THE EFFECT OF RICE HUSKS AND mTiO$_2$ ON THE THERMAL PROPERTIES OF LLDPE/RH/mTiO$_2$ BIOCOMPOSITES

Emi GOVORČIN BAJSIĆ, Mario MEHEŠ, Ljerka KRATOFIL KREHULA, Ana PERŠIĆ, Veljko FILIPAN, Igor SUTLOVIĆ

University of Zagreb, Faculty of Chemical Engineering and Technology, Zagreb, Croatia, EU,
egovor@fkit.hr; mmehes@fkit.hr; krehula@fkit.hr; apersic@fkit.hr; vfilipan@fkit.hr; isutlo@fkit.hr

Abstract

Petroleum-based products as Linear low-density polyethylene (LLDPE) are most commonly used in packaging of products like food, pharmaceuticals, cosmetics and detergents because of his low cost, good mechanical properties, easy processing and flexibility. However the lack of LLDPE as non-degradable packaging material has a major impact on environmental pollution.During the last few decades, petroleum-based products because of improper management and disposal practice cause serious environmental pollution problems that could persist for centuries. This has raised growing concern about degradable polymers and promoted develop of new synthetic plastics with plants (biopolymers) which can be biodegradable and may replace currently used plastics at least in some of the fields. Rice husk (RH) is one of the major agricultural residues produced as a byproduct during the rice milling process and it can be widely used due to its properties. The incorporation of RH into polymer matrices provides advantageous characteristics, such as biodegradability, low cost, light weight, toughness, and resistance to weathering. The aim of this study was to examine the influence of the RH content and mTiO$_2$ on the thermal properties of LLDPE. In addition to RH, rutile (mTiO$_2$) was added due to its antibacterial and photocatalityc properties as well as resistance to high temperatures. LLDPE/RH/mTiO$_2$ biocomposites were prepared by mixing RH in content of 10, 20, 30, 40 and 50 wt % and 5 wt % of mTiO$_2$ in the neat LLDPE in a Brabender mixer. By DSC techniques phase transitions, TGA technique the thermal stability while by DMA technique viscoelastic properties of the LLDPE/RH/mTiO$_2$ biocomposites were obtained with the respect of RH content and addition of mTiO2. According to DSC results for LLDPE/RH/mTiO$_2$ biocomposites changes in the melting (T_m) and crystallisation (T_c) temperature indicated that there was some degree of interaction between LLDPE, RH and mTiO$_2$. The TGA results show that the LLDPE is more thermally stable with addition of mTiO$_2$. The viscoelastic properties were improved with the addition of mTiO$_2$.

Keywords: Linear low density polyethylene, rice husks, mTiO$_2$, biocomposites, thermal properties

1.   INTRODUCTION

During the last few decades, polymer composites because of their superior properties such as high strength to weight ratio, good electrical insulation, ability to transfer load, and easy and inexpensive processing have been of interest to industry and academia. However, petroleum-based products creates ecological and enviromental problems due to non-biodegradable polymers which release harmful chemicals and toxic gases. This results in synthesis of polymers for the production of biodegradable polymers by inexpensive and renewable resources such as cellulose, starch, lignin, proteins and vegetable oils has attracted the attention of scientists around the world and has shown a promising path to the sustainable development of new products. Biodegradable polymers/fibers are biocompatible and degrade in the surounding enviroments without causing any environmental pollution. Natural fibers such as banana,rice husks, jute, sisal and hemp have advantages such as low cost, less weight, easy to process and bio-degradable compared to the synthetic fibers.[1] Because of that natural fibers can be used an alternative material to conventional synthetic fibers such as glass, carbon, boron and kevlar fibers. Most natural fibers consist of cellulose, hemicelluloses,lignin and other

