EFFECTS OF WOOD FLOUR ON THE MECHANICAL, THERMAL AND MORPHOLOGICAL PROPERTIES OF POLY (L-LACTIC ACID)-CHITOSAN BIOPOLYMER COMPOSITES

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ABSTRACT

The aim of this paper was to investigate the effects of wood flour on the mechanical, morphological and thermal properties of poly (L-lactic acid) (PLA)-chitosan biopolymer composites produced by compression molding. The composites were characterized by a combination of mechanical properties, scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The addition of chitosan to PLA matrix reduced the tensile strength from 57,1 MPa for pure PLA to 34,3 MPa for 5% chitosan and 11,5 MPa for 10% chitosan, and the flexure strength from 72,3 MPa for pure PLLA to 30,4 MPa for 5% chitosan and 24,6 MPa for 10% chitosan. The change trend in the young's modulus was found to be similar as compare with the tensile strength. However, the flexure modulus generally increased with the addition of the chitosan as comparison with pure PLA. The mechanical properties of the PLA-chitosan blends with wood flour were found to be lower than theirs of the pure PLA. According to SEM images, some holes and small voids at various diameters on the fractured section of the all composites were seen. T_{onset}, $T_{10\%}$, $T_{50\%}$, $T_{85\%}$ of the pure PLA decreased with the addition of both chitosan and wood flour. Thermal stability of the PLA-chitosan blends was determined to be better than the PLA-chitosan composites with wood flour.

Keywords: Bio-based composites, DSC analysis, mechanical properties, *Pinus sylvestris*, TGA analysis, wood flour.

INTRODUCTION

In recent years, polylactic acid (PLA) has gained interest due to being made from renewable resources and biodegradability and an alternative to petroleum-based polymers. The concern of non-biodegradable polymers is its end of life use. Therefore, biodegradable biopolymers such as polylactic acid (PLA), polyhydroxybutyrate (PHB), polycaprolactone (PCL) can be an alternative solution for environmental problems (Abdelwahab *et al.* 2012, Ebadi-dehaghani *et al.* 2016). PLA is produced either by the polycondensation of lactic acid or by the ring opening polymerization of lactide. Lactide obtained from the fermentation of renewable sugar source, such as corn or sugar beets is a cyclic dimmer prepared by depolymerization of lactic acid (Rhim *et al.* 2009). PLA has received great interest due to its high mechanical properties, biodegradability and biocompatibility (Garlotta 2001, Wu and Wu 2006). In the early stages of biopolymers, commercial biopolymers were used in limited areas, such as preparation of medical devices (bone surgery, suture, and chemotherapy, etc.) due to high production costs. As production cost of PLA has been lowered by new technologies, applications and large-scale production. Usage area of PLA has been extended to other commodity areas such as packaging, textiles and composite materials (Drumright *et al.* 2000). PLA applications have a significant potential for the commercial packaging industry duo to stiff films of high transparency and can be processed using readily available production technologies. However, brittleness and other properties such as low thermal stability,

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Maderas. Ciencia y tecnología 21(4): 611 - 618, 2019

Universidad del Bío-Bío

medium gas barrier properties and low solvent resistance of the pure polymer limit its food packaging applications (Petersen *et al.* 2001). Moreover, thermal properties, toughness, water vapor and gas barrier properties of PLA are lower to those of classical petroleum-based polymers (Maazouz *et al.* 2011). To overcome these drawbacks, many approaches have been established, including copolymerization, compounding with nanofillers and blending with other polymers (Ying *et al.* 2007, Fukushima *et al.* 2009, Wu *et al.* 2006). Many studies have focused on blending PLA with other biopolymers (chitosan, starch, PHBV, PBAT, PHB) (Wu *et al.* 2006, Zhao *et al.* 2013, Abdelwahab *et al.* 2012, Armentano *et al.* 2015).

