



MIGRATION AND LEACHING OF PLASTICIZER FROM PLASTICIZED POLY(L-LACTIDE)/OLIVE STONE FLOUR COMPOSITES

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Abstract

Thermally induced migration of tributylacetyl citrate (TBAC) from plasticized poly(L-lactide) (PLLA) and plasticized PLLA/olive stone flour (OSF) composites were investigated. Isothermal heating was conducted at 120°C and 150°C in a vented oven. Change of thermal properties was investigated by differential scanning calorimetry (DSC). The weight loss of plasticizer increases with heating time and at 120°C is lesser than at 150°C. Migration of TBAC results in cracks and changed colour of material. The plasticized PLLA/OSF composites showed resistance to cracking. As the amount of OSF increases the resistance to cracking increases. Kinetic analysis of TBAC migration shows that activation energy related to concentration of plasticizer (ΔE_a) of all compositions is almost the same leading to the conclusion that OSF doesn't affect the thermally induced migration. DSC analysis reveals that thermal properties of material are greatly influenced by migration temperature, independently of its composition. Migration of plasticizer increase T_g , T_m , T_c and X_c of material and that increase is more pronounced at 150°C. Increase of OSF content in the plasticized PLLA/OSF composites hasn't showed any influence. DSC analysis confirmed migration test results.

1 Introduction

As the interest for acceptable environmental solutions grows the interest for biodegradable polymers grows, too. Poly(L-lactide) is biodegradable, semicrystalline, thermoplastic aliphatic polyester and its main positive feature beside biodegradability is production from renewable resources. It is synthesized from lactic acid produced by fermentation of sugar or starch feedstock like potato, corn, wheat, sugarcane etc [1]. It can be used in medicine for the internal fixation of bone fractures, in the pharmaceutical applications, in packaging industry for food and non-food sector, in agricultural field, fiber technology [2-4]. Still, its production costs are relatively high. PLLA is also brittle polymer with glass transition temperature around 60°C and melting point around 160°C. Consequently, some additives have to be used to obtain usable and concurrent material on the market for mentioned applications.

To reduce PLLA brittleness tributylacetyl citrate (TBAC) can be used as a plasticizer. TBAC is non-toxic citrate ester produced from citric acid and it can be used as the non-toxic additive for different purposes [5]. Beside TBAC and all other citrate esters, plasticizers such as poly(ethylene glycol), glucosemonoesters, partially fatty acid esters, oligomeric lactic acid and glycerol were also used to improve the flexibility and impact resistance of PLLA [6]. The effective plasticization of semicrystalline polymers broadens the range of its application but



the most important issue is a migration of plasticizer to the surface of the polymeric material and than in the environment.

Migration and leaching of plasticizer molecules from polymers is a process that determines material's usable lifetime. Whether the plasticizers leach out to a liquid or migrate to gaseous or solid surrounding, polymers become inappropriate for desired application. With loss of plasticizer polymeric material regains the properties of unnpasticized polymer. Adequate plasticizer has to be miscible with polymer, creating homogeneous and non-toxic blend, especially in the case of plasticizer for the food packaging materials [7]. Evaporation during processing or usage at elevated temperature is not desired [7]. Mobility of the plasticizer molecules generally rises as temperature increases and the loss of plasticizer may occur. Thermally induced plasticizer migration at 100°C and 135°C of acetyl triethyl citrate from PLA/starch blend and at 125°C and 150°C of TBAC from plasticized PLA/ carbon black composites was investigated [8,9].

Olive stone flour (OSF) is fine flour produced by milling of olive stones, composed of cellulose, hemicelluloses, lignin, water, some fat, proteins and free sugars [10]. It can be used as a filler to reduce price of the final product. Lignocellulosic materials have a lot of positive features like low density, low requirements on processing equipment, no abrasion during processing, abundance and biodegradability [11]. The biodegradability of OSF is determined by the composition.