low molecular weight compounds. Over the last years, remarkable attention has been paid to eco-friendly, sustainable materials for various applications. In this context, rice husks (RH) was used as reinforcing element in green polymer composites. RH is characterized by its abundance, renewability, low-price, low density and high strength to weight ratio. Polymer composites incorporating fillers can result in materials with improved the different properties such as mechanical, thermal, flame retardancy and water absorption behaviour [2]. The improvement of mechanical and thermal properties can be achieved by the addition of inorganic filler namely titanium dioxide (TiO_2). TiO_2 is a versatile material with interesting characteristics biocompatible, chemical stability, high reactivity, antibacterial properties, electrochemical properties, low cost, and safe production. Thermal analysis (TA) is one of the group of techniques, which is used in the characterization of polymeric materials to give information, which are often unavailable via using other techniques. Therefore, thermal analysis is a perfect and versatile tool for characterizing composite materials in a wide temperature range.In this work thermogravimetry (TG), differential scanning calorimetry (DSC) and dynamic-mechanical analysis (DMA) were used to characterize the influence of RH and microsized TiO_2 on the thermal and dynamic-mechanical properties.In the aim to develop biocomposites with better biodegradation properties RH particles were added in the LLDPE polymer. For expect is that the RH particles will stimulate biodegradation process of synthetic LLDPE polymer.This study is the preliminary for the further investigations which will be directed on the determination of photocatalytic effect of $mTiO_2$ in the LLDPE/RH biocomposites and biodegradation process.

2. EXPERIMENTAL

2.1. Materials

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/cm^3 was supplied from Equate Pertrochemical Company, Kuwait. The rice husk (RH) was donated from rice factory in Kocani, Macedonia, and the rice cultivar was 'Sant Andrea' (Oryza sativa L. 'Sant Andrea'), Italy. Microsized TiO_2 (Aeroxide P25, Titania, Titanium dioxide) in the form of white powder, molecular weight 79.87 $gmol^{-1}$ and density of 3.9 $g\ cm^{-3}$ was purchased from Sigma-Aldrich Chemistry.

2.2. Preparation of biocomposites

In this work, two series of biocomposites formulation of LLDPE reinforced rice husk without and with TiO_2 incorporation were prepared. LLDPE biocomposites containing RH (content 10-50 wt%) and 5 wt% of $microTiO_2$ were prepared by the melt-mixing in the Brabender kneading chamber at 155 °C for 5 minutes (screw rotation speed was 60 rpm). The RH were chopped to small size in IKA-WERKE M20 mixer and dried in an air-circulating oven at 105 °C for 24 h to remove any residual water prior to mixing with LLDPE. The biocomposites 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

The viscoelastic properties (storage modulus E' and loss modulus E'') of the LLDPE and LLDPE/RH biocomposites without and with $mTiO_2$ were measured using a dynamic mechanical analyser (DMA 983, TA Instruments). The measurements were performed at a frequency of 1 Hz and at a oscillation amplitude of 0.2 mm. The temperature range was from -100 °C to 120 °C at a heating rate of 3 °C/min. The specimen dimensions were 20 x 13 x1 mm. The samples were cooled to -100 ºC using liquid nitrogen.

DSC analysis was carried out using a differential scanning calorimeter DSC Mettler Toledo 822e. The measurements were carried out in the temperature range from -100 to 150 °C at a heating rate of 10 C/min, in two heating/cooling cycles and inert atmosphere of nitrogen. Samples of 9-10 mg were placed into aluminium pans with a lid and were hermetically-sealed. Thermal parameters such as melting temperature (T_m),

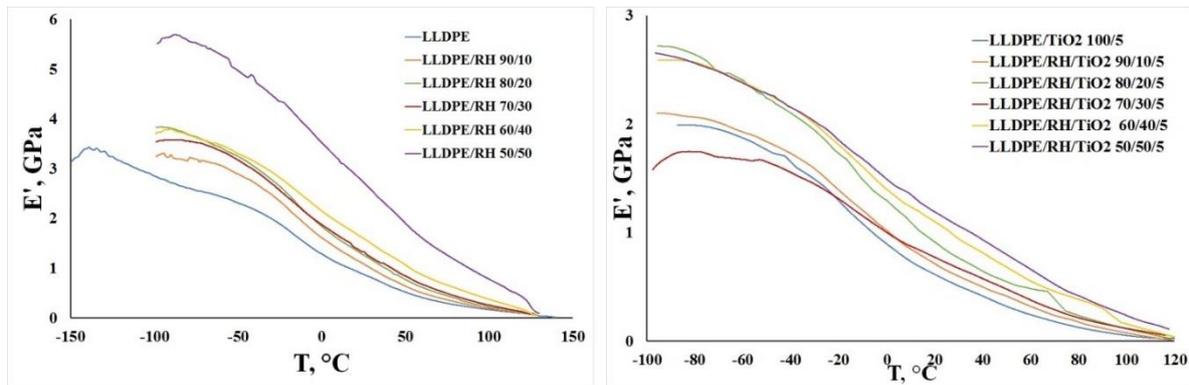crystallization temperature (T_c), heat of melting (ΔH_m) and the percentage of crystallinity (X_c), of the studied biocomposites were analyzed.