Chitin, one of the biopolymers is a polysaccharide made up of N-acetyl-glucosamine and N-glucosamine units. When the N-acetyl-glucosamine units are more than 50%, the biopolymer is called chitin (Khor and Lim 2003). Chitosan is a linear cationic polysaccharide obtained by deacetylation of chitin derived from crustaceans such as crabs and shrimp. Since chitosan is a non-toxic, biocompatible and cost-effective material, this polymer is mainly used for biomedical and agricultural purposes (Sinha *et al.* 2004). Chitosan is known to interact with cells and cellular lysozyme degrades chitosan in-vivo (Tomihata and Ikada 1997).

The aim of this study was to investigate the effects of wood flour as reinforcing filler on the mechanical, thermal and morphology properties of polylactic acid (PLA)-chitosan blends.

MATERIALS AND METHODS

Materials

Poly L-lactic acid (PLLA) was supplied by Good Fellow, England. Density of PLLA has 1,24 g/cm³. Chitosan (CAS: 9012-76-4) having properties such as average Mn 5000, wt 310000-375000 Da, 60% oligosaccharide and > 75% deacetylation was obtained from Sigma-Aldrich (Germany). Wood flour was prepared with grinding of Scots Pine (*Pinus sylvestris* L.) which was supplied from a local mill. All materials were stored in sealed containers after being oven dried to 24 hours at 103±2°C for wood flour, at 50°C for polylactic acid (PLA) and chitosan. The scots pine wood composes of 71,4% carbohydrates; 27,6% lignin; 0,4% ash, and 06% extractives (Kilic *et al.* 2010). Chitosan composes of β-(1→4)-linked D-glucosamine and N-acetyl-D-glucosamine (Das and Patra 2017).

Compounding

Biopolymers and wood flour were blended with speed mixer and then the blends were compounded using a twin screw extruder with 16 mm screw diameter and L/D ratio of 20 (Aysa Instruments, Turkey). Rotor speed and process temperature was set at 65 rpm and 165°C, respectively. The extruded blends were passed across a water bath and they was pelletized. The extruded blends were ground in a grinder (Aysa Instruments, Turkey), and then the pellets dried to 24 hours before compression molding. The temperature used for compressing molding, the compression pressure and pressure duration was 175 °C, 25 bars, and 5 min, respectively. Three panels with dimension of 20 x 20 x 3 mm³ for each formulation were produced with the compression molding, and mechanical test samples were obtained with cutting of the panels according to the related standards in the characterization section. The mechanical samples were prepared with sizing of the panels by a saw cutter. Ten replicates for the mechanical testing of all formulation were prepared. Experimental design of the PLA-chitosan blends and their composites with wood flour is shown in Table 1.

Table 1: Experimental design of the PLA-chitosan blends and their composites with wood flour.

	Polylactic acid-PLA (%)	**Chitosan (%)**	**Wood Flour (%)**
Neat PLA	100	0	
PLA5	95	5	
PLA10	90	10	
PLA5-10%	85,5	4,5	10
PLA5-20%	76	4	20
PLA10-10%	81	9	10
PLA10-20%	72	8	20

Effects of wood flour... Altuntas and Aydemir

Maderas. Ciencia y tecnología 21(4): 611 - 618, 2019

Characterization

The tension tests were conducted according to the American Society of Testing and Materials (ASTM) standard D 638-14. All the tension tests were done at a rate of 0,5 cm /min. The flexure tests were conducted according to ASTM D 790-17, Test Method 1, Procedure A, i.e. three-point loading system. The tests were run at a test speed of 1,27 mm/min. The impact tests were conducted according to ASTM D 256-10. A mechanical tester with 5 kN loading capacity (Zwick, Austria) was used to the mechanical testing. The results obtained were presented as an average for tested samples.

TGA was tested using Hitachi STA 7300 analyzer with a heating rate of 10°C/min from room temperature to 600°C, under nitrogen with a flow rate 20 ml/min to avoid sample oxidation.

DSC analysis of the samples was performed using a Perkin Elmer 6000 analyzer on samples of about 5 mg. For all specimens, testing was adopted heat/cool methods. All samples were heated to 25°C to 300°C at a ramp rate 10°C/min and cooled with same ramp. Melting temperature (T_m), crystallization temperature (T_c), glass transition temperature (T_g), glass transition enthalpy (ΔH_g), melting enthalpy (ΔH_m), crystallization enthalpy (ΔH_c), crystallinity (X_c) of the materials was determined from thermograms.

