INFLUENCE OF DIFFERENT PROCESSING TECHNIQUES ON THE THERMAL PROPERTIES OF POLY(L-LACTIDE)/OLIVE STONE FLOUR COMPOSITES

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Abstract
The aim of this work was to find the best processing technique for poly(L-lactide)/olive stone flour (PLLA/OSF) composites. Processing with horizontal single-screw extruder gave non-homogenous composites and was abandoned. The composites prepared using vertical twin-screw compounder followed by injection moulding and Brabender plastograph without and with pressing in hydraulic press were used for thermal analyses by differential scanning calorimetry (DSC). It was established that thermal properties of PLLA/OSF composites depend on the processing technique. To obtain most reliable results PLLA/OSF composites have to be prepared on Brabender plastograph.

1 Introduction

Poly(L-lactide) (PLLA) has been used for production of a broad array of products in the last few decades. So, researchers generally know how to process this brittle thermoplastic biodegradable polyester synthesised from renewable resources. If this polymer is used for production of composites with organic fillers than each new filler will bring new approach to processing. Olive stone flour (OSF) is organic filler produced by milling olive stones and its use is very interesting from economical and environmental point of view. As PLLA/OSF composites are new composites there is no information about their processing. It is assumed that thermal properties of PLLA/OSF composites will depend on the thermal history, i.e. on the processing procedure of PLLA composites, such as film casting, extrusion, injection moulding, compression moulding, foaming, pultrusion etc. Some of above mentioned processing techniques have been successfully applied for preparation of different PLLA composites, but not yet for the composites with OSF. Proper processing technique is very important for material with desired properties. Investigation of the long hemp fiber/PLA composites produced using different processing conditions revealed that the composites produced by film stacking gave the best result in terms of mechanical performance [1]. The studies that can be found in the literature point out two important considerations for a suitable processing technique: the impact of processing on the filler and the impact of processing on the polymer degradation [2]. Quality of the processed material also depends on variation in raw material quality, differences in bulk density of natural filler, which can lead to feeding problems and poor dispersion of the filler within a matrix as well as the poor compatibility of the filler and the matrix, poor thermal stability of the filler, etc. [2]. The aim of this work was

to find the best processing technique for PLLA/OSF composites. For the preparation of PLLA/OSF composites horizontal single-screw extruder, vertical twin-screw compounder with injection moulding and Brabender plastograph without and with pressing in hydraulic press were used. The influence of processing technique on the thermal properties of composites was investigated by differential scanning calorimetry.

2 Materials and testing methods

2.1 Materials

Poly(L-lactide), Biomer L9000, in pellet form, was purchased from Biomer (Germany), $\overline{M_v} \approx 58700$ ($[\eta]_{25^0C} = 165$ cm^{3}g^{-1} in chloroform) [3]. Olive stone flour, Jeluxyl OM 3000, was purchased from Jelu-Werk (Germany). Original OSF was sieved to obtain the finest fraction from 50 to 150 mesh size. PLLA pellets and OSF were dried in a vented oven at 100°C for 8 h prior to processing to remove moisture.

2.2 Sample preparation

PLLA was blended with various amounts of OSF, Table 1, using three different processing techniques.

Sample	PLLA [weight parts]	OSF [weight parts]
PLLA 1x	100	0
PLLA 2x	100	10
PLLA 3x	100	20
PLLA 4x	100	30

x - processing techniques: a - horizontal single-screw extruder,
b - vertical twin screw compounder,
c_1 - Brabender plastograph without pressing,
c_2 - Brabender plastograph with pressing.

Table 1. Composition of PLLA/OSF composites.

First processing technique was extrusion on horizontal single-screw extruder (Dynisco, Qualitest, Canada). The optimum rotation speed was 150 rpm and the optimum temperature was 170ºC. PLLA and OSF were also extruded on vertical twin-screw compounder (Xplore, Netherland) at 180°C, 70 rpm, with nitrogen as a protective gas. Direct moulding was performed using injection moulding machine (Xplore, Netherland) at 25°C. Third processing technique was blending on Brabender plastograph at 170°C for 3 min at 70 rpm. PLLA/OSF composites were than removed from the plastograph as small clumps and moulded at 175°C in a hydraulic hot press. After moulding samples where cooled down to room temperature and the specimen of 30×10×1 mm were obtained. Figure 1 shows used processing equipment.

