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STUDY ON ADSORPTION OF ESSENTIAL OILS ON POLYLACTIC ACID MICROPARTICLES

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Polylactic acid (PLA) is a biodegradable polymer that is widely used in medical devices, drug delivery systems, fibers for packaging containers and textiles. However, given that interactions between the polymer and the materials in contact with it affect its applications, it is important to study its adsorption and diffusion properties. The adsorption capacity of different polylactic acid particles regarding different additives, e.g. essential oils (*Thymus vulgaris, Melissa officinalis* and *Foeniculum vulgare*), was investigated. PLA microparticles of various sizes were prepared by a solvent emulsification evaporation method. In this study, the specific adsorption of essential oils on PLA microparticles was also investigated, which is related to the solubility parameters of essential oils. The experiments were performed using three different solutions of essential oils and ethanol as a solvent. Two sets of PLA microparticles were prepared with different solvents using three different particle sizes. PLA microparticles exhibited different adsorption properties depending on the solvent that was used for their production. Samples of particles prepared using the solvent dichloromethane had a higher essential oil uptake than those prepared with chloroform. The uptake of essential oil solution did not change significantly (~60%) by varying either the type of solvent used for PLA preparation or PLA particle size. The solubility of the essential oils affects the specific adsorption of essential oils on the microparticles. Among the components of the Hansen solubility parameters (HSPs), the polarity of essential oils is strongly related to adsorption.

Keywords: polylactic acid, microparticles, essential oil adsorption, Hansen solubility parameters

1. Introduction

Biodegradable polymers are important feedstocks in industry as they offer an environmentally-friendly alternative to fossil-based polymers in biomedical, agricultural and household applications [1]. PLA is an aliphatic polyester as well as one of the most commercially available, bio-based, biodegradable and biocompatible polymers. PLA is commonly considered for different applications such as in drug delivery systems, tissue engineering, packaging and textiles. The fields of application of this polymer are limited by certain properties, e.g. its low mechanical strength or hydrophobicity [2]-[3]. Different additives, e.g. essential oils, can be incorporated into biodegradable polymers to improve their functional properties [4]. Different types of essential oils such as thyme, cinnamon, oregano and basil are incorporated into biodegradable polymer films, e.g. for the development of food packaging films to enhance antimicrobial properties [5]. Essential oils also act as plasticizers in polymers. Due to their plasticizing properties, the structural and mechanical properties of such polymers can be altered [6], thereby also changing the sorption properties of PLA.

Interactions between essential oils and PLA have been studied by several researchers (Dusankova et al., Martins et al., Dicastillo et al.) using different processing methods [7]-[9] and are mainly determined by the composition of the essential oil and its polarity.

Dusankova et al. studied PLA microspheres containing different components of essential oils. They found that the more polar components adsorb better in the microspheres than the more apolar ones, as PLA itself is polar [7]. Martins et al. came to a similar conclusion. When the incorporation and release of the components of the essential oils thymol and p-cymene were studied, the diffusion rate of these components through the PLA matrix differed significantly (diffusion coefficient was 1.99×10^{-16} m^2/s for thymol and 4.34×10^{-16} m^2/s for p-cymene), which could be explained by their difference in polarity [8].

In our work, the adsorption properties of polylactic acid particles regarding different essential oils like those from lemon balm, fennel and thyme were investigated. The microparticles were prepared by a solvent emulsification evaporation method [10]. The structure of the polymer particles formed is critical, as their particle size distribution and porosity influence their adsorption properties. The properties of the particles that are

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Table 1. Notation for the microparticles

Sample name	PLA-solution – solvent type	Average size, µm
PLA_DKM_50	Dichloromethane (*DKM*)	57±12
PLA_DKM_100		116±21
PLA_DKM_200		207±57
PLA_K_50	Chloroform (*K*)	56±14
PLA_K_100		121±31
PLA_K_200		198±40

produced by the solvent emulsification evaporation method are mostly affected by the concentration of the PLA solution, type and amount of surfactant as well as the mixing speed. Besides the concentration of the PLA solution, its composition is also important [11]. The organic solvent in which PLA is dissolved will affect the structure of the microparticles produced [10], [12]. Shi et al. found that PLA particles prepared using chloroform as the solvent were less porous than those prepared in ethyl acetate [12].