The samples were observed with an environmental scanning electron microscopy (ESEM), the Tescan MAIA3 XMU-SEM at an acceleration voltage of 5 kV. All samples surface was sputter-coated with gold using a Denton sputter coater for enhanced conductivity.

For the tensile and flexural strength, tensile and flexural modulus of elasticity and impact strength values, all multiple comparisons were first subjected to an analysis of variance (ANOVA) at the 99% confidence level, and significant differences between mean values of the samples were determined using Duncan's multiple range test. The significant differences between the samples were shown with letters, such as A, B, C, and D.

RESULTS AND DISCUSSION

Mechanical properties

The effects of wood flour on the mechanical properties of polylactic acid-chitosan biopolymer blends were investigated, and according to the obtained results (one-way ANOVA and Duncan test), the changes in both in groups and among the groups were found to be statistically significant. Table 2 shows mechanical properties such as tensile strength, young's modulus, flexure strength, flexure modulus, and izod impact strength of the all composites. The addition of chitosan to PLA matrix reduced the tensile strength from 57,1 MPa for neat PLA to 34,3 MPa for 5% chitosan and 11,5 MPa for 10% chitosan, and the flexure strength from 72,3 MPa to 30,4 MPa for 5% chitosan, 24,6 MPa for 10% chitosan. Therefore; it can be said that chitosan has to be a negative effect on the mechanical properties of neat PLA. The addition of wood flour was found to generally decrease the mechanical properties of PLA-chitosan blends. When loadings of wood flour were raised from 10% to 20%, the tensile strength of chitosan-PLA blends increased to the composites with both 5% and 10% chitosan. However; both the tensile strength of all the PLA-chitosan composites with wood flour were found to be lower as comparison with neat PLA. The change trend in the young's modulus was found to be similar as compare with the tensile strength expect for 10% chitosan-PLA blends with 20% wood flour. The young's modulus of 10% chitosan-PLA biopolymer composites increased as 3,3% with 20% wood flour, and the young's modulus of the other all composites decreased, and the largest decrease ratio was found to be 22,6%. As results, the addition of the chitosan effected more the tensile strength as compare with young's modulus.

Table 2: Mechanical properties of the PLA-chitosan composites.