Figure 1. Processing machine: a) horizontal single-screw extruder; b) vertical twin screw compounder; c) Brabender plastograph.

2.3 DSC analysis

Thermal characteristics of the samples were investigated using differential scanning calorimeter (DSC-4, Perkin-Elmer, USA) without intracooler and differential scanning calorimeter (DSC 823, Mettler-Toledo, Swiss) equipped with intracooler. Both instruments were calibrated with indium (T_m=156.8°C, ΔH_m=58.47 Jg^{-1}), and their DSC data are comparable. Before the start of measurements the system was stabilized from 0.5 to 1 hour. The closed aluminium pans were used and the measurements were performed under nitrogen atmosphere (flow rate was 30 cm^3min^{-1}). Sample weight was approx. 20 mg. The samples were heated from -50°C to 200°C at 10°Cmin^{-1} (first heating cycle), than cooled down to -50°C at 20°Cmin^{-1} (cooling cycle) and finally heated from -50°C to 200°C at 20°Cmin^{-1} (second heating cycle). Due to the impossibility to achieve temperatures below 25°C on DSC-4, measuring range was from 30 to 200°C. The crystallization temperature (T_c) and the melting temperature (T_m) were taken as the peak temperature of the crystallization exotherm and the melting endotherm, respectively, whereas the glass transition temperature (T_g) was taken as the inflection point of the specific heat decrement at the glass transition region. Melting and crystallization characteristics were determined from the first heating and first cooling scan while the glass transition was determined from the second heating.

Crystalline content in PLLA, X_c, was calculated according the Equation (1) [4]:

$$X_c(\%) = \frac{\Delta H_m + \Sigma \Delta H_{cc}}{\Delta H_{100\%} \times w_{PLLA}} \quad (1)$$

where ΔH_m is the melting enthalpy of the sample, ΔH_{cc} is the cold crystallization enthalpy of the sample, $\Delta H_{100\%}$ is the melting enthalpy for 100% crystalline PLLA (93 Jg^{-1}) and w is the weight fraction of PLLA in the sample.

3 Results and discussion

PLLA/OSF composites were prepared after determination of the optimum processing conditions for all processing techniques, Figure 2. Pure PLLA is colourless but composites with OSF are brown. As OSF content increases colour of composites is getting darker.

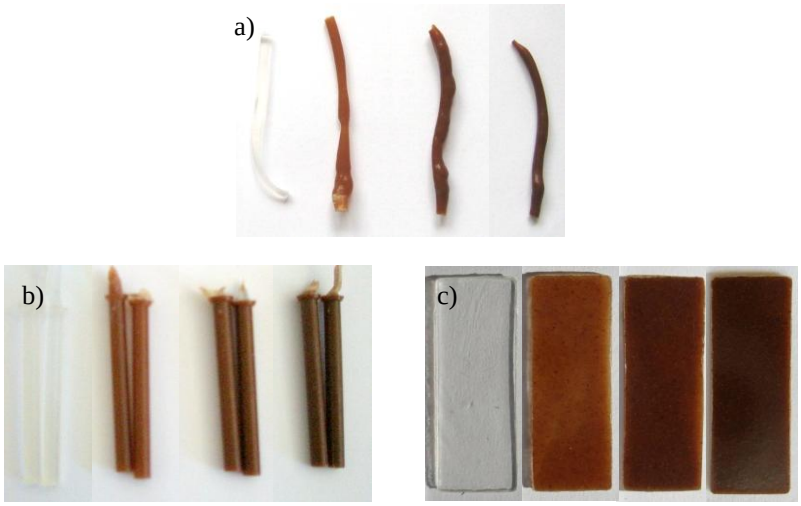

Figure 2. PLLA/OSF composites prepared by different processing techniques: a) extrusion on the horizontal single-screw extruder; b) extrusion on the vertical twin screw compounder; c) blending on the Brabender plastograph.

