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Method for the Determination of Solvent Sorption of Polylactic Acid and the Effect of Essential Oils on the Sorption Properties

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Abstract: The investigation of the adsorption and diffusion properties of polylactic acid (*PLA*) is very important, because during the application of the polymer, interactions can occur between the polymer and its environment that can affect its properties and application. The aim of our work was to investigate a method for determining the solvent sorption capacity of *PLA* and to investigate how different additives, such as essential oils, affect the solvent sorption properties of the polymer. Experiments were carried out to explore the correlation between the solvent uptake of two different types of *PLA* granules and the solubility parameter of the selected 5 essential oils (*Melissa officinalis*, *Mentha piperita*, *Foeniculum vulgare*, *Majorana hortensi*, *Thymus vulgaris*) for 3 solvents. It was observed, that application of essential oils was changed the solvent uptake of the granules differently. While one granule solvent uptake decreased on average by 2–3 wt.%, the other increased by a similar amount. The difference of sorption capacity of pure and essential oil containing solvent were between 20–190%. The specific essential oil uptake was highest in solutions with a concentration of 2.00 mg/mL, about 2.00 mg *EO*/g *PLA*. In alcoholic solutions we observed a relation between the solvent uptake of *PLA* and the solubility parameter of the relevant essential oil.

Keywords: polylactic acid; Hansen solubility parameter; solvent adsorption; essential oil adsorption

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1. Introduction

Essential oils (*EOs*) contain a number of volatile and natural bioactive compounds (terpenes, hydrocarbons). For example, thyme oil is widely used in perfumes, cosmetics, rosemary and peppermint oil in medicines and these can be applied as food preservatives [1–3]. Investigation of the adsorption and diffusion properties of essential oils in biodegradable polymers is important to increase the applicability of these polymers.

The importance of biodegradable polymers is constantly growing in industry. Application of them could be good choice to replace fossil-based polymers for packaging and medical applications. Polylactic acid (*PLA*) is one of them that is used more and more extensively for applications in medical devices, medical implants, tissue engineering, drug delivery fibers of packaging containers, textiles. Its fields of application are limited by certain properties, such as the poor mechanical strength of the polymer [4–7].

Essential oils provide antimicrobial property to *PLA* but they act as a plasticizer as well [8,9]. Along with the latter effect, structural, mechanical and thermal properties of the polymer could be more or less altered [10]. Among the mechanical properties of the polymer, for example, the tensile strength of the polymer decreases and the elongation at break increases. The change in mechanical properties upon plasticization depends mainly on the composition and polarity of the essential oils [11].

The change in the properties of the polymer matrix probably can be associated with the polarity of essential oil components. On this basis, it should be investigated whether the adsorption properties of essential oils on a polymer can be related to the Hansen solubility parameters (*HSP*). The Hansen solubility parameter characterizes the affinity of

the polymer for various organic compounds [12,13]. The *HSP* consists of three parameters: the parameter representing contribution to dispersion forces (δ_d), the parameter indicating polar interactions (δ_p) and the parameter representing the formation of H-bonds (δ_h). The *HSP* values of solvents that dissolve the polymer will be closer to the *HSP* value of the polymer than those that do not dissolve the polymer [14].

The sorption of essential oils in the polymer depends on several factors, including the composition of the essential oil, its polarity, and the properties of the polymer. The essential oil absorption of polymers also depends on the method by which the active ingredient is incorporated into the polymer. Due to hydrophobicity at the surface of granules, instability, and volatility of essential oil composition, it could be easily evaporated and lost during preparation [3]. Martins et al. has investigated the adsorption through encapsulation and the release of essential oil components, like thymol and p-cymol from *PLA*-based microcapsules [15]. They confirmed a preferential encapsulation of apolar compounds in detriment of polar compounds of thyme oil. The maximum amount of thyme oil encapsulated was 65% [16,17]. Microparticles encapsulated with orange essential oil were prepared by Xiao et al. by improved emulsifying solvent evaporation method. An encapsulation efficiency of 93.23% was achieved, with a loading capacity was 19.17% [18]. Villegas et al. investigated the impregnation of cinnamaldehyde using supercritical impregnation method with supercritical CO_2. The impregnation yield was between 8–13 wt.% [19]. Helal et al. synthesized poly (lactic-co-glycolic) acid (*PLGA*) particles and entrapped three essential oil components (eugenol, linalool, and geraniol) inside these *PLGA* particles by using the continuous flow-focusing microfluidic method. The encapsulation efficiencies of essential oil components in *PLGA* particles were 95.14%, 79.68%, and 71.34% and loading capacities were 8.88%, 8.38%, and 5.65% [20].

