitude of 0.3 mm. The heating rate was 3 °C/min. The samples were cooled to -100 °C using liquid nitrogen.

In order to obtain the thermal stability thermogravimetric analysis was performed under a nitrogen atmosphere (60 ml/min) on a TA Instruments Q500 system analyzer. Samples of approximately 10 mg were heated from 25 °C to 600 °C at a heating rate of 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. Thermal behaviour of LLDPE/RH biocomposites

The thermal behavior of LLDPE/RH biocomposites was investigated by means of DSC measurement. The DSC curves during heating and cooling of the neat LLDPE and LLDPE/RH biocomposites are shown in **Figures 1a** and **1b** respectively.

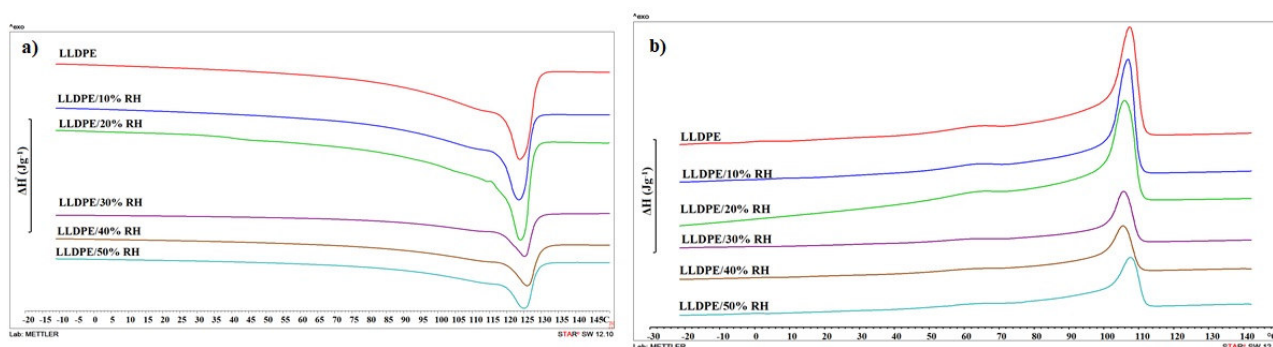


Figure 1 DSC curves of the neat LLDPE and LLDPE/RH biocomposites during heating (a) and cooling (b)

The DSC heating curve of the neat LLDPE (**Figure 1 a**) shows melting temperature (T_m) at 123.1 °C and crystallization temperature at 108.0 °C. **Table 1** gives the peak melting and crystallization temperatures and the heat of melting (ΔH_m). From DSC curves and the T_m values in **Table 1** it can be seen very small (2 °C) change in the T_m of the LLDPE crystalline phase by incorporation of RH and with the increase of their content. The added RH had no significant effect on the polymer melting point. The addition of the RH has decreased the crystallization temperature, T_c . This decrease in T_c suggested on the slower crystallization of LLDPE with the addition of RH. Degree of crystallinity, χ_c , for LLDPE and LLDPE/RH biocomposite was determined according to Equation (1) and it increases at lower content of RH (10 and 20 wt%) (**Table 1**), what means that RH act as nucleating agents for LLDPE. In regard to the χ_c it is seen that the increase of the RH content (30, 40, 50 wt %) reduces the χ_c , which suggests that the highest reduction in the crystalline phase of the LLDPE obtained.

$$\chi = \left(\frac{\Delta H_m}{\Delta H_m^0 \times \left(1 - \frac{\%RH}{100}\right)} \right) \times 100 \quad (1)$$

where:

ΔH_m - the value of melting enthalpy read from the surface of melting endotherm (Jg^{-1})

ΔH_m^0 - the melting enthalpy of 100 % crystalline LLDPE (293,0 Jg^{-1}).

Table 1 DSC results after 2nd heating/cooling cycle of the neat LLDPE and LLDPE/RH biocomposites

Sample	T_m (°C)	T_c (°C)	ΔH_m (Jg^{-1})	χ_c (%)
LLDPE	123.1	108.0	118.18	40.33
LLDPE /10 % RH	123.0	107.7	115.37	43.75
LLDPE /20 % RH	123.4	106.7	120.12	51.25
LLDPE /30 % RH	125.0	106.0	50.41	24.58
LLDPE /40 % RH	125.8	105.8	55.34	31.48
LLDPE + 50 % RH	124.7	108.0	58.11	39.67

3.2. Results of Thermogravimetric Analysis (TGA)

A TG analysis was very useful technique to determine quantitatively the degradation behavior, the composition of the materials and thermal stability. In this study the thermal stability of the neat LLDPE and LLDPE/RH biocomposites was investigated. The decomposition temperature for each step and the residue of the neat LLDPE and LLDPE/RH biocomposites under nitrogen atmosphere are observed from **Figure 2**.