Thermogravimetric (TG) and Differential Thermogravimetric (DTG) measurements were performed with TA Instruments Q500 system analyzer to obtained the thermal stability of the neat LLDPE and LLDPE/RH biocomposites without and with mTiO$_2$. Samples of approximately 10 mg was heated from 25 $^\circ$C to 600 $^\circ$C at a heating rate of 10 $^\circ$C /min under a nitrogen atmosphere (60 ml/min).

3.   RESULTS AND DISCUSSION
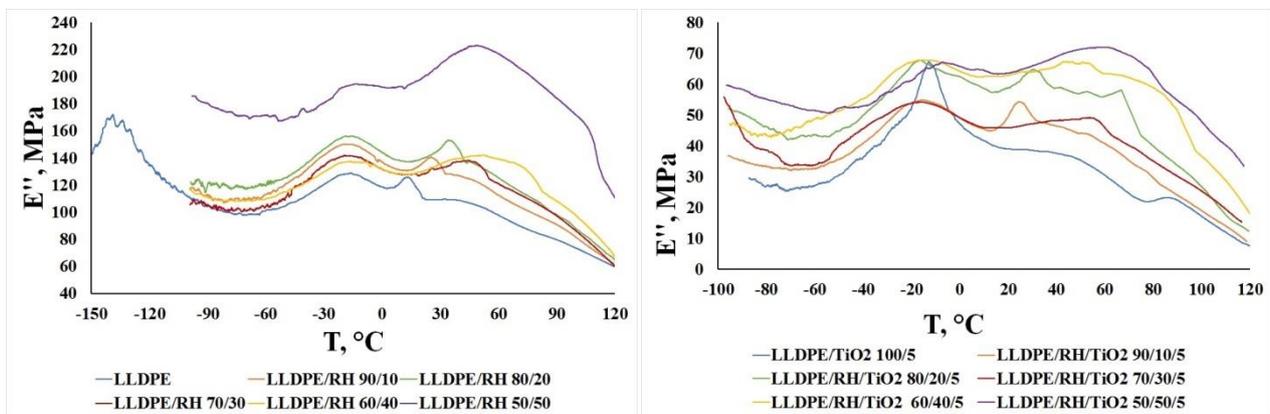
3.1.   Dynamic Mechanical Analysis (DMA)

Dynamic mechanical analysis (DMA) has become a widely used technique for the determination of the loss modulus, E'', storage modulus, E', and tanδ. Generally, the DMA properties of a composite material depend presence and content of the additives like filler, compatibiliser, and the mode of testing. The storage modulus E' of the neat LLDPE and LLDPE/RH biocomposites without and with TiO$_2$, shown in **Figure 1.**

Figure 1 Storage modulus (E') as a function of temperature of the neat LLDPE and LLDPE/RH biocomposites without and with TiO$_2$

The values of (E') at 25 $^\circ$C for the neat LLDPE and LLDPE/RH biocomposites without and with mTiO$_2$ are reported in **Table 1** and **Table 2.** As can be observed, the E' values increased with the increase of the RH content in the biocomposites without and with mTiO$_2$, due to the reinforcement imparted by the fillers that allowed greater stress transfer at the interface.

Figure 2 Loss modulus (E'') as a function of temperature of the neat LLDPE and LLDPE/RH biocomposites without and with mTiO$_2$

Figure 2 shows the temperature dependence of the loss modulus, E'' of the neat LLDPE and LLDPE/RH biocomposites without and with $mTiO_2$. For all biocomposites two relaxations are clearly observed in this temperature range. The low-temperature peak is related to the glass transition (T_g) of the amorphous LLDPE fractions. The high-temperature peak corresponds to the α_h transition related to the LLDPE crystalline fractions [3]. The E'' values corresponding to the T_g increased with incorporation of the $mTiO_2$ (**Table 2**). It may be attributed to the presence of $mTiO_2$ can enhance interaction between LLDPE matrix and RH in the biocomposites. A good interfacial interaction can be evaluated based on capability of $mTiO_2$ particles in restricting the mobility of polymer chain. As it is seen, that the α_h transition peak is significantly shifted to higher temperatures by the addition of RH (**Table 1**) and $mTiO_2$ (**Table 2**). Sirotkin et al. [4] suggest that in polyethylene α_h relaxation temperature increases with the lamellar thickness, irrespective of grade or crystallinity and is associated with c-shear within the crystalline lamellae.