Martins et al. the release test of the essential oil components from *PLA*-based microparticles showed that the rate of release is higher during the first hour, than the amount of the active component released is set to a constant value. This may be due to diffusion through the *PLA* matrix in the first hours, while the release mechanism later depends mainly on the molar mass of the *PLA*. The diffusion of thymol occurs more rapidly through the polymer, probably due to the difference in polarity between the two components [15,21]. Similar release mechanism was observed by other researchers like Biswal et al., Dusankova et al. [22,23]. Dusankova et al. has studied the preparation and characterization of *PLA* microspheres containing different essential oil constituents. The polar essential oil component is more adsorbed in the microspheres than the more apolar components since the *PLA* itself is polar [23].

Not only the polarity of the components but also the δ_h component of their solubility parameter can be associated with the change in the properties of the polymer. Sato et al. tested the properties of *PLA* films in 60 kinds of organic solvent according to the solubility parameters of solvents. They concluded that the hydrogen binding parameter of the solubility parameters is more determinant in the solubility and swelling properties of the polymer than the other two solubility parameter component [24].

The aim of our work was to develop a method to determine the solvent adsorption capacity of polylactic acid particles. We investigated the effect of different additives on the solvent sorption properties of the polymer and how its related to the solubility parameter of essential oils. The experiment was carried out with five different essential oil solutions in three different concentrations (1 wt.%, 1.5 wt.% and 2 wt.%). Solutions were prepared with various solvents such as ethanol, methanol and hexane. Adsorption studies were carried out on two granules with different properties (different degrees of crystallinity and different purity).

2. Materials and Methods

2.1. Materials

Two different types of *PLA* granules have been used: Nature Works Ingeo Biopolymer 4043D, and Nature Works Ingeo Biopolymer 3D850 (NatureWorks, Plymouth, MN, USA).

Five essential oils were used for the experiment: *Melissa officinalis* (lemongrass essential oil, Neuston Healthcare Kft., Budapest, Hungary), *Mentha piperita* (peppermint essential oil, Neuston Healthcare Kft., Budapest, Hungary), *Foeniculum* vulgare (fennel essential oil, Neuston Healthcare Kft., Budapest, Hungary), *Majorana hortensis* (marjoram essential oil, Neuston Healthcare Kft., Budapest, Hungary), *Thynus vulgaris* (thyme essential oil, Neuston Healthcare Kft., Budapest, Hungary). All commercial essential oils are 100% pure natural essential oils produced by steam distillation.

2.2. Methods

PLA granules were pre-dried at 80 °C for 4 h in a dryer (Binder FD 53, BINDER GmbH, Tuttlingen, Germany) to adjust their water content. For the solvent uptake measurement, 2.000 g of *PLA* granules were weighed on an analytical balance (Ohaus Adventurer AR3130, Ohaus, China) in a pre-weighed dry test tube, then 2.000 g of volatile oil solution was added to it in a given concentration (1 wt.%, 1.5 wt.% and 2 wt.%). The granules were soaked for 24 h, then the samples were separated by filtration. The granules were dried in a dryer at 80 °C to constant weight. The composition of the residual solution was analyzed by gas chromatography.

The essential oil solutions were analyzed by Gas Chromatography. The GC analyses were performed on GC 2010 Shimadzu (Shimadzu, Kyoto Japan) with an Equity-1 column (30.0 m × 0.25 mm; film thickness 0.25 µm) with a FID detector. Injector and detector temperatures were set to 280 °C. The injected volume was 1 µL. The heating rate was 10 °C/min from 50 °C to 280 °C.