Consequently, in our work, the adsorption of essential oils on PLA microparticles as a function of the PLA particle size was investigated. To modify the particle size distribution, the concentration of PLA solution was changed during the emulsification method.

2. Experimental

2.1. Materials

NatureWorks Ingeo Biopolymer 3D850 PLA granules, dichloromethane (>99.8%, Fisher), chloroform (technical grade, stabilized with ~0.6% of ethanol, VWR) and polyvinyl alcohol (fully hydrolyzed, M_w approx. 60,000; Merck) were used to prepare the PLA microparticles. To measure the degree of adsorption, ethanol (99.8% G.R., ISO reagent, Lach-Ner, s.r.o.) and three kinds of essential oils: *Melissa officinalis* (from lemon balm, Neuston Healthcare Kft.), *Foeniculum vulgare* (from fennel, Neuston Healthcare Kft.) and *Thymus vulgaris* (from thyme, Neuston Healthcare Kft.) were used.

2.2. Methods

Microparticles were prepared based on a solvent emulsification evaporation method. The particles were prepared as follows: firstly, 200 ml of PLA solution of a given concentration (2.5, 5.0 and 7.5 wt. %) using dichloromethane or chloroform as a solvent; secondly, the solution was added to 400 ml of 1 wt. % polyvinyl alcohol (PVA) solution. The emulsion was stirred with a magnetic stirrer at 820 rpm for 24 or 48 hours, depending on the solvent used (dichloromethane or chloroform, respectively). After filtering and washing, the solid particles were dried in a Binder FD 53 oven at 50 °C for 24 hours.

To determine the average diameter and size distribution of the particles, an image was taken using an optical microscope (Lacerta, zoom: 40x). The particle size was determined from the images using the program ImageJ.

To measure the degree of adsorption, 1.000 g of PLA particles were weighed on an Ohaus Adventurer AR3130 analytical balance in a pre-weighed dry test tube, then 2.000 g of a 1.00 mg/ml ethanolic solution of essential oil was added to it. The microparticles were soaked for 24 hours before the samples were separated by filtration.

The essential oil concentrations of the residual ethanolic solutions were analyzed by UV-Vis spectrophotometry. The absorption spectra of the samples were recorded between 200 and 800 nm using an Agilent Cary 60 UV-Vis Spectrophotometer.

Differential scanning calorimetry (DSC) was performed with a NETZSCH DSC 214 Polyma differential scanning calorimeter. The measurements were carried out under a 60 ml/min N_2 flow rate according to the following protocol: first the sample was heated from 20 to 200 °C at a heating rate of 10 °C/min before being cooled from 200 to 20 °C at a cooling rate of 10 °C/min then reheated from 20 to 200 °C at the same heating rate.

Notation was applied to the samples, e.g. *PLA_K_100_EL*. The first letter refers to the solvent that was used for PLA preparation (*DKM* for dichloromethane and *K* for chloroform), the number refers to the size of the microparticles (*Table 1*). At the end of the sample identification, the first letter refers to the type of solvent used for essential oil solution (*E* for ethanol) and the last letter refers to the essential oil, namely *L* for lemon balm, *T* for thyme and *F* for fennel.

3. Results and Discussions

3.1. Microparticle properties

The properties of the microparticles such as their particle size distribution are shown in *Fig.1*. As the concentration of the PLA solution increased, the size of the particles produced also increased. The correlation between the concentration of PLA solution and the diameter of the particles is linear. The solvent emulsification evaporation method mainly produced spherical particles that did not aggregate (*Fig.2*).