Although the Figure 2a shows the homogenous composites that are processed with the horizontal single-screw extruder the result wasn't as satisfactory as it is visible from Figure 3. During feeding of feeding hoper with PLLA granules and OSF powder the powder fell down on the bottom of the feeding hoper while PLLA granules remained on the top of the feeding hoper. Dispersion of OSF in extruded sticks of PLLA/OSF composites was non-homogenous. To obtain the homogenous samples it was necessary to eliminate part of the sample at the beginning of extrusion and also at the end of extrusion. This processing procedure obviously can't give repeatable sample composition.

Figure 3. PLLA 2a samples produced on the horizontal single-screw extruder.

While working on the vertical twin-screw compounder with injection moulding small "dead" corners inside the extruder were observed, where the components of PLLA/OSF composites were trapped and has not been 100% mixed. This was not the case during working with the Brabender plastograph. Brabender plastograph allow good visual control of the homogeneity of the composites and the operating temperature was lower for about 10°C. Lower processing temperature is important when it comes to PLLA and its thermal decomposition at elevated temperatures. Therefore, preparation on the horizontal single-screw extruder was abandoned while samples prepared on the vertical twin-screw compounder with injection moulding and the Brabender plastograph without and with pressing in hydraulic press were thermally analyzed by DSC. DSC curves obtained from all heating/cooling scans of PLLA/OSF composites prepared on the Brabender plastograph without pressing are shown in Figures 4-6.

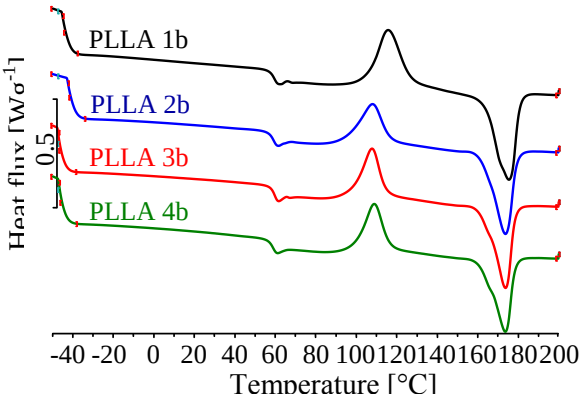

Figure 4. DSC curves of the first heating scan for PLLA/OSF composites prepared on the Brabender plastograph without pressing.

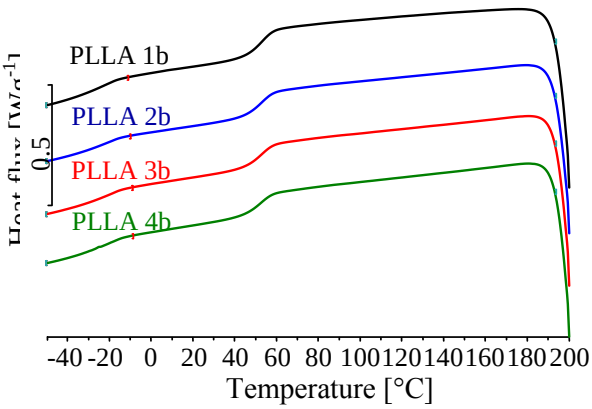

Figure 5. DSC curves of the cooling scan for PLLA /OSF composites prepared on the Brabender plastograph without pressing.

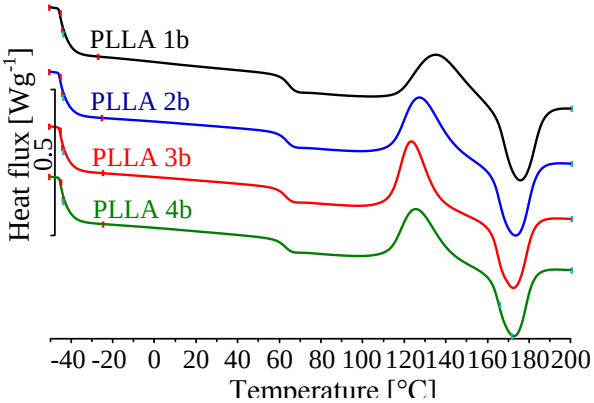

Figure 6. DSC curves of the second heating scan for PLLA/OSF composites prepared on the Brabender plastograph without pressing.