The objective of the present investigations is to study the thermally induced migration of TBAC at two different temperatures from plasticized PLLA and plasticized PLLA/OSF composites. Through kinetic analysis the migration rates and the activation energy related to concentration of plasticizer (ΔE_a) could be obtained [12]. The influence of plasticizer loss on the thermal properties of the composites was investigated by differential scanning calorimetry.

2 Experimental

2.1 Materials

Poly(L-lactide), Biomer L9000, in pellet form was purchased from Biomer (Germany), $\overline{M}_n \approx 58700$ ($[\eta]_{25^\circ C} = 165 \text{ cm}^3 \text{ g}^{-1}$ in chloroform) [13]. Tributylacetyl citrate was purchased from Merck KgaA (Germany), $M_r = 402.88 \text{ gmol}^{-1}$. 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 and TBAC, Table 1, using a Brabender plastograph operating at 170°C for 3 min at 70 rpm. Plasticized PLLA and plasticized 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 at a room temperature and the specimen of 30×10×1 mm were obtained. The samples where prepared in triplicates.



Sample	PLLA / weight parts	TBAC / weight parts	OSF / weight parts
PLLA 1	100	30	0
PLLA 2	100	30	10
PLLA 3	100	30	20
PLLA 4	100	30	30

Table 1 Composition of plasticized PLLA and plasticized PLLA/OSF composites

2.3 Plasticizer migration

The samples were placed in a vented oven at isothermal temperatures of 120 and 150°C. In defined time intervals (0, 30, 60, 120, 180, 300, 420, 660 and 1440 min) the samples were weighted. Before weighting the surface were cleaned up from the migrated plasticizer and cooled at a room temperature. The weight loss of the plasticizer was assumed as the total weight loss of the samples during heating time (t) and calculated according to Equation 1:

$$\text{weight loss}(\%) = \frac{m_0 - m_t}{m_0} \times 100 \quad (1)$$

where m_0 is the weight before migration and m_t is the weight of after migration at t .

2.4 DSC analysis

The thermal characteristics of the samples were determined using differential scanning calorimeter (DSC 823, Mettler-Toledo) equipped with intracooler. The closed aluminium pans were used and the measurements were performed under nitrogen atmosphere (flow rate was $30 \text{ cm}^3 \text{ min}^{-1}$). Weight of the samples was approx. 20 mg. They 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). The crystallization temperature from the melt (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.

Crystallinity degree, X_c , of PLLA was calculated according the Equation 2 [14]:

$$X_c(\%) = \frac{\Delta H_m + \sum \Delta H_{cc}}{\Delta H_{100\%} \times w_{PLLA}} \quad (2)$$

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. Theory

Thermally induced migration of plasticizers from polymer materials can be described by first order kinetic equation [12]:



$$\ln \frac{C}{C_0} = -K \times t \quad (3)$$

where C is the residual weight concentration of plasticizer, C_0 is the initial weight concentration of plasticizer in the blend, K is general constant of the migration and t is the time of migration.

Migration is a process connected with a gradient of concentration and it is fastest at a beginning. Influence of the temperature on the migration rate (K) can be described by Arrhenius-like equation [12]:

$$K = K_0 \exp\left(\frac{-\Delta E_a}{RT}\right) \quad (4)$$

where K_0 is a constant, ΔE_a is activation energy related to concentration of plasticizer, R is the gas constant and T is the absolute temperature. Higher temperatures accelerate the migration of plasticizer while lower temperatures decelerate it. The value of K can be determined by Equation 3 as a slope of $\ln(C/C_0)-t$ lines and than ΔE_a using Equation 5[12]:

$$\Delta E_a = \frac{R \ln\left(\frac{K_1}{K_2}\right)}{\frac{1}{T_2} - \frac{1}{T_1}} \quad (5)$$

where K_1 is the migration rate at T_1 and K_2 is the migration rate at T_2 .

4. Results and discussion

4.1 Plasticizer migration

The weight loss, assumed as the weight loss of the plasticizer, was calculated as an arithmetic mean of three measured values. The change of weight loss as a function of time at 120°C and 150°C is shown in Figure 1.