Differential scanning calorimetry (*DSC*) was performed with NETZSCH DSC 214 Polyma (NETZSCH, Selb, Germany) instrument. The measurements were carried out under 60 mL/min N_2 flow rate according to the following protocol: first heating from 20 to 200 °C with 10 °C/min heating rate, than first cooling from 200 to 20 °C with 10 °C/min cooling rate, finally a second heating from 20 to 200 °C with 10 °C/min heating rate.

To investigate how solvent uptake is related to the Hansen solubility parameter (δ_t) of essential oils, the solubility parameters of essential oils were determined. The Hoftyzer-Van Krevele group contribution method was used to determine the solubility parameters of the main components of essential oils. Solubility parameters of a solution are a linear function of composition. In our work, the volume fraction for each component was used for calculate the solubility parameters of solutions [14,25].

In this work a three-letter code was used to identify the samples. The first letter refers to the type of granules, the second refers to the type of solvent and the last letter refers to essential oil. The number refers to the concentration of the essential oil solution (Table 1).

Table 1. Notation for the samples.

Granules		Solvents		Essential Oils		Solution Concentration	
F	3D850 *PLA*	*E*	Ethanol	*L*	Lemongrass essential oil	*1*	1 wt.%
S	4043D *PLA*	*M*	Methanol	*M*	Marjoram essential oil	*1.5*	1.5 wt.%
		H	Hexane	*T*	Thyme essential oil	*2*	2 wt.%
				P	Peppermint essential oil		
				F	Fennel essential oil		

3. Results

3.1. Granules Solvent Sorption

We measured the solvent adsorption of the two granules in pure solvents and concluded that the granules *S* solvent sorption was 46.4% higher of ethanol, 50.7% of methanol and 54.0% of hexane than in the granules *F* This may be because *F* granules are more heat-resistant and crystalline than *S* granules [26,27]. The purity of granules is also different. IR spectrophotometric method was used to determine that the *PLA* content of the granules *F* was 94% and for the other granules it was 89%.

We have carried out preliminary experiments (which are not included in this report) in order to find out the swelling behavior of the granules in different solvents. We found that there was no measurable change in granules diameters in alcohols over the 14-day period studied. In hexane solvent, the granules diameter increased by 4%.

3.1.1. Solvent Sorption in Ethanol Solutions

In essential oil solutions the solvent sorption of the *S* granules for each essential oil was less than 5.0 wt.% which was measured in pure ethanol. (Figure 1a). The opposite is true for granules *F*. In the case of the *F* granules the solvent uptake was higher in the presence of essential oil than in pure ethanol solvent. The solvent adsorption was greater than 2.3 wt.%. (Figure 1b). The solvent sorption of *S* granules in the presence of essential oil is close to solvent uptake of *F* granules in pure ethanol.