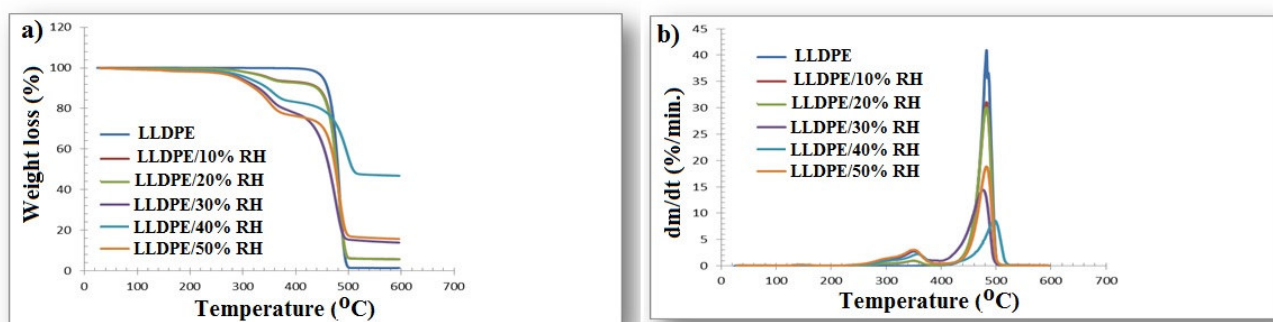


Figure 2 TG curves a) and DTG curves b) of the neat LLDPE and LLDPE/RH biocomposites

The TGA results are presented in **Table 2** which including the initial degradation temperature (T_{ini}), the temperature corresponding to final temperature of thermal degradation (T_{end}) temperature at the maximum rate of degradation (T_{max}) and the residual mass of the composites at 600 °C. From the **Figure 2a** can be seen that the TG curve displays a main degradation step and almost no residue (1.41 %) is left for the neat LLDPE. The DTG curve (**Figure 2b**) shows a single peak with an inflection point at 482.9 °C where LLDPE degraded at the maximum rate. DTG curves showed the three stage degradation behavior for the LLDPE/RH biocomposites. The first stage, between 100 and 200 °C represented the loss of water that inside RH, the second stage corresponds to the degradation of RH while the third stage of degradation corresponds to the degradation of LDPE. The final decomposition temperature of the LLDPE/RH biocomposites in the present research work is closer to T_{fin} of LLDPE. From **Table 2**, it is clear that the addition of RH decreased the thermal stability of the biocomposites, also the thermal stability decreased with increasing RH content. This is due to the lower thermal stability of the RH. The residue at 600 °C increased with increasing RH content (**Table 2**).

Table 2 TGA results of the neat LLDPE and LLDPE/RH biocomposites

Sample	T_{ini} (°C)	T_{fin} (°C)	T_{max}^1 (°C)	T_{max}^2 (°C)	Residue at 600°C (%)
LLDPE	451.5	494.5	/	482.9	1.41
LLDPE/10 % RH	350.4	495.6	349.3	482.8	5.77
LLDPE/20 % RH	347.3	494.4	350.9	482.3	5.68
LLDPE/30 % RH	293.9	490.3	351.6	475.9	13.96
LLDPE/40 % RH	309.0	510.3	357.0	497.3	46.88
LLDPE/50 % RH	288.2	494.0	349.9	482.6	15.76

3.3. Dynamic Mechanical Analysis (DMA) results

DMA allows measurement of the storage modulus (E') characteristic of the stiffness, and loss modulus (E'') characteristic of damping at different temperatures. **Figure 3** shows the storage modulus (E') and loss modulus (E'') of the neat LLDPE and RH reinforced LLDPE biocomposites as a function of temperature.

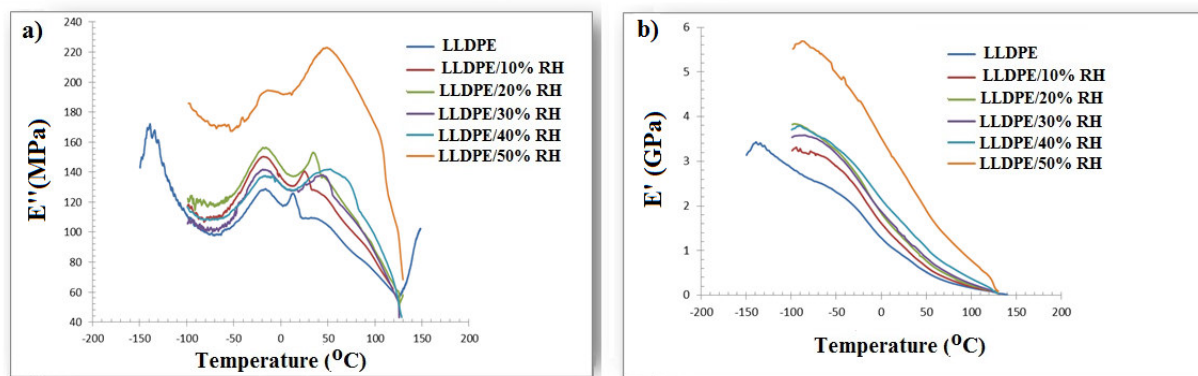


Figure 3 DMA curves of Loss modulus a) and Storage modulus b) of the neat LLDPE and LLDPE biocomposites