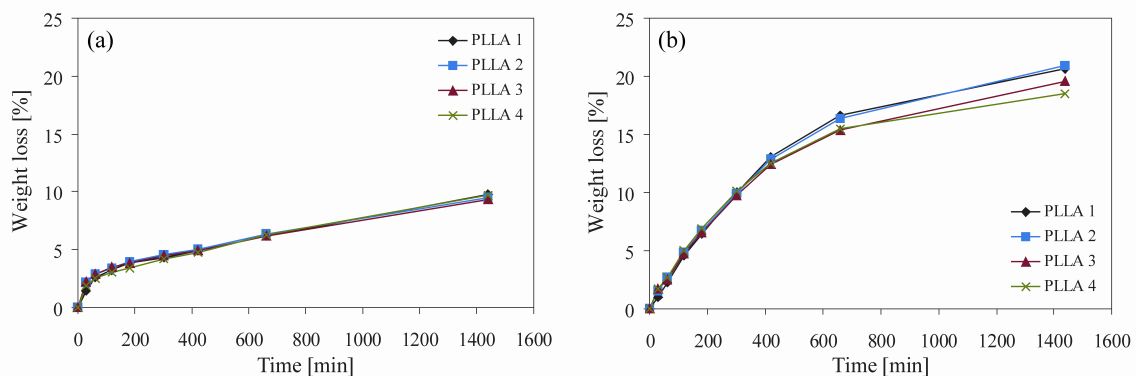


Figure 1. Weight loss of plasticized PLLA and plasticized PLLA/OSF composites after heating at: (a) 120°C; (b) 150°C



The loss of the plasticizer increases with time and at 120°C is lower than at 150°C. Zhang and Sun also found that higher temperature favours the plasticizer migration [8]. The weight loss at 120°C of plasticized PLLA and plasticized PLLA/OSF composites is almost the same during whole period of heating. After 1440 min 50% of TBAC amount migrate from all samples. Addition of OSF has no influence on TBAC migration and the rate of weight loss is highest in first 60 min. The rate of weight loss at 150°C is highest at first 200 min for all samples. Also, all samples exhibit the same weight loss in the first 400 min. Further weight loss is inversely proportional to OSF content. After 1440 min almost all TBAC migrate from the samples. Although the difference is observed the reducing effect of OSF on TBAC at 150°C is poor.

It is well known that loss of plasticizer from plasticized material can cause macroscopic change of material properties during usage and also it can contaminate surrounding area. The samples of plasticized PLLA and PLLA/OSF composites before and after migration induced by heating at 120°C and 150°C are presented in Figure 2.

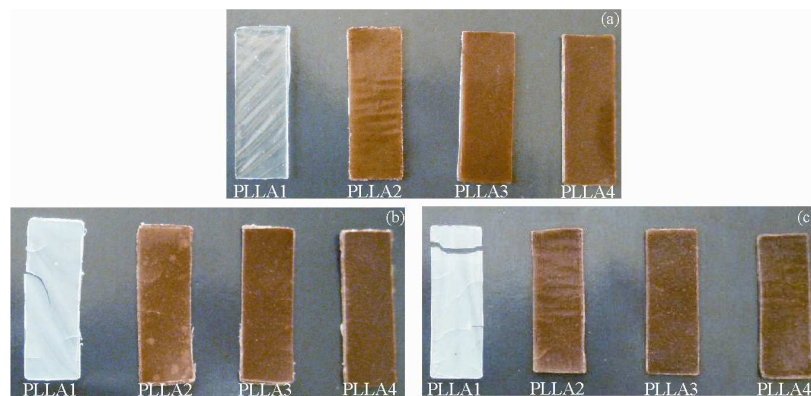


Figure 2. Plasticized PLLA and plasticized PLLA/OSF composites: (a) before migration; (b) after migration at 120°C; (c) after migration at 150°C