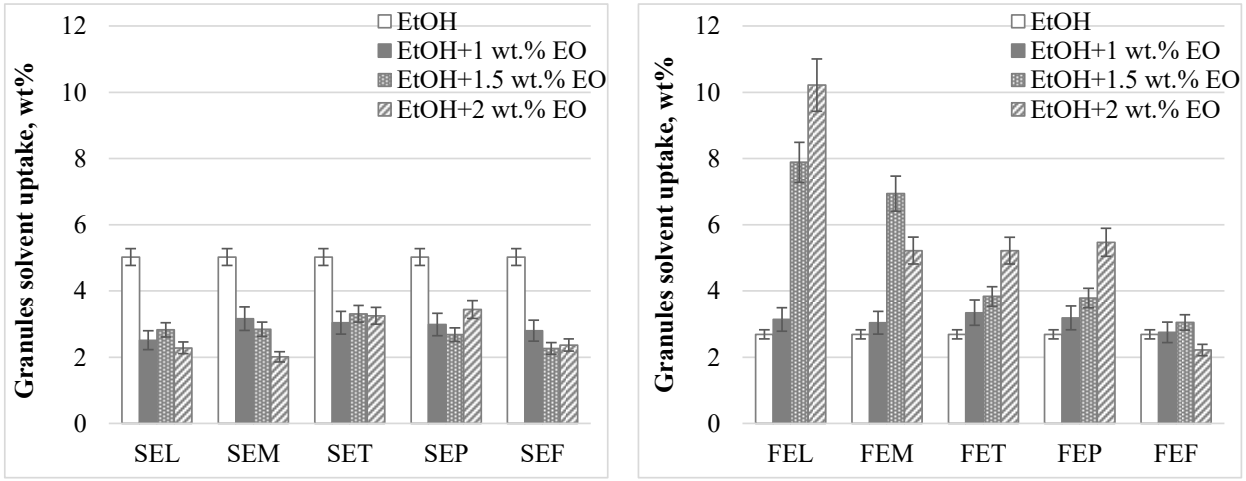
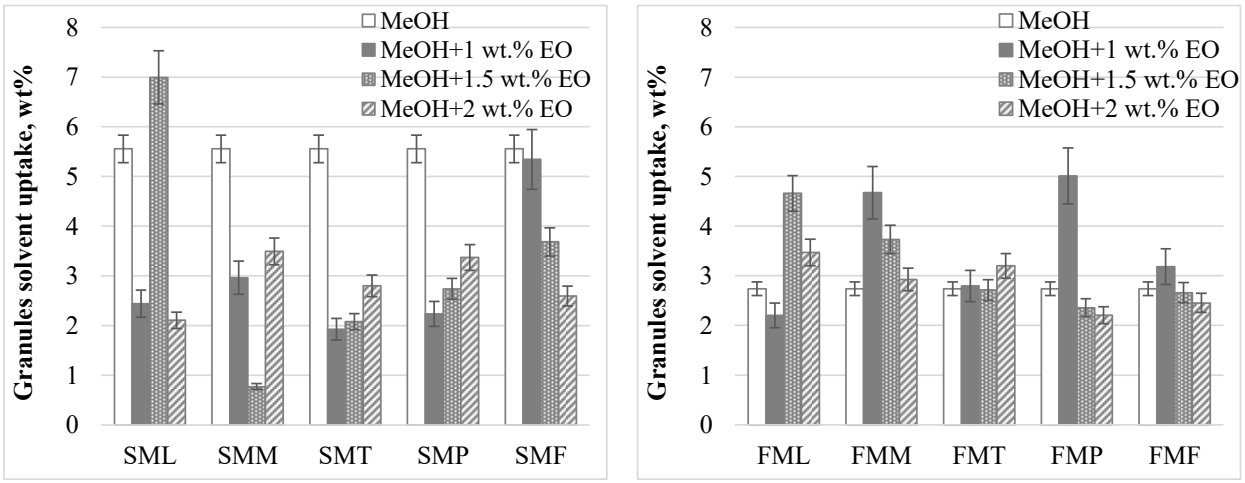


Figure 1. Solvent uptake in ethanol at different concentration of essential oil: (**a**) 4043D granules; (**b**) 3D850 granules.

The amount of adsorbed solvent was decreased with the increase of the concentration of solutions at sample *SEM*. The other samples adsorption capability changed differently (*SEL*, *SET*, *SEP* and *SEF* samples). The solvent sorption of the *S* granules was between 2.0 wt.% and 3.4 wt.%. Compared to *S* samples, for *FET*, *FEM*, *FEL* and *FEP* samples, solvent uptake increases with increasing essential oil concentration. Lemongrass essential oil had the most effect on solvent uptake. By increasing the concentration of the lemongrass essential oil solution from 0 wt.% to 1 wt.%, 1.5 wt.% and 2 wt.%, the amount of solvent adsorbed increased by 1.2 times, 2.9 times and 3.8 times, respectively. There was no significant change in the solvent sorption of the granules in the *FEF* sample (±0.42 wt.%).

3.1.2. Solvent Sorption in Methanol Solutions

The solvent sorption of the *F* and *S* granules in methanol solvent were 2.7 wt.% and 5.5 wt.%. Granules *S* solvent sorption properties in methanol were similar to those in ethanol. The weight change of the *S* granules for each essential oil is less than in pure ethanol (less than 5.5 wt.%), exception of sample *SML1.5* (Figure 2a). Based on the results, we found that in the presence of essential oils (at least 2 of 5), the solvent uptake increased for *F* granules (Figure 2b) compared to pure solvent (>2.7 wt.%).



(**a**) (**b**)

Figure 2. Solvent uptake in methanol at different concentration of essential oil: (**a**) 4043D granules; (**b**) 3D850 granules.