The values of the thermal characteristics obtained form DSC curves are presented in Figures 7-12 and Table 2. PLLA/OSF composites prepared on the vertical twin-screw compounder show cold crystallization temperature (T_{cc}), pre-melting crystallization temperature (T_{pmc}) and crystallization from the melt (T_{mc}) while PLLA/OSF composites prepared on the Brabender plastograph without and with pressing show T_{cc} only, Figure 7, 8 and 10. Pre-melting crystallization in PLLA often happens. It absence is a proof of a great importance of influence of processing techniques on the properties of the polymer.

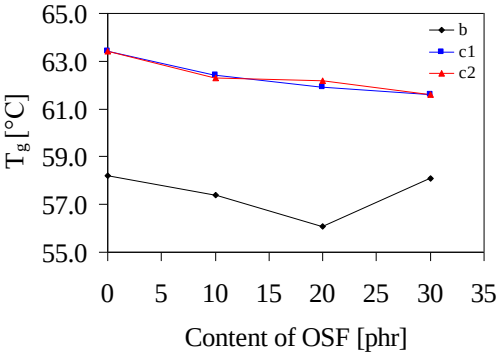

Figure 7. Dependence of T_g on OSF content in the composites prepared by different processing techniques

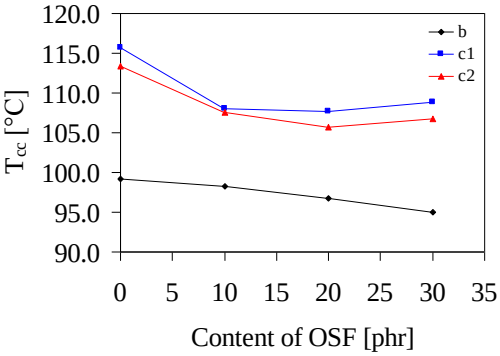

Figure 8. Dependence of T_{cc} on OSF content in the composites prepared by different processing techniques

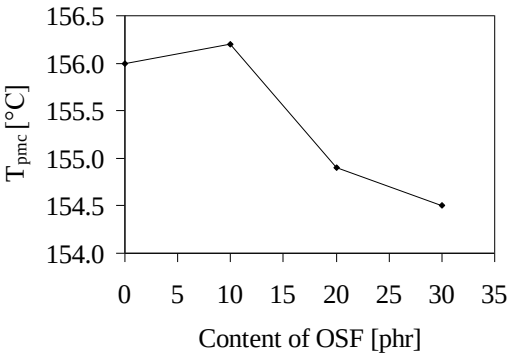

Figure 9. Dependence of T_{pmc} on OSF content in the composites prepared by vertical twin-screw compounder

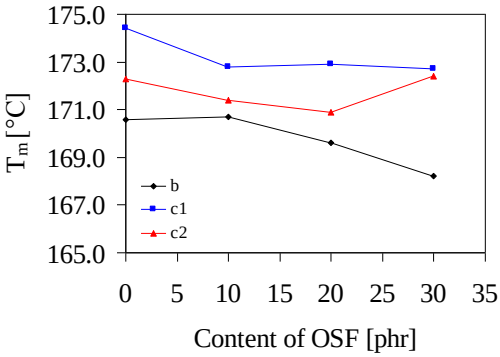

Figure 10. Dependence of T_m on OSF content in the composites prepared by different processing techniques

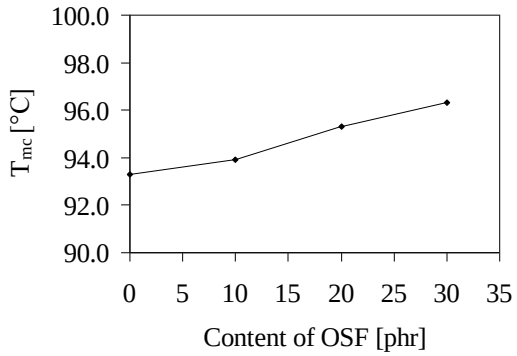

Figure 11. Dependence of T_{mc} on OSF content in the composites prepared by vertical twin-screw compounder