The E'' curves of the neat LLDPE and LLDPE/RH biocomposites with different RH content as a function of temperature is shown in **Figure 3a**. All curves exhibit two relaxation peaks in the range of temperature analyzed. The low relaxation peak is related to the glass-rubber transition of the amorphous phase of LLDPE and is taken as the glass transition temperature (T_g) [5,6]. It can be seen that the area under these peaks decreases with RH content and this is easily related to the decreasing LLDPE concentration in the biocomposites. The high temperature peak corresponds to the α_h transition related to the LLDPE crystalline fractions [5,6]. The glass transition temperature, T_g , obtained from E'' and temperature α_h transition are shown in **Table 3**. The LLDPE T_g determined from the E'' curves showed a marginal decreasing in the presence of RH, from -16 to -17 $^{\circ}\text{C}$. As the RH content increased the mobility of LLDPE chains increased. **Figure 3b** shows the temperature dependence of the storage modulus (E') for the neat LLDPE and LLDPE/RH biocomposites with different RH content. It was observed that E' of all the biocomposites increased with higher RH content across the entire temperature range due to the enhanced stiffness, as can be seen from **Figure 3b** and **Table 3**. Increasing the RH content a significant improvement of stiffness was verified. This is the expected effect caused by the addition of more rigid fillers into semi-rigid polymer matrices.

Table 3 TGA results of the neat LLDPE and LLDPE/RH biocomposites

Sample	T_g ($^{\circ}\text{C}$)	α_h ($^{\circ}\text{C}$)	$E'_{25^{\circ}\text{C}}$ (GPa)
LLDPE	-16.6	12.6	0.8730
LLDPE /10% RH	-17.2	25.4	1.086
LLDPE /20% RH	-17.2	35.2	1.265
LLDPE /30% RH	-18.0	44.4	1.327
LLDPE /40% RH	-17.2	50.2	1.600
LLDPE /50% RH	-14.6	48.2	2.727

4. CONCLUSION

The DSC results showed that the addition of the RH and increasing the RH content in the LLDPE/RH biocomposites increased the crystallinity degree of the biocomposites at lower filler concentration of RH (10 and 20 wt.%) due to nucleating ability of RH. But the crystallinity degree was reduced on addition 30, 40 and 50 wt % of RH. This may be attributed to the presence of the higher concentration of the silica from the RH in the crystal structure of LLDPE. The melting temperature of the biocomposites was not significantly changed,

the T_m was slightly increased with increasing RH content (30, 40 and 50 wt % of RH). In terms of thermal stability it has been found that the addition of RH decreased the thermal stability of the neat LLDPE. Initial degradation temperature of LLDPE/RH biocomposites decreased with the increasing of RH content suggesting that the biocomposites are less thermally stable. The results obtained by DMA analysis show a decrease of glass transition temperature (T_g) of LLDPE when it was blended with RH, mobility of LLDPE chains increased.

REFERENCES

- [1] TANG, X.Z.; KUMAR, P.; ALAVI, S.; SANDEEP, K.P. Recent Advances in Biopolymers and Biopolymer-Based Nanocomposites for Food Packaging Materials *Critical Reviews in Food Science and Nutrition*. 2012, vol.52, no. 5, pp. 426-442.
- [2] WANG, W., SAIN, M. and COOPER, P. A. Hygrothermal weathering of rice hull/HDPE composites under extreme, climatic conditions. *Polymer Degradation and Stability*, 2005, vol. 90, no.3, pp. 540-545.
- [3] THWE, M. M. and LIAO, K. Effects of environmental aging on the mechanical properties of bamboo-glass fiber reinforced polymer matrix hybrid composites. *Composite. Part A Applied Science and Manufacturing*, 2002, vol. 33, no. 1, pp. 43-52.
- [4] ROWELL, R. M., in: Emerging Technologies for Materials and Chemicals, ROWELL, R. M., SCHULTZ, T. P., NARAYAN, R., Eds., 1992, 12, 476,
- [5] YEONG-TARNG, S. and HUI-CHUN, C. DSC and DMA studies on silane-grafted and water-crosslinked LDPE/LLDPE blends. *Journal of Applied Polymer Science*, 2001, vol.81, no.7, pp.1808-1816.
- [6] KONTOU, E. A. and NIAOUNAKIS, M, Thermo-mechanical properties of LLDPE/SiO₂ nanocomposites, *Polymer*, 2006, vol.47, no. 4, 1267-1280.