In the case of solutions of thyme and peppermint essential oil, it has been observed that increasing the concentration of essential oil leads to increased solvent uptake of *S* granules. For example, for *SMP* samples, increasing the concentration from 1 wt.% to 1.5 wt.% and 2 wt.% increased the amount of solvent adsorbed from 2.2 wt.% to 2.7 wt.% and 3.4 wt.%, respectively. For *FMM* and *FML* samples, the amount of solvent adsorbed is increased by at least 26.7%. The exceptions are samples *FML1* and *FMM2*, where the solvent uptake decreased (by 20%) or didn't change (2.9 wt.%). For the *FMT* sample, the solvent uptake of the particles didn't change significantly (±0.37 wt.%). In the case of samples of *FMM*, *FMP* and *FMF*, we also found that increasing the essential oil concentration of the solution decreases the amount of solvent absorbed.

3.1.3. Solvent Sorption in Hexane Solutions

Using hexane as a solvent, the solvent sorption of the granules was lower in the pure solvent than in ethanol and methanol. It was 3.7 wt.% for granules *S* and 1.7 wt.% for granules *F*. We found that for the *S* samples, there is no similar relation between the concentration of essential oil in the solution and the amount of solvent absorbed (Figure 3a). The solvent uptake of the granules *S* in the presence of each essential oil is lower (<3.0 wt.%) than for pure hexane in the presence of essential oil. For granules *F*, the solvent uptake of each sample was greater (>2.0 wt.%) than or equal (around 1.7 wt.%) to the solvent uptake of the sample without essential oil. (Figure 3b).

In the case of the *SHL* and *SHF* samples, in 1.5 wt.% solutions the granules solvent uptake was maximal while for the *SHM* and *SHP* samples it was minimal at this concentration. For the *SHT* sample there is not significant change (~1.3 wt.%) in the solvent uptake of the granules. For samples of *FHL*, *FHM*, *FHT* and *FHF*, we found that the solvent uptake increases by increasing the concentration of essential oil from 1 wt.% to 1.5 wt.% by 81.3%, 31.0%, 14.5% and 11.1%. However, by further increasing the concentration to 2 wt.%, the solvent uptake is reduced.

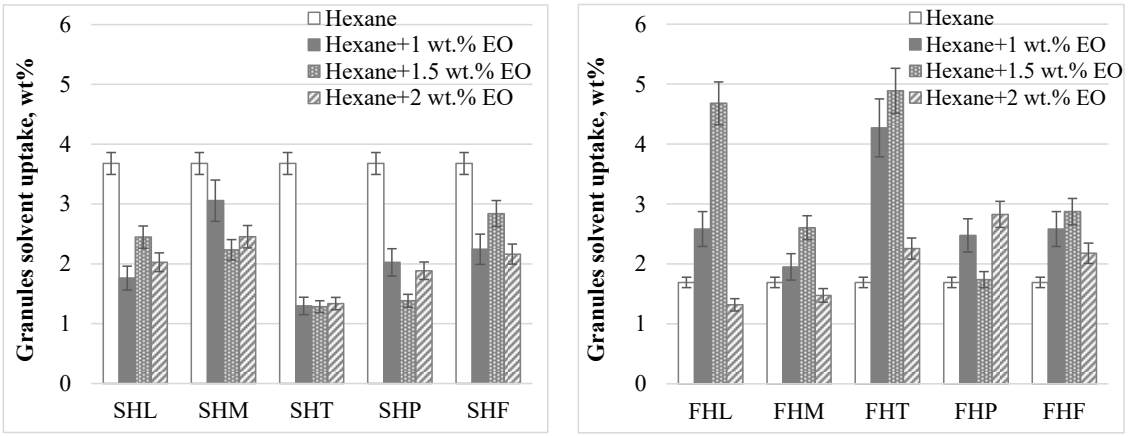


Figure 3. Solvent uptake in hexane at different concentration of essential oil: (**a**) 4043D granules; (**b**) 3D850 granules.

3.2. Granules Essential Oil

3.2.1. Essential Oil Adsorption in Ethanol Solutions

Based on the results of measurements with ethanol solutions, we found that in the case of *SEL*, *FEL*, *SEP*, *FEP*, *SEM*, *FET* and *SEF* samples, as the concentration of essential oil in the solution increases, the amount of essential oil adsorbed by the granules increases. Similar correlation was not found for the *FEF* sample, while for the *SET* sample the opposite was observed: as the concentration of essential oil in the solution increases, the amount of essential oil adsorbed by the granules decreases (Figure 4).