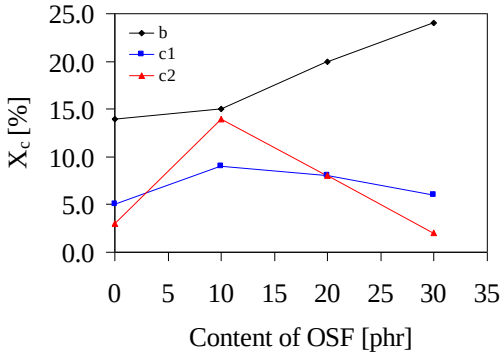

Figure 12. Dependence of X_c on OSF content in the composites prepared by different processing techniques

Sample	Δc_p / $Jg^{-1}°C^{-1}$	$-\Delta H_{cc}$ / Jg^{-1}	$-\Delta H_{pmc}$ / Jg^{-1}	ΔH_m / Jg^{-1}	$-\Delta H_{mc}$ / Jg^{-1}
PLLA 1b	0.300	29.00	2.63	44.77	15.08
PLLA 2b	0.299	26.87	2.36	41.92	14.30
PLLA 3b	0.159	22.98	2.33	41.11	20.39
PLLA 4b	0.106	20.50	1.09	38.56	28.33
PLLA $1c_1$	0.368	23.04		27.81	
PLLA $2c_1$	0.310	16.37		23.75	
PLLA $3c_1$	0.286	16.06		22.21	
PLLA $4c_1$	0.266	15.24		19.81	
PLLA $1c_2$	0.368	23.61		26.01	
PLLA $2c_2$	0.328	12.30		23.94	
PLLA $3c_2$	0.309	15.53		21.05	
PLLA $4c_2$	0.282	19.27		20.70	

Table 2. Other DSC characteristics of PLLA/OSF composites prepared by different processing techniques.

T_g of the composites prepared on the Brabender plastograph without or with pressing is almost the same but there is a significant difference between this T_g and T_g of the composites processed on the vertical twin-screw compounder. It is evident form the Figure 7 that T_g of the composites prepared on the vertical twin-screw compounder is lower than T_g of the composites obtained by other processing techniques for around 6°C. T_g decreases with increase of OSF weight parts in the composites for all processing techniques. Considerable deviation is present in the composite with 30 weight parts of the filler prepared on the vertical twin-screw compounder. In the case of T_{cc} the composites prepared on the Brabender plastograph without or with pressing have again almost the same value of T_{cc}. But, T_{cc} of the same composites prepared on the vertical twin-screw compounder is lower for 10 to 16°C, Figure 8, and pattern of T_{cc} change with OSF addition is also different. PLLA/OSF composites prepared by the different processing techniques have different values of T_m with addition of OSF, Figure 10. The composites prepared on the Brabender plastograph without pressing have the highest values of T_m (172.7-174.4°C) and it is possible that in these composites thermal degradation of the polymer is the lowest. T_m decreases with addition of OSF, but increase of OSF content brings no significant change. If the same composites are prepared with additional pressing, they have lower values of T_m (170.9-172.4°C), as is expected, due to the additional processing step. T_m decreases with OSF addition till 20 weight parts of OSF but with addition of 30 weight parts it suddenly increases. PLLA/OSF composites prepared on the vertical twin-screw compounder have the lowest values of T_m (168.2-170.7°C). Addition of OSF decreases T_m of the composites. Furthermore, the melting