3.2. Solution uptake by microparticles

Regarding the uptake of ethanolic solution of essential oil by the particles prepared from a PLA solution prepared in dichloromethane, it was concluded that the solution uptake increases slightly by 10% on average as the particle size increases. However, the presence of essential oils in the solutions did not significantly affect the solution uptake of the particles. For a given particle size, the solution uptake was practically the same for all examined solutions. The average solution uptake by

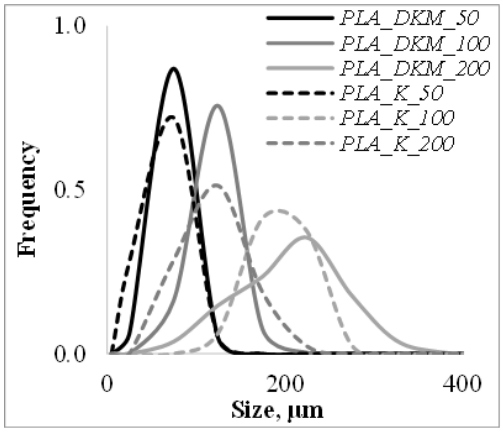

Figure 1. Particle size distribution of the different PLA microparticles

particles 50, 100 and 200 µm in diameter is ~60, ~66 and ~75%, respectively.

3.3. Adsorption of essential oils on microparticles

The different types of PLA microparticles exhibited different adsorption properties (*Figs.3* and *4*) regarding various essential oils.

It was found that in the case of lemon balm, the uptake of essential oils by *PLA_DKM* particles from ethanolic solutions and the specific amount of the essential oil adsorbed increased as the particle size increased, while the degree of uptake and adsorption decreased in the case of ethanolic solutions of thyme and fennel. Lemon balm essential oil yielded an outstanding result. In this case, by increasing the particle size from 50 to 100 µm and then to 200 µm, the degree of essential oil uptake increased by 19% and then by a further 16%.

It was concluded that the effect of *PLA_K* particle size on the specific adsorption of thyme and fennel essential oils is insignificant, there is no correlation between the amount of essential oil adsorbed and the particle size. However, in the case of the lemon balm

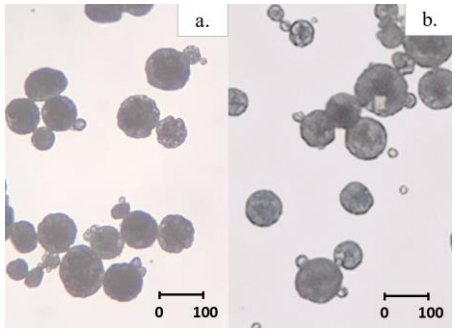

Figure 2. Images of the microparticles: a.) PLA_K_100 and b.) PLA_DKM_100

essential oil, the degree of specific adsorption increased as the particle size increased.

In general, it was concluded that for *PLA_DKM* particles, the essential oil uptake mainly resulted from the differences between the microparticles (degree of crystallinity, size, porosity) and the types of essential oils present in the solutions. Nonetheless, in the case of *PLA_K* particles, the specific amount of essential oil adsorbed on the surface or in the pores of the particles did not change significantly as the particle size changed, rather each essential oil was adsorbed differently on the particles. The particles prepared by using dichloromethane as a solvent had a higher specific essential oil adsorption (0.8-3.4 mg EO/g PLA) than particles prepared in chloroform (0.6-1.6 mg EO/g PLA). Variation in the adsorption properties of the particles was probably caused by the differences in their structure. The different solvents used in the production process caused the particles to solidify at different rates, leading to possible differences in their internal structure and porosity.

3.4. The correlation between adsorption properties in light of the Hansen solubility parameters (HSPs)

Adsorption properties are affected by the composition and properties of the adsorbate. The connection between