After 1440 min at 120°C all samples show small cracks and change of colour. Plasticized PLLA with OSF show higher crack resistance than plasticized PLLA without OSF. The change of colour can be evidence of increase of PLLA crystallinity and/or thermal degradation. In the case of plasticized PLLA transparent and colourless sample becomes opaque and white and it can be concluded that the change of crystallinity degree is the main reason. In the case of plasticized PLLA/OSF composites this doubt stays, because OSF is brown and the samples are brown, too. Samples become darker with few white spots and lines. After 1440 min at 150°C the influence of migration is even more visible and the samples are more cracked and broken (especially plasticized PLLA). The change of colour of all samples is also more pronounced. On loss of plasticizer the flexibility is worsened, i.e. samples become more rigid and easy breakable. The plasticized PLLA/OSF composites show stability to crack and the main reason is presence of OSF. As the amount of OSF increases the stability to crack increases. Obviously, OSF acts as a binding material even after higher loss of TBAC.

To be able to perform kinetic analysis of the migration of plasticizer it was necessary to conduct this investigation at two different temperatures. Figure 3 represents the linear dependence of $\ln(C/C_0)$ on t for all compositions at 120°C and 150°C obtained using first order kinetic equation (Equation 3).

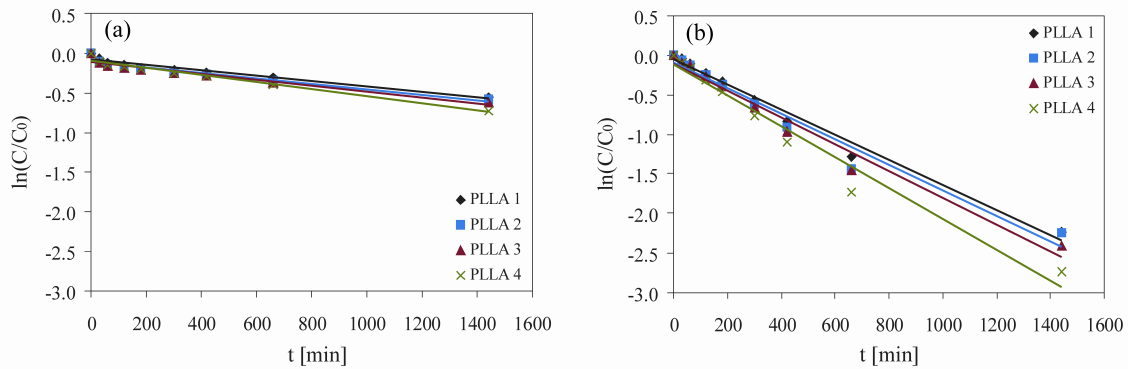


Figure 3. Kinetic dependence of $\ln(C/C_0)$ on t for plasticized PLLA and plasticized PLLA/OSF composites after heating at: (a) 120°C; (b) 150°C

All experimental data fit the equation at a correlation coefficient of 0.97 at 120°C and 0.95 at 150°C. The slope of $\ln(C/C_0)$ - t lines represents the migration rate (K), Table 2. K is higher at higher temperature and at 120°C it is almost the same for all compositions. At 150°C it has slight trend to increases with addition of OSF. For PLLA 1, PLLA 2 and PLLA 3 it can be regarded as the same but it differs for PLLA 4. ΔE_a of TBAC migration was calculated according to Equation 5. The values of ΔE_a are presented in Table 2.

Sample	$K_1 \times 10^{-3} [\text{min}^{-1}]$	$K_2 \times 10^{-3} [\text{min}^{-1}]$	$\Delta E_a [\text{kJmol}^{-1}]$
PLLA 1	0.3	1.6	71
PLLA 2	0.4	1.6	70
PLLA 3	0.4	1.7	70
PLLA 4	0.4	2.0	68

Table 2 Migration rate and activation energy of TBAC of plasticized PLLA and plasticized PLLA/OSF composites

ΔE_a of plasticizer migration from all samples is almost the same leading to the conclusion that OSF doesn't affect the thermally induced migration of TBAC. On the contrary, Wang et al. confirmed that carbon black restrains the migration of TBAC in the plasticized PLA/CB composites [9].