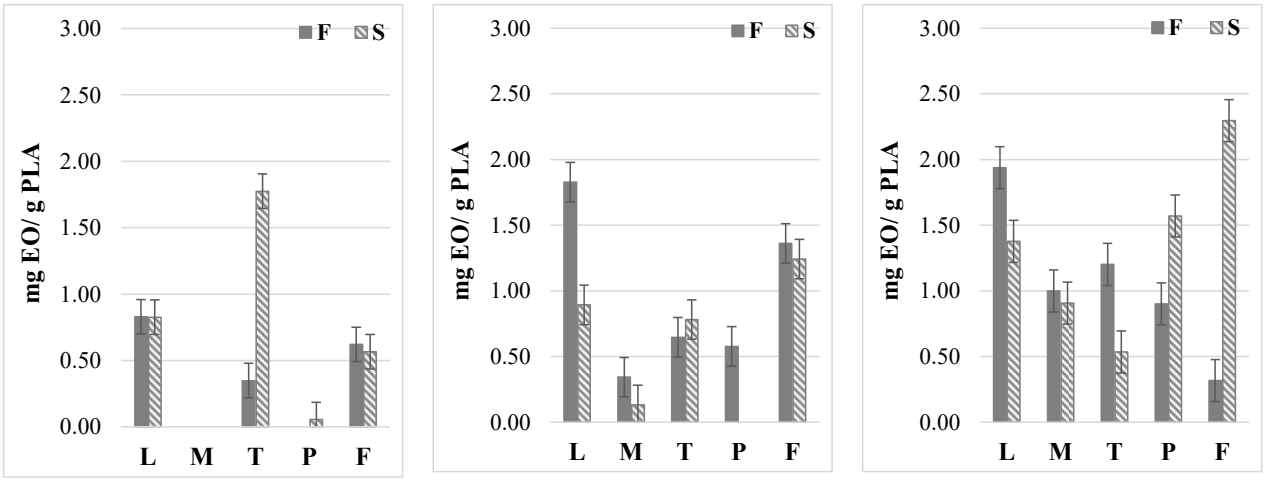


Figure 4. The specific amount of essential oil in ethanol solutions at different concentrations: (**a**) 1 wt.% solution; (**b**) 1.5 wt.% solutions; (**c**) 2 wt.% solutions.

In the case of the *FEL*, *FET*, *FEF* and *FEP* samples, in the presence of the essential oils the solvent uptake of the granules *F* increased, which is directly proportional to the amount of adsorbed essential oil. In the presence of lemongrass essential oil by increasing the concentration of essential oil from 1 wt.% to 1.5 wt.% the amount of solvent adsorbed increased by 2.5 times and the amount of adsorbed essential oil also increased by 2.2 times. By further increasing the concentration, solvent uptake increased by 1.3 times, and the amount of essential oil adsorbed by 1.05 times. In the case of *FET1* and *FET1.5* samples, the amount of the thyme essential oil bound by the *PLA* increased by 85.8%, but this did not

cause a significant difference in solvent uptake (±0.03 wt.%). For *FEP1.5* and *FEP2* samples by increasing the concentration the essential oil uptake increased by 56.1% and the solvent sorption increased by 44.3%.

In the case of the *SEL*, *SET*, *SEF* and *SEM* samples, in the presence of the essential oils the solvent uptake of the granules *S* decreased, which is inversely proportional to the amount of adsorbed essential oil. However, when using peppermint essential oil, the amount of solvent adsorbed is directly proportional to the amount of essential oil adsorbed. For *SEF1*, the solvent sorption of the *PLA* granules was the highest (2.80 wt.%) and the adsorbed amount of essential oil the lowest (0.6 mg *EO*/g *PLA*) among the three samples. For *SEF1.5* and *SEF2* samples the amount of adsorbed essential oil increased by 2 and 4 times but this caused no further change in solvent uptake (±0.03 wt.%). In the presence of peppermint essential oil, the amount of essential oil adsorbed increased from 0.06 to 1.57 mg *EO*/g *PLA* by increasing the concentration of essential oil from 1 to 2 wt.%. This caused only a 15% increase in solvent uptake.