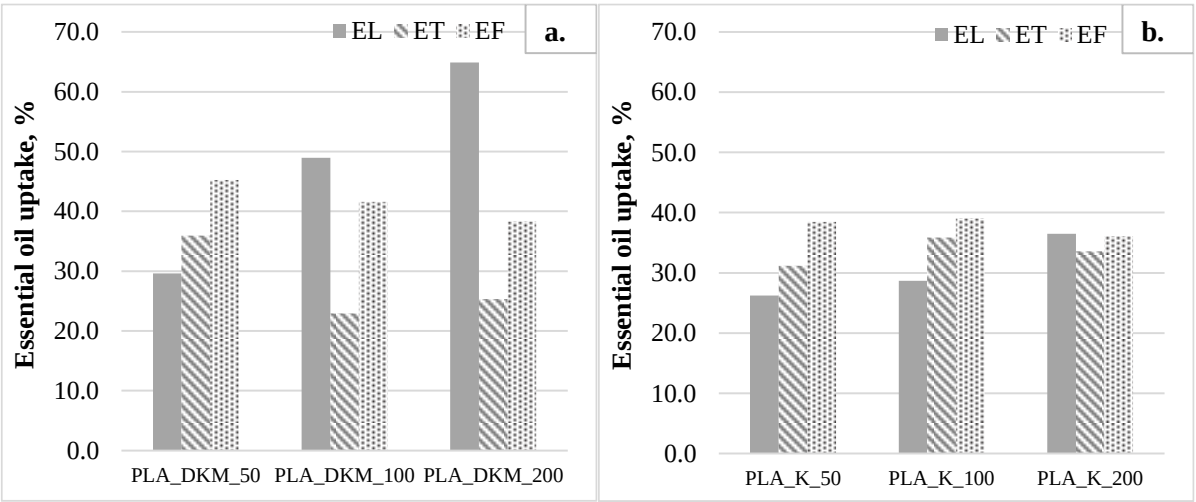

Figure 3. Essential oil uptake (%) by the microparticles in the case of a.) particles prepared in dichloromethane and b.) particles prepared in chloroform

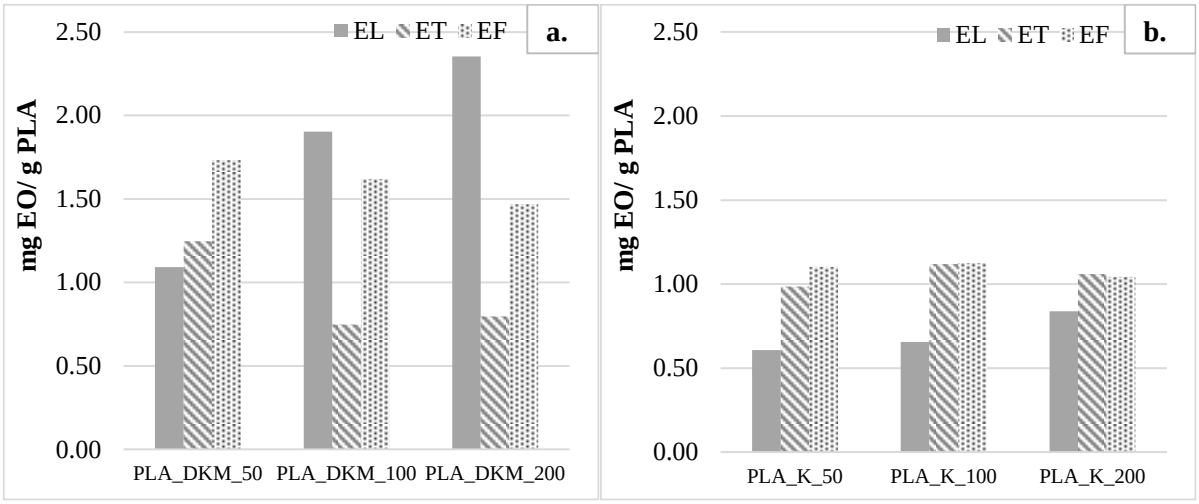

Figure 4. Specific adsorption of essential oil (EO) on microparticles (mg EO/g PLA) in the case of a.) particles prepared in dichloromethane and b.) particles prepared in chloroform

the solubility of essential oils and the adsorption properties of PLA was investigated. Solubility can be characterized by the HSPs, which describe the affinity of the polymer for different organic substances. Hansen total solubility parameter (δ_t) is composed of three parameters, one indicating the contribution to the dispersion forces (δ_d), another characterising the polar interactions (δ_p) and one more demonstrating the formation of H-bonds (δ_h). These solubility parameters can be determined using different methods such as the group contribution method (Hoftyzer-Van Krevelen method) [13]-[15].

The specific amount of essential oil adsorbed on PLA can be related to the total solubility parameter or one of its components. Since different essential oils have different solubility parameters depending on their composition (*Table 2*), the specific adsorption on PLA is different for different essential oils.