4.2 DSC analysis

DSC was used to study the thermal properties of plasticized PLLA and plasticized PLLA/OSF composites before and after plasticizer migration at 120°C and 150°C. The thermograms obtained from the heating and the cooling cycles are shown in Figure 4, 5 and 6.

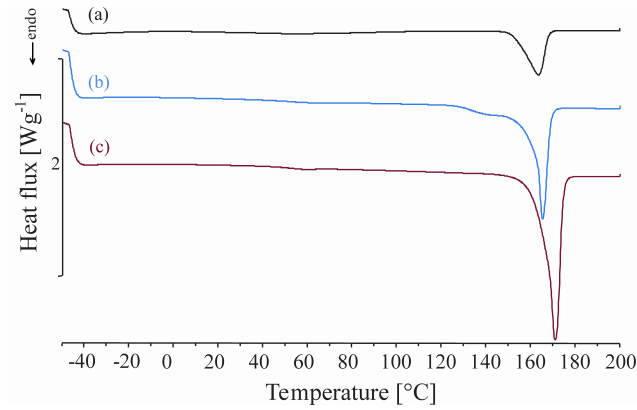


Figure 4. DSC thermograms of the first heating cycle of PLLA 1: (a) before migration; (b) migration at 120°C; (c) migration at 150°C

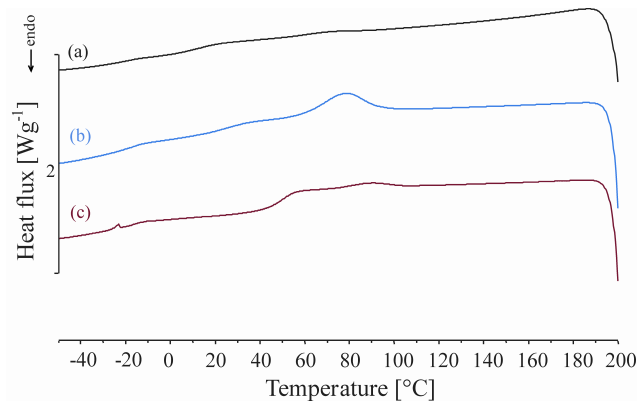


Figure 5. DSC thermograms of the cooling cycle of PLLA 1: (a) before migration; (b) after migration at 120°C; (c) after migration at 150°C

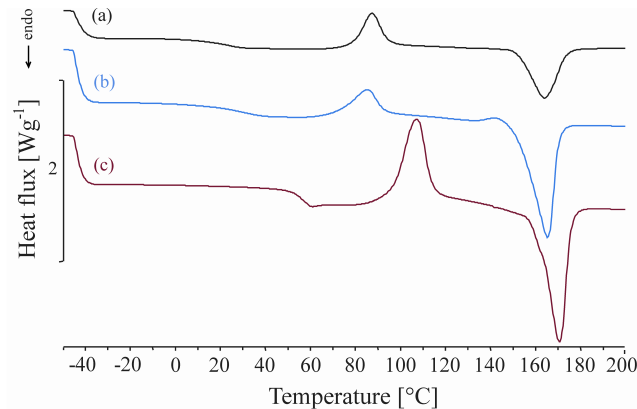


Figure 6. DSC thermograms of the second heating cycle of PLLA 1: (a) before migration; (b) after migration at 120°C; (c) after migration at 150°C

Thermal characteristics obtained from the thermograms are presented in Table 3. From the first heating cycle the melting data was obtained while the glass transition data was obtained from the second heating cycle. The cooling cycle gives information about the crystallization from the melt.