Table 1 DMA results of the neat LLDPE and LLDPE/RH biocomposites without $mTiO_2$
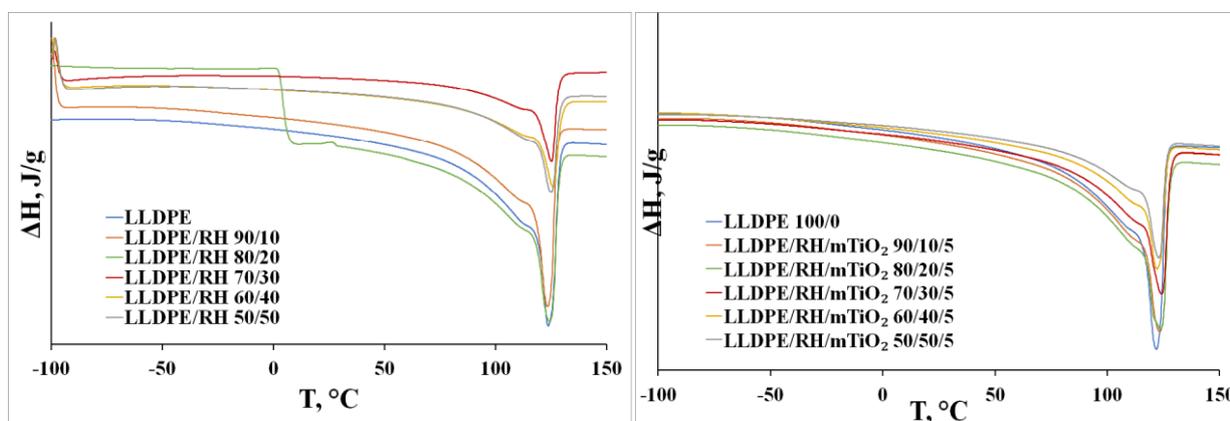
Sample	LLDPE100/0	LLDPE/RH 90/10	LLDPE/RH 80/20	LLDPE/RH 70/30	LLDPE/RH 60/40	LLDPE/RH 50/50
T_g(°C)	-16.4	-18.9	-16.3	-16.8	-16.5	-10.0
α_h (°C)	12.5	24.9	34.0	44.2	51.5	48.5
$E'_{25°C}$(GPa)	0.876	1.086	1.264	1.333	1.600	2.725

Table 2 DMA results of the neat LLDPE and LLDPE/RH biocomposites with $mTiO_2$

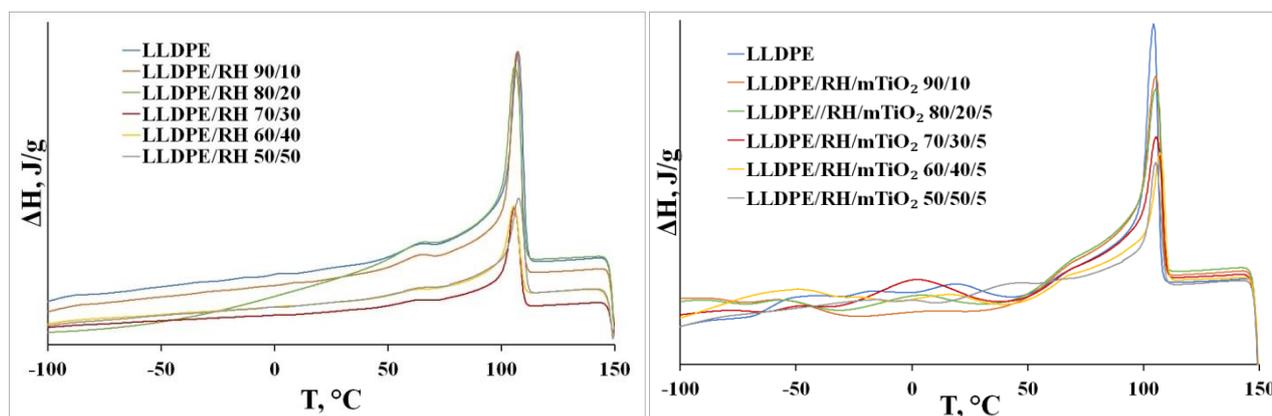| Sample	LLDPE/TiO₂10 0/5	LLDPE/RH/TiO₂ 90/10/5	LLDPE/RH/TiO₂ 80/20/5	LLDPE/RH/TiO₂ 70/30/5	LLDPE/RH/TiO₂ 60/40/5	LLDPE/RH/TiO₂ 50/50/5
T_g(°C)	-12.70	-15.38	-16.20	-14.90	-14.00	-7.08
α_h (°C)	25.75	24.31	30.42	53.92	46.76	56.87
$E'_{25°C}$(GPa)	0.5600	0.6500	0.8325	0.7210	1.0270	1.1250