endoterms of PLLA/OSF composites prepared by the Brabender plastograph without and with pressing are bimodal, i.e. a small "shoulder" is visible on the melting endotherm which is not a case with the samples prepared by the vertical twin-screw compounder with injection moulding. This may indicate the presence of multiple crystal forms of PLLA or the consequences of morphological changes during heating (e.g. changes in lamella thickness and size of spherulites). Change of X_c with addition of the filler is also quite different between the composites prepared on the vertical twin-screw compounder and the Brabender plastograph without or with pressing, Figure 12. Namely, the values of X_c of the composites prepared on the Brabender plastograph without pressing (5-9%) and with pressing (2-14%) are different but the pattern of its irregular change with the filler addition is the same. Again, PLLA/OSF composites prepared on the vertical twin-screw compounder have completely different values of X_c (14-24%) and way of its change whit OSF addition, i.e. X_c increases with OSF addition. It is assumed that the values of degree of crystallinity is not just a result of the filler addition but also the applied processing technique. The support for this conclusion is also a fact that original granules of PLLA have a crystallinity about 49% [5]. Generally, if the cooling rate during composites preparation is higher the crystallinity content is lower. It is also possible that during certain processing conditions olive stone flour in PLLA/OSF composites act as a nucleating agent and also as an "obstacle" to mobility of polymer chains during crystallization. Achieved crystallinity in PLLA/OSF composites in this case can be result of these opposing effects.

Taking into account all described factors it is clear that the thermal properties and crystallinity of polymer matrix depend on processing conditions. Difference in processing condition of PLLA composites prepared on the Brabender plastograph without and with pressing gave a slightly different thermal properties of the composites. If those data are compared with data obtained for the composites prepared on the vertical twin-screw compounder with injection moulding, there is difference between them. As T_g, T_{cc} and T_m of neat PLLA prepared on the vertical twin-screw compounder with injection moulding are lower than those prepared on the Brabender plastograph without and with pressing, it is possible to conclude that partial thermal degradation of PLLA occurs during extrusion resulting in lower molecular weight PLLA and consequently lower values of the transition temperatures. The same situation is with the composites, too. In the extruder or other processing equipments, PLA can undergo thermal degradation, leading to the formation of lactide monomers and other byproducts [6].

Specific heat capacity (Δc_p), cold crystallization enthalpy (ΔH_{cc}), pre-melting crystallization enthalpy (ΔH_{pmc}) and melting enthalpy (ΔH_m), except crystallization from the melt enthalpy (ΔH_{mc}), decrease with increas of OSF content for all prepared composites. In the case of ΔH_{mc} change is inverse. The values of mentioned thermal characteristics for the composites prepared on the Brabender plastograph without and with pressing are almost the same (for the existing thermal transitions). For the composites prepared on the vertical twin-screw compounder with injection moulding Δc_p has lower values (0.106-0.300$Jg^{-1}°C^{-1}$) and ΔH_{cc} (-20.50-(-29.00) Jg^{-1}) has higer values as ΔH_m (38.56-44.77Jg^{-1}) from the composites prepared on the Brabender plastograph without or with pressing. ΔH_m is almost twice larger from ΔH_m (19.81-27.81 Jg^{-1} and 20.70-26.01 Jg^{-1}) for the composites prepared on the Brabender plastograph without or with pressing. From this values it is also evident that there is no significant differences in thermal properties between the composites prepared on the Brabender plastograph without or with pressing compared to the composites prepared on the vertical twin-screw compounder with injection moulding.

4 Conclusions

Different processing techniques of PLLA/OSF composites affect the thermal properties of the investigated composites. Thermal properties and crystallinity of the composites prepared on

the Brabender plastograph without or with pressing differ, but less than the properties of the composites prepared on the vertical twin-screw compounder with injection moulding. The values of the glass transition temperature, the cold crystallization temperature and the melting temperature after processing of neat PLLA and PLLA/OSF composites on the vertical twin-screw compounder with injection moulding are lower than after processing on the Brabender plastograph without and with pressing. It is possible that during extrusion of the samples thermal degradation takes place. In order to exclude, as much as possible, the thermal degradation of the polymer during the preparation of the composites Brabender plastograph without or with pressing should be used. As the final products used by consumers have to be additionally shaped into desired workpiece, further investigation has to be done with the composites prepared on the Brabender plastograph with pressing into different moulds.

5 References

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