Sample		T_g [°C]	Δc_p [Jg ⁻¹ °C ⁻¹]	T_m [°C]	ΔH_m [Jg ⁻¹]	T_c [°C]	ΔH_c [Jg ⁻¹]	X_c [%]
Before migration	PLLA 1	19	0.286	163	23.2	71	-0.9	32
	PLLA 2	16	0.248	161	21.3	72	-1.3	32
	PLLA 3	16	0.252	161	20.0	72	-1.4	32
	PLLA 4	16	0.218	161	18.9	72	-1.6	33
After migration at 120°C	PLLA 1	27	0.416	164	52.3	79	-12.4	66
	PLLA 2	25	0.415	164	47.4	77	-11.4	65
	PLLA 3	26	0.310	163	46.7	78	-14.8	68
	PLLA 4	26	0.293	162	44.3	78	-13.3	69
After migration at 150°C	PLLA 1	55	0.560	169	69.0	90	-2.0	77
	PLLA 2	53	0.498	168	65.2	89	-2.3	78
	PLLA 3	52	0.484	168	59.3	88	-2.7	77
	PLLA 4	54	0.437	168	52.6	89	-1.2	74

* Δc_p , specific heat capacity; ΔH_c , crystallization enthalpy from the melt.

Table 3 Thermal characteristics of plasticized PLLA and plasticized PLLA/OSF composites before and after plasticizer migration at 120°C and 150°C

The thermograms of the first heating cycle of PLLA 1 (Figure 4) show only the melting peak before and after migration of TBAC at 120°C and 150°C. After migration at 120°C the main endothermic peak has a shoulder around 145°C but this isn't visible after migration at 150°C. The shoulder is the evidence of the presence of more than one crystallographic form or crystals morphology change induced by plasticizer migration on isothermal heating at lower temperature. The melting peak is sharper and higher as the migration temperature increases because higher TBAC loss enables PLLA to form crystals easier. T_m and ΔH_m increases as temperature and consequently migration increases. The crystallization induces an evident increase of X_c with temperature, too. Table 3 shows that cooling of PLLA 1 at cooling rate 20°Cmin⁻¹ enables only minor crystallization from the melt before migration but after migration at 120°C the cooling rate is not a limiting factor for crystallization. This is probably related with a change of crystallographic form or crystals morphology. T_c increases with increases of migration temperature. After thermal treatment at 150°C, crystallization from melt is slightly higher than before treatment. The second heating scan (Figure 6) shows that as temperature of migration increases T_g and Δc_p of PLLA 1 increases, too. This is the main proof that with higher plasticizer loss material approaches T_g of unplasticized PLLA which is 63°C [15]. Properties of the plasticized PLLA weren't changed significantly upon OSF addition. T_g and T_m decrease for few degrees but with further increases of OSF content no change happens. Only Δc_p and ΔH_m decrease as OSF content increases. T_c and X_c of all plasticized composites were practically the same. Plasticized PLLA/OSF composites show after migration at different temperatures the same behaviour as plasticized PLLA. The shoulder for PLLA 2, PLLA 3 and PLLA 4 is at 143°C, 140°C and 137°C, respectively. Values of T_g , T_m and T_c after migration are slightly lower in the presence of OSF. An increase of OSF amount show only minor influence on PLLA crystallization degree due to the plasticizer migration.

5. Conclusions

The thermally induced migration of TBAC from plasticized PLLA and plasticized PLLA/OSF composites at two temperatures and the thermal analysis of these materials before and after



migration have been carried out. The weight loss of plasticizer increases with time and at 120°C is lower than at 150°C. At 120°C the rate of weight loss is highest in first 60 min but at 150°C in first 200 min for all samples. OSF acts as a binding material even after higher loss of TBAC. ΔE_a of all compositions is almost the same what leads to conclusion that OSF doesn't affect the thermally induced migration of TBAC. With progress of migration cracking of the plasticized samples (some of them were broken) and change of colour take place. Plasticizer loss results in rigid and easy breakable samples. Plasticized PLLA/OSF composites show resistance to crack and the main reason is presence of OSF. As the amount of OSF increases the resistance to crack increases. DSC analysis revealed that migration at 120°C and 150°C change thermal properties of the materials. T_g , T_m , T_c and X_c increase as the migration temperature increases. Addition of OSF to plasticized PLLA has minor influence on its thermal properties at both temperatures. Increase of OSF amounts in the plasticized PLLA/OSF composites hasn't any influence.

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