3.2.2. Essential Oil Adsorption in Methanol Solutions

We found that in the case of *SMP*, *FMF*, and *SMF* samples, increasing the concentration of essential oil in the solution increases the specific amount of essential oil taken up by the granules. For *FMP* and *SMT* samples the opposite was observed: as the concentration of essential oil in the solution increases, the amount of essential oil adsorbed by the granules decreases. Similar correlation was not found in the case of lemongrass essential oil (Figure 5).

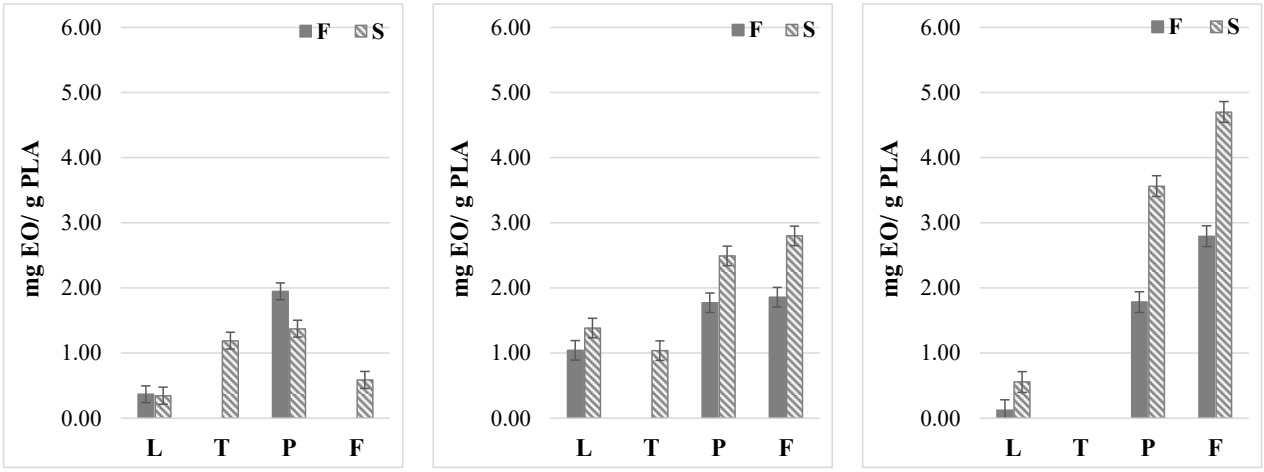


Figure 5. The specific amount of essential oil in methanol solutions at different concentrations: (**a**) 1 wt.% solution; (**b**) 1.5 wt.% solutions; (**c**) 2 wt.% solutions.

In the case of the *FML* and *SMP* samples, in the presence of the essential oils the solvent uptake of the granules *F* increased, which is directly proportional to the amount of adsorbed essential oil. For *FML1* and *FML1.5* with the increasing concentration of the solution as the essential oil uptake increased by 2.8 times, the solvent sorption increased by 2.1 times.

In the case of the *SML*, *SMT*, *SMF* and *FMF* samples, in the presence of the essential oils the solvent uptake of the granules *S* decreased, which is inversely proportional to the amount of adsorbed essential oil. For *SML1* and *SML2* samples with the increasing concentration of the solution as the essential oil uptake increased by 60%, the solvent sorption decreased by 13.5%. Samples *FMF1.5* and *FMF2* showed similar behavior, as the concentration of the solution increased, the essential oil sorption also increased (by 50%), but the solvent adsorption decreased (by 8%). However, the increase in the specific

amount of essential oil (the difference was about 1.00 mg *EO*/g *PLA*) did not cause a significant difference in solvent uptake (the difference was 0.2 wt.%). The *SML1.5* sample behaved differently from. *SML1* and *SML2* samples. Of the three samples, this sample had the highest essential oil sorption (1.39 mg *EO*/g *PLA*) and the highest solvent sorption (7.0 wt.%). For the *SMT* and *FMP* samples, the amount of solvent absorbed and essential oil adsorbed did not change significantly with increasing thyme essential oil concentration.