3.2. Thermal behaviour of biocomposites

Differential scanning calorimetry (DSC) was used to investigate the effect of the RH and $mTiO_2$ filler on the thermal properties of biocomposites. The DSC curves of 2nd heating and cooling cycles of the neat LLDPE and LLDPE/RH biocomposites without and with $mTiO_2$ are shown in **Figure 3** and **Figure 4,** respectively.

Figure 3 DSC curves of 2nd heating cycle for the neat LLDPE and LLDPE/RH biocomposites without and with $mTiO_2$

The effect of RH content and introduction of $mTiO_2$ on T_m for the LLDPE/RH biocomposites is presented in **Table 3** and shows no significant changed in T_m for the biocomposites. The DSC curves of the neat LLDPE

and LDPE/RH biocomposites without and with mTiO₂ during the 2nd cooling cycle are shown in **Figure 4**. The determined crystallization temperature, T_c, values are listed in **Table 3** and **Table 4**. The T_c of the biocomposites had slightly shifted to a higher temperature compared to the neat LLDPE with the incorporation of RH and mTiO₂. A change in crystallization temperature in the presence of fillers reflects changes in the nature of relaxation processes occurring in thin layers at the polymer-phase interface. A low shoulder observed in the low point of temperature side of the cooling peak of the LLDPE indicating paracrystalline structure.

Figure 4 DSC curves of 2nd cooling cycle for the neat LLDPE and LLDPE/RH biocomposites without and with mTiO₂

Table 3 DSC results after 2nd heating/cooling cycle of the neat LLDPE and LLDPE/RH biocomposites without mTiO₂

Sample	LLDPE100/0	LLDPE/RH 90/10	LLDPE/RH 80/20	LLDPE/RH 70/30	LLDPE/RH 60/40	LLDPE/RH 50/50
T_m (°C)	120.8	122.5	124.0	123.4	123.6	123.7
T_c (°C)	104.2	105.5	104.3	105.1	105.5	106.1
ΔH_m (Jg^{-1})	118.41	113.80	105.01	92.99	75.02	63.36
χ_c (%)	40.4	43.2	44.8	45.3	42.7	43.2

Table 4 DSC results after 2nd heating/cooling cycle of the neat LLDPE and LLDPE/RH biocomposites with mTiO₂

Sample	LLDPE/TiO₂ 100/5	LLDPE/RH/TiO₂ 90/10/5	LLDPE/RH/TiO₂ 80/20/5	LLDPE/RH/TiO₂ 70/30/5	LLDPE/RH/TiO₂ 60/40/5	LLDPE/RH/TiO₂ 50/50/5
T_m (°C)	121.3	122.1	124.0	123.6	121.6	122.6
T_c (°C)	104.9	105.8	104.3	105.8	107.6	105.4
ΔH_m (Jg^{-1})	125.4	120.6	119.94	94.6	76.16	60.9
χ_c (%)	42,8	48.1	53.9	48.6	45.6	44.0

The crystallinity of LLDPE and LLDPE/RH biocomposite without and with mTiO₂ (χ_c %) was calculated according to Equation (1). A increase of the crystallinity can be observed when the mTiO₂ are incorporated in the LLDPE/RH biocomposites (**Table 4**). These results can be explained by the strong nucleation ability of the mTiO₂ on LLDPE.