A correlation between the adsorbed amount of the essential oil and $\Delta\delta_{p,EO}$ was observed. ($\Delta\delta_{p,EO}$ shows how much the δ_p of an essential oil differs from that of PLA.) In the case of *PLA_DKM* particles, the specific adsorption decreased as $\Delta\delta_{p,EO}$ increased (*Fig.5*). In contrast, it was found that the specific amount of essential oil adsorbed on *PLA_K* particles deviated in the case of $\Delta\delta_{p,EO}$ less than 5.5 ($MPa^{1/2}$).

3.5. Thermal properties of the PLA particles

DSC was used to evaluate the thermal properties of the samples. The glass transition (T_g), cold crystallization (T_{cc}) and melting temperatures (T_m) of the PLA particles were determined during the second heating of the DSC measurement.

The degree of crystallinity (X_C%) was calculated from the enthalpy of melting (ΔH_m) and the enthalpy of cold crystallization (ΔH_{cc}), taking into account an enthalpy of melting (ΔH_m^0) of 94 kJ/kg for 100% crystalline *PLA* [16]-[17]:

$$X_C\% = [(\Delta H_m - \Delta H_{cc})/\Delta H_m] \times 100 \quad (1)$$

Both types of PLA particles exhibited two exothermic, cold crystallization peaks and an endothermic melting peak (*Fig.6*). For both *PLA_DKM* and *PLA_K* particles, the glass transition occurred at ~61°C (61.3±0.6 and 60.9±0.3°C, respectively) and the melting at 177°C (177.3±0.8 and 176.6±0.3°C, respectively). However, a difference is observed in the cold crystallization temperatures between the two types of particles. For the *PLA_K* and *PLA_DKM* particles, the first cold crystallization peaks appeared at 96.7±0.6°C and 104.4±0.2°C, respectively. The probable reason for this is that during the emulsification method, the particles solidified at different rates based on the organic solvent used for the PLA solution. As the particles solidified at different rates, their structure and porosity vary. The thermal properties of the granules did not change even when the concentration of the PLA solution was changed during their preparation. The degree of crystallinity of the *PLA_K* particles was approximately 25.0±0.7%, while that of *PLA_DKM* was different. The degree of

Table 2. Hansen solubility parameters (HSPs) of the materials

Material	δ_d ($MPa^{1/2}$)	δ_p ($MPa^{1/2}$)	δ_h ($MPa^{1/2}$)	δ_t ($MPa^{1/2}$)
PLA	18.6	9.9	6.0	21.9
Ethanol	15.1	8.4	18.3	25.2
Lemon balm essential oil	16.4	4.6	5.1	17.8
Thyme essential oil	21.5	3.3	9.6	23.8
Fennel essential oil	24.3	3.9	28.0	37.3