3.2.3. Essential Oil Adsorption in Hexane Solutions

Based on the results of tests carried out with hexane solvent, we found that in the case of *SHL*, *FHT*, *SHP*, *FHP* and *SHF* samples, the amount of solvent absorbed by the *PLA* and the amount of essential oil adsorbed by the *PLA* are inversely proportional. (Figure 6).

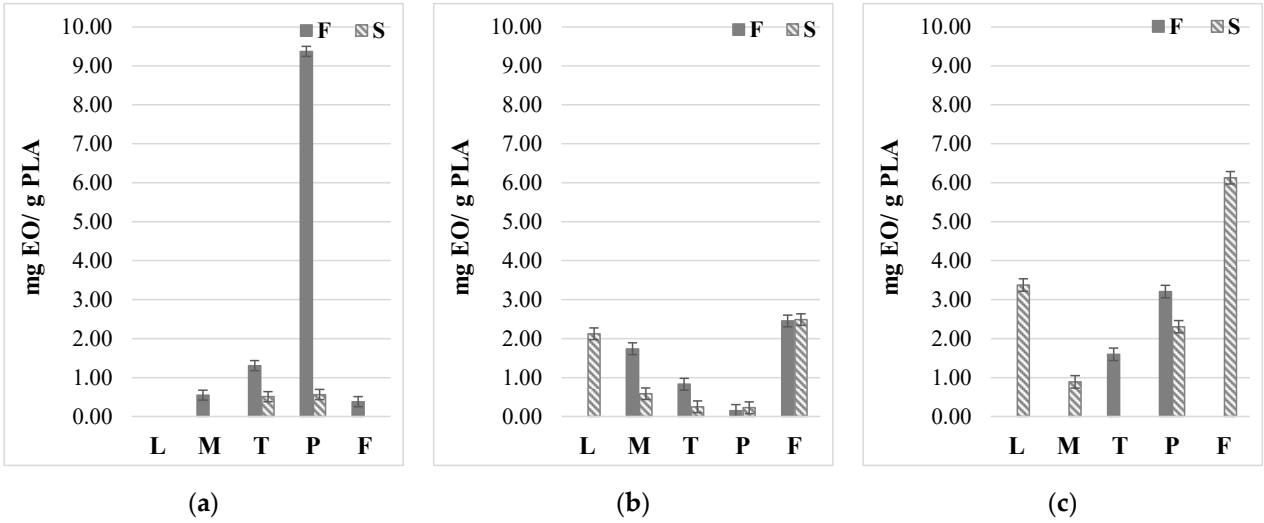


Figure 6. The specific amount of essential oil in hexane solutions at different concentrations: (**a**) 1 wt.% solution; (**b**) 1.5 wt.% solutions; (**c**) 2 wt.% solutions.

For *SHL1.5* and *SHL2* samples as the concentration of essential oil increases (by 0.5 wt.%), the amount of solvent absorbed decreases (by 17.1%), while the amount of adsorbed essential oil increases (by 37.1%). The *SHP* and *SHF* sample series showed similar results. In the case *FHT* and *FHP* samples, the amount of the adsorbed essential oil doesn't depend on the concentration of the essential oil in the solution. For the *SHT* samples we found that the amount of essential oil absorbed by the *PLA* decreased (by 51.4%) with increasing concentration of the solution, but this did not affect the granules solvent uptake ($\pm$0.03 wt.%).

In the case of the *FHM*, *SHM* and *FHF* samples, in the presence of the essential oils the solvent uptake of the granules *F* increased, which is directly proportional to the amount of adsorbed essential oil. As the concentration of essential oil solutions increases, the amount of solvent absorbed and the amount of essential oil adsorbed increases. For example, for *FHM1* and *FHM1.5* samples the essential oil uptake increased by 3.1 times and the solvent sorption increased by 31%.

3.3. Correlation with the Hansen Solubility Parameter

Table 2 contains the solubility parameter and the relative energy difference (*RED*) value for each essential oil and solvent [18]. The solubility parameters of essential oils were calculated using the Hoftyzer-Van Krevele method. Solubility parameters of a solution are a linear function of composition. The solubility parameter components can be calculated on the basis of the molecular structure using the