$$\chi c = \left(\frac{\Delta H_m^0}{\Delta H_m^{100} x \left(1 - \frac{\% RH}{100} \right)} \right) x100 \tag{1}$$
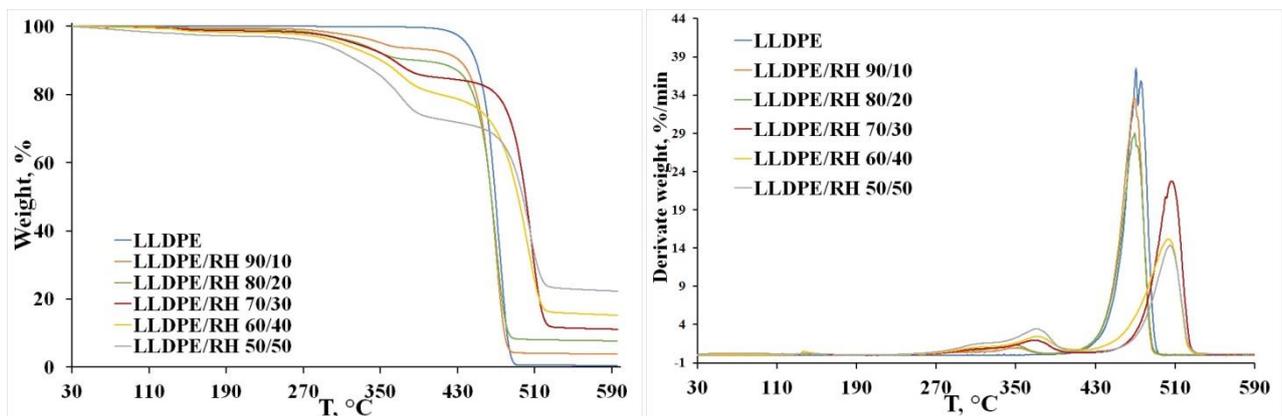
where:

ΔH_m^0 - the value of melting enthalpy read from the surface of melting endotherm (Jg^{-1})

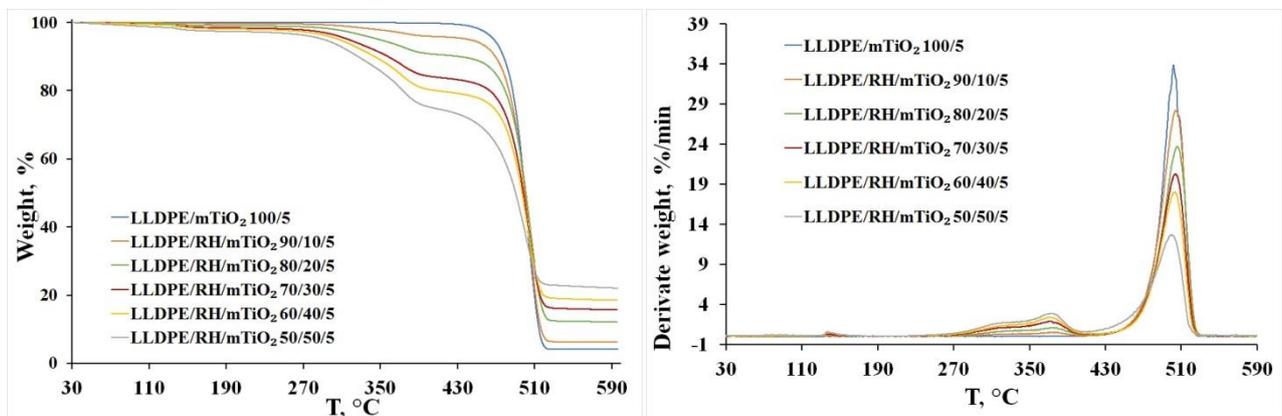ΔH_m^{100} - the melting enthalpy of 100 % crystalline LLDPE (293,0 Jg^{-1}).

3.3.   Results of Thermogravimetric Analysis (TGA)

A TG analysis was very useful tehnique 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 without and with mTiO$_2$ was investigated. The TG and DTG curves of LLDPE/RH biocomposites without and with mTiO$_2$ are represented in **Figure 5** and **Figure 6**, respectively.

Figure 5 TG and DTG curves of the neat LLDPE and LLDPE/RH biocomposites without mTiO$_2$

Figure 6 TG and DTG curves of the neat LLDPE and LLDPE/RH biocomposites with mTiO$_2$