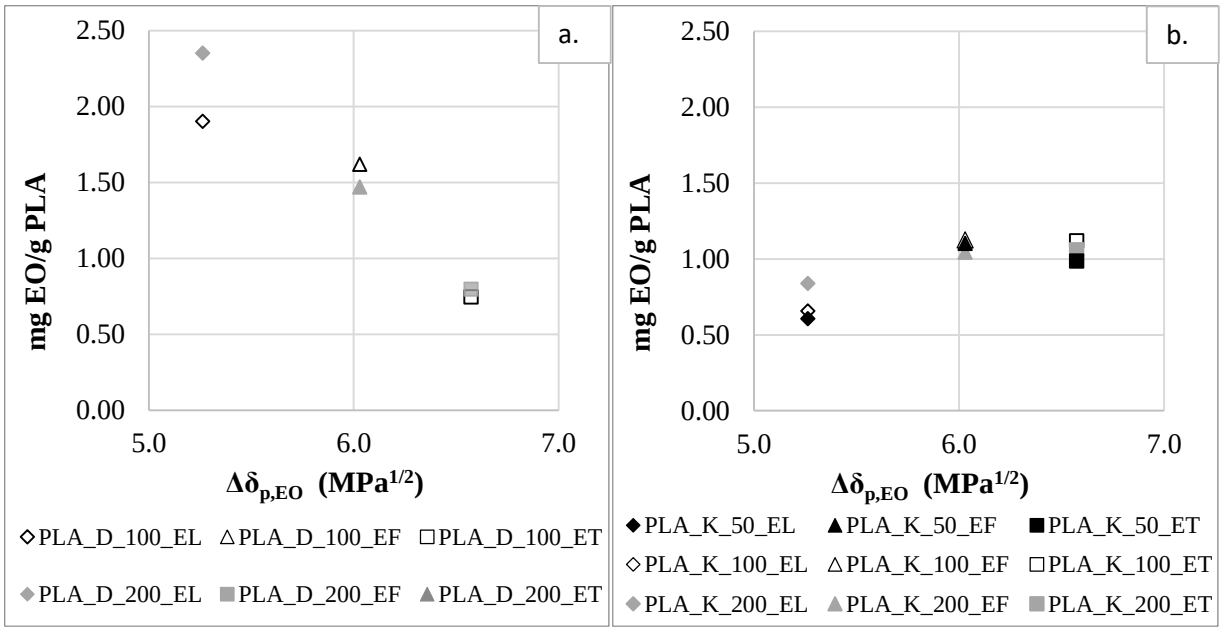

Figure 5. Correlation between the HSPs and the specific adsorption of essential oil (EO) on microparticles (mg EO/ g PLA) in the case of a.) particles prepared in dichloromethane and b.) particles prepared in chloroform

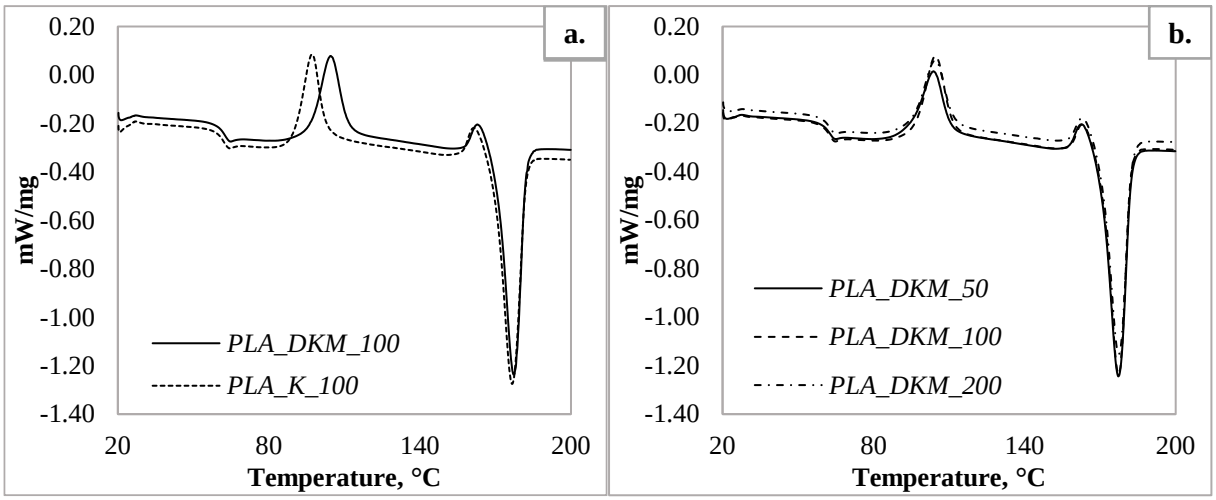

Figure 6. The second heating DSC curves of the PLA granules and microparticles in the case of a.) their different types and b.) their different sizes

crystallinity of the *PLA_DKM_50*, *PLA_DKM_100* and *PLA_DKM_200* particles was 24.3±0.4, 19.6±0.7 and 21.5±0.8, respectively.

After the degree of adsorption was measured, the thermal properties of the microparticles did not change due to their interaction with the essential oils (*Fig.7*). However, the adsorption of essential oils had an effect on the degree of crystallinity of the particles, as the degree of crystallinity of the *PLA_DKM* particles increased by ~2% and that of *PLA_K_50* particles increased to ~30%.