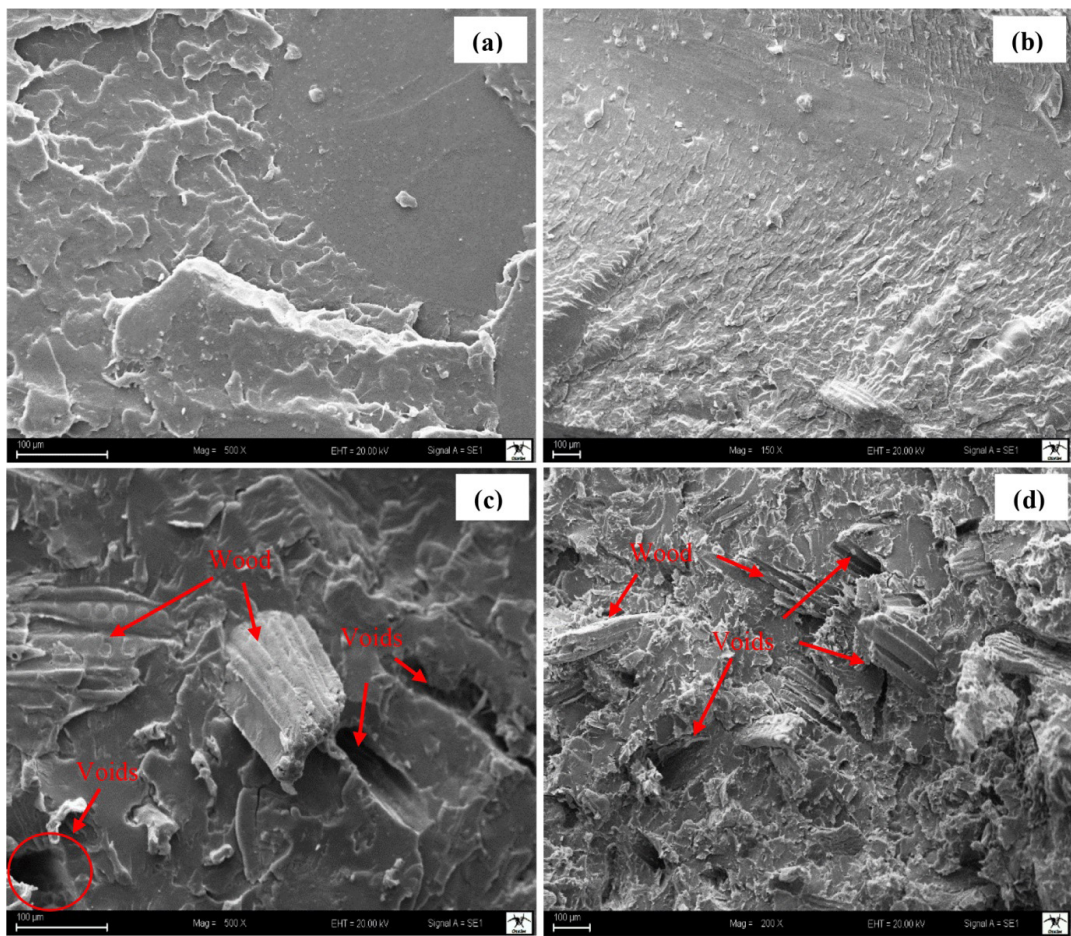| Compositions	Tensile Strength (MPa)	Young's modulus (MPa)	Flexure Strength (MPa)	Flexure Modulus (GPa)	Izod Impact Strength (kJ/m²)
Neat PLA	57,1 A	1,5 CD	72,3 C	3,1 A	2,8 D
PLA5	34,3 B	1,4 BCD	30,4 C	3,3 A	2,5 C
PLA5-10%	13,9 F	1,3 A	16,4 A	3,2 A	2,3 C
PLA5-20%	19,7 EF	1,4 B	20,8 B	3,5 B	1,3 B
PLA10	11,5 C	1,1 BCD	24,6 B	4,4 C	1,2 B
PLA10-10%	15,9 DE	1,4 BC	21,8 B	3,9 B	1,3 B
PLA10-20%	17 CD	1,5 D	23,6 B	4,4 C	1,0 A

As seen to Table 2, the flexure strength values of the neat PLA (72,3 MPa) decreased with the addition of the chitosan to 30,4 MPa for 5% chitosan and 24,6 MPa for 10% chitosan. When the loading of the chitosan to PLA matrix raised, the flexure strength was found to decrease more. The addition of wood flour to PLA-chitosan blends also decreased to the flexure strength of PLA-chitosan blends for both 10% and 20% loadings. The change trend in the flexure modulus value of the PLA-chitosan composites was found to be not similar as compare with young's modulus/tensile strength and flexure strength. Because the addition of the chitosan increased at 7,5% for 5% chitosan and 42,3% for 10% chitosan the flexure modulus of the all PLA-chitosan blends. The addition of the wood flour to the chitosan-PLA blends provided an improvement on the flexure modulus of the PLA-chitosan blends as comparison with pure PLA. Although the addition of the chitosan generally decreased the flexure strength, the addition of the chitosan and wood flour increased the flexure modulus of the all PLA-chitosan composites. The izod impact strength values of the PLA-chitosan composites were given in Table 2.

The addition of the chitosan decreased to 10.7% for 5% chitosan and 57,1% for 10% chitosan to the izod IS of the all PLA-chitosan composites. The izod IS of the chitosan-PLA blends generally decreased with the loading of wood flour. The maximum decrease in the izod IS was found at 54,2% for 10% chitosan-PLA with 20% wood flour. An incompatibility between chitosan and PLA was reported by Suyatma *et al.* (2003). Therefore, it can be said that the addition of the chitosan decreased all the mechanical properties such as young's modulus, tensile strength, flexure strength except for flexure modulus. In this study, the wood flour was found to provide some improvements on the mechanical properties of the PLA-chitosan blends. In another study, the addition of wood flour to the PLA matrix was determined to increase the mechanical properties of the PLA composites (Shah *et al.* 2008). In a similar study, the addition of chitosan was raised from 0% to 30 %, tensile strength of PLA-chitosan blends was found to decrease. The decrease of the tensile strength with increasing content of chitosan was found to provide an increase in young's modulus (Quiroz-Castillo *et al.* 2015).