Table 2 shows the initial degradation temperature ($T_{ini.}$), the temperature corresponding to final temperature of thermal degradation (T_{end}) and the residual mass of the biocomposites at 600 °C. As can be seen from the DTG curve LLDPE degrades in one degradation stage while the both LLDPE/RH biocomposites series degrades up to three degradation stages. The first two stages corresponding to those of RH (due to the loss of water in RH and to the thermal decomposition of hemicellulose, cellulose and lignin in RH) and the third one was due to thermal degradation of LLDPE. As expected, the area of the first two peaks in the DTG curves increases with the RH content, whereas the area of the third peak decreases with it. The increase in RH content in the LLDPE/RH biocomposites decreased the thermal stability of biocomposites. This is due to the lower thermal stability of the RH. In addition, the weight loss starts at the higher temperature for biocomposites with mTiO$_2$. It shows that thermal stability of LLDPE/RH biocomposites was significantly improved by the incorporation of mTiO$_2$. The value of the residual at 600°C of LDPE/RH biocomposites increase with increasing

RH content and it was mainly related to the silica content of RH (96%). It can be seen that the residue of LLDPE/RH/mTiO$_2$ biocomposites is a little higher than that of LLDPE/RH biocomposites.

Table 5 TGA results of the neat LLDPE and LLDPE/RH biocomposites without mTiO$_2$

Sample	LLDPE10 0/0	LLDPE/RH 90/10	LLDPE/RH 80/20	LLDPE/RH 70/30	LLDPE/RH 60/40	LLDPE/RH 50/50
$T_{ini.}$ (ºC)	439.8	352.9	329.4	324.4	310.6	308.1
$T_{fin.}$ (ºC)	484.1	480.7	481.3	520.2	516.5	517.6
Residue at 600ºC	0.515	3.8	7.7	11.1	15.2	22.3

Table 6 TGA results of the neat LLDPE and LLDPE/RH biocomposites with mTiO$_2$

Sample	LLDPE/TiO$_2$ 100/5	LLDPE/RH/TiO$_2$ 90/10/5	LLDPE/RH/TiO$_2$ 80/20/5	LLDPE/RH/TiO$_2$ 70/30/5	LLDPE/RH/TiO$_2$ 60/40/5	LLDPE/RH/TiO$_2$ 50/50/5
$T_{ini.}$ (ºC)	467.6	467.9	467.8	468.2	475.1	457.5
$T_{fin.}$ (ºC)	513.7	515.7	467.8	522.4	525.0	512.6
Residue at 600ºC	4.1	6.2	12.2	15.7	18.5	22.2

4. CONCLUSION

In this study we prepared the LLDPE/RH biocomposites with different content of RH particles and withouth and with the addition of TiO$_2$ with the aim to investigate the effect of RH and mTiO$_2$ on the phase transitions, viscoelastic properties and thermal stability. For expect is that the RH particles and mTiO$_2$ will improve thermal properties important in the application of this biocomposites as packing materials. By adding and increasing the content of RH the storage modulus (E') for the LLDPE/RH biocomposites was higher than that of the neat LLDPE, because of the increasing stiffness of the biocomposites. The incorporation of mTiO$_2$ as filler to LLDPE/RH biocomposites, the T$_g$ increases due to the reduced segmental mobility of LLDPE. On the other side the presence of the RH and mTiO$_2$ does not affect T$_m$ of the LLDPE/RH biocomposites. DSC results indicate that the addition of mTiO$_2$ favors the nucleation process; thus, the *Xc* values of the LLDPE/RH/mTiO$_2$ biocomposites are higher than those of LLDPE/RH biocomposites. On the bases of TGA measurements the incorporation of the mTiO$_2$ gives rise to a considerable increase of the thermal stability of LLDPE/RH biocomposites.

REFERENCES

[1] VAISANEN T., DAS O., TOMPPO L. A review on new bio-based constituents for natural fiber-polymer composites, *Journal of Cleaner Production*. 2017, vol. 149, pp. 582-596. Available from: https://doi.org/10.1016/j.jclepro.2017.02.132.

[2] PRAVEENKUMARA J., GIRIJAPPA Y. G., Thyavihalli, PUTTEGOWDA M., RANGAPPA S. M., SIENGCHIN S. Effect of natural filler materials on fiber reinforced hybrid polymer composites: An Overview, *Journal of Natural Fibers*. 2020, vol. 19, pp.1-16. Available from: https://doi.org/10.1080/15440478.2020.1854145.

[3] TURI, E. A. "Thermal Characterization of Polymeric Materials". 2nd Edition. Academic Press, 1997, pp 2420.

[4] SIROTKIN, R. O., BROOKS, N. W. The Dynamic Mechanical Relaxation Behavior of Polyethylene Copolymers Cast from Solution. *Polymer*. 2001, vol.42, pp. 9801-9808. Available from: https://doi.org/10.1016/S0032-3861(01)00535-3.