The degree of crystallinity of the *PLA_K_100* and *PLA_K_200* particles was not influenced by which essential oil was used.

Based on the results, it was found that the thermal properties of the PLA microparticles are affected by the type of solvent used during their preparation rather than by the concentration of the PLA solution used. It was concluded that the thermal properties of the microparticles were not changed by the adsorption of essential oils. Therefore, the amount of essential oil adsorbed was insufficient to cause a significant change to the PLA structure.

4. Conclusion

In our work, the adsorption properties of polylactic acid particles for lemon balm, fennel and thyme essential oils were investigated. The adsorption of these essential oils on the PLA particles was investigated as a function of particle size (50, 100 and 200 μm).

It was concluded that the adsorption of essential oils is affected by both differences between types of microparticles (degree of crystallinity, size, porosity) and the types of essential oils present in the solutions of *PLA_DKM* samples. Although the specific amount of essential oil adsorbed on the surface or in the pores of *PLA_K* particles did not change significantly as the

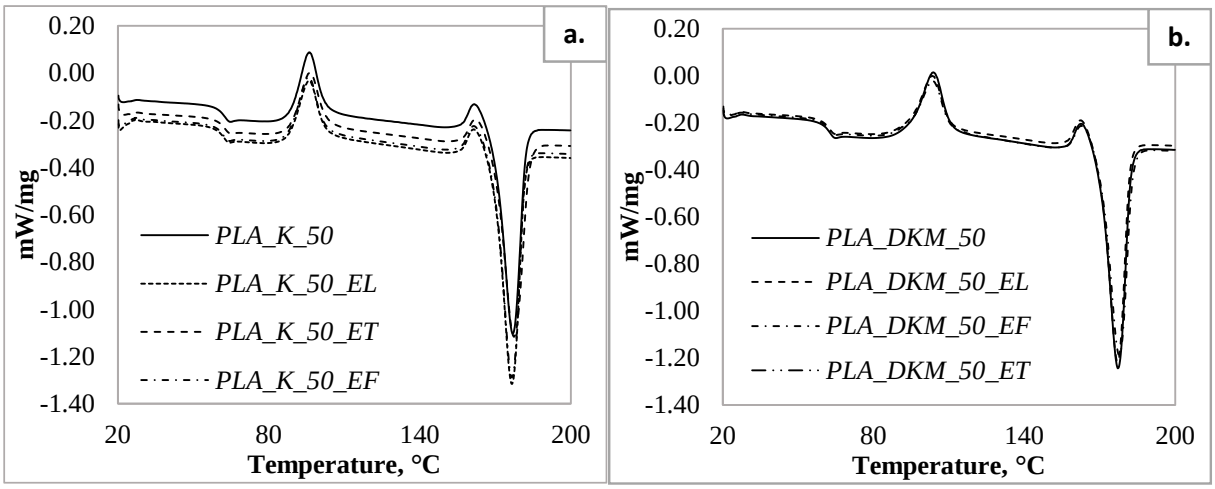

Figure 7. The second heating DSC curves of the PLA microparticles after measuring the adsorption of a.) particles prepared in chloroform and b.) particles prepared in dichloromethane.

particle size varied, the degree of adsorption of the essential oils on the particles varied. The particles that were prepared in dichloromethane as a solvent, exhibited a higher specific adsorption of 0.8-3.4 mg EO/g PLA compared to particles prepared in chloroform of 0.6-1.6 mg EO/g PLA. The difference in the adsorption properties of the particles is probably caused by variations in their structure. The different solvents used in the production process caused the particles to solidify at various rates, which may lead to differences in their internal structure and porosity.

The reason for differences in the degree of adsorption of the essential oils is variation in the composition of the essential oil solutions, which is characterized by the HSPs. In ethanolic solutions, a correlation between the adsorbed amount of the essential oil and the δ_p component of the total HSPs was observed.

Based on the results, it was determined that the thermal properties of the PLA microparticles are affected by the type of solvent used during their preparation rather than by the concentration of PLA solution applied. It was concluded that the thermal properties of the microparticles were not affected by the degree of adsorption.

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