Scanning electron microscopy (SEM)

SEM images of the PLA-chitosan composites for 5% chitosan (a) and 10% chitosan (b), and the blends with 10% wood flour (c), 20% wood flour (d) were given in Figure 1.

Effects of wood flour... Altuntas and Aydemir

Maderas. Ciencia y tecnología 21(4): 611 - 618, 2019

Figure 1: SEM images of the PLA-chitosan composites ((a): 5% chitosan, (b): 10% chitosan, (c): the blends with 10% wood flour, (d): the blends with 20% wood flour).

The blending was homogenously provided according to SEM images in Figure 1a and Figure 1b, and any voids in the inner structure of the chitosan-PLA blends cannot be determined. The morphological properties of the blends changed with addition of the wood flour, and some holes between wood flour and the matrix blends were found. In a study on the morphological properties of PLA-chitosan composites, it was found that the PLA-chitosan fractured surfaces were covered with fillers, and a number of micro voids and holes throughout the fractured surface. The fractured surface was also determined to be smooth and homogeneous surfaces upon incorporation of CS in the PLA matrix (Zakaria *et al.* 2013). The similar results were obtained by Shah *et al.* (2008).

Thermogravimetric analysis (TGA/DTG)

The TGA curves of the PLA-chitosan composites were given in Figure 2. Three stages of mass loss are associated with the TGA curve after heating from 25°C to 900°C. The first stage, which is up to 250°C, is usually associated with the release of moisture, humidity or other volatiles from the biopolymer. The second stage (up to about 500°C) corresponds to volatilization stages of thermally degraded units and show relatively big DTG curve in Figure 2. The final third stage extends to the ending test temperature at 650 °C in association with more than 83,9 wt. % of loss for 5% chitosan-PLA blends with 20% wood flour. The results of T_{onset}, $T_{10\%}$, $T_{50\%}$, $T_{85\%}$ and mass loss at 600°C were listed in Table 2.

Maderas. Ciencia y tecnología 21(4): 611 - 618, 2019

Universidad del Bío-Bío
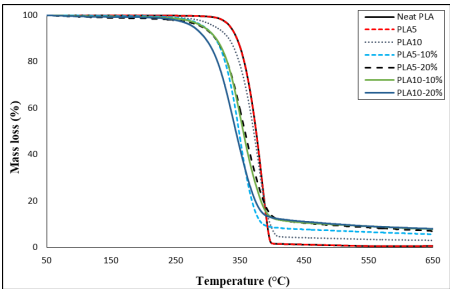
Figure 2: The TGA curves of the PLA-chitosan composites.

As seen as Table 3, T_{onset}, $T_{10\%}$, $T_{50\%}$, $T_{85\%}$ of the PLA-chitosan composites decreased with the addition of both chitosan and wood flour. Thermal stability of the biopolymer blends was determined to be better than the PLA-chitosan composites with wood flour. The maximum and minimum temperature for $T_{50\%}$ were determined as 344°C for 10% chitosan-PLA blends with 20% wood flour and 376°C for neat PLA, respectively. The mass loss of the PLA-chitosan composites was found to decrease from 99% for neat PLA to 84% for 5% chitosan-PLA blends with 20% wood flour. The thermal decomposition temperature (T_{onset}, $T_{10\%}$, $T_{50\%}$, $T_{85\%}$) and mass losses of the PLA-chitosan blends were found to be lower than the neat PLA matrix. As a result, it can be said that both chitosan and wood flour decreased the thermal stability of the neat PLA. In a study, Bonilla *et al.* (2015) found that the incorporation of chitosan did not promote significant changes in the thermal behavior of neat PLA. The similar results were obtained by Quiroz-Castillo *et al.* (2015).

Table 3: The summary of TGA curves of PLA-chitosan composites.

Composites	T_{onset} (°C)	$T_{10\%}$ (°C)	$T_{50\%}$ (°C)	$T_{85\%}$ (°C)	Mass loss (%)
Neat PLA	355	347	376	391	99
PLA5	336	346	375	390	95
PLA10	347	332	371	392	92
PLA5-10%	331	311	348	374	88
PLA5-20%	322	312	358	395	84
PLA10-10%	326	313	355	391	86
PLA10-20%	313	296	344	385	93

Differential scanning calorimetry (DSC)

T_g, T_m, T_c, X_c and the enthalpies of the PLA-chitosan composites were given in Table 4. DSC analysis was conducted with cooling and heating of the neat biopolymers and the PLA-chitosan composites. T_g, T_c and T_m changed with the loadings of the chitosan and wood flour. The highest value of T_g was found as 58°C for neat PLA, and 55°C for 10% chitosan-PLA biopolymer blends. T_g decreased with the addition of the wood flour. Both T_m and T_c decreased with chitosan and wood flour. The maximum and minimum temperature value in the T_m and T_c of the PLA-chitosan composites were determined as 147°C for 5% chitosan-PLA blends and 119°C for 10% chitosan-PLA blends with 20% wood flour, and 134°C for 5% chitosan-PLA blends with 10% wood flour and 108°C for 5% chitosan-PLA blends. X_c values of the PLA-chitosan composites increased with the addition of the chitosan, and the maximum X_c was found as 35% for 10% chitosan-PLA blends. However, the addition of the wood flour to biopolymer blend matrix was determined to decrease the X_c of the PLA-chitosan composites with wood flour. The maximum and minimum X_c of the PLA-chitosan composites was measured as 26% for 10% chitosan-PLA blends with 20% wood flour and 20% for 5% chitosan-PLA blends with 20% wood flour. In a study conducted on the thermal properties of chitosan-polylactic acid, it was found that the increase of the chitosan addition in the composite films caused to a decrease in the T_g values. The decreasing in T_g values was found to be due to additional action of chitosan - most probably the increased hydrophilicity of the composite films causes higher amount of bound water, which acts as a plasticizer (Marudova *et al.* 2015, Bonilla *et al.* 2015, Quiroz-castillo *et al.* 2014). In another study, no significant effects of the chitosan addition on the T_g and T_m values was observed, which can be due to the lack of miscibility of both polymers. However; crystallization temperature (T_c) of the composites significantly increased with the addition of chitosan particles (Bonilla *et al.* 2015).

Effects of wood flour... Altuntas and Aydemir

Maderas. Ciencia y tecnología 21(4): 611 - 618, 2019

Table 4: The summary of DSC results of PLA-chitosan composites.

Composites	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	X_c (%)
Neat PLA	58	150	22	127	24
PLA5	53	147	29	108	33
PLA10	55	139	30	115	35
PLA5-10%	53	134	20	116	24
PLA5-20%	50	138	15	119	20
PLA10-10%	50	138	21	116	25
PLA10-20%	54	137	19	119	26

CONCLUSIONS

Chitosan was efficiently blended with PLA matrices by extrusion in 5% and 10% of the biopolymer matrix. The addition of wood flour to PLA-chitosan blends were added with the addition of 10% and 20%. The presence of chitosan decreased the all mechanical properties such as tensile strength, young's modulus, flexure strength and izod impact strength except for flexure modulus. In the fractured surfaces of PLA-chitosan blends, some micro voids and holes between polymer matrix and fillers were determined. TGA analysis showed that the addition of both chitosan and wood flour were decreased the thermal stability of the pure PLA. According DSC analysis, Tg, Tc and Tm of the PLA-chitosan composites were found to be lower than neat PLA. As a result, the addition of chitosan can be said to have a negative effect on the mechanical and thermal properties of the PLA and the wood flour provided some improvements on the all mechanical and thermal properties of PLA-chitosan composites. New studies should be conducted to find the effects of the chitosan on blending of chitosan with polylactic acid and the reinforcing of wood flour of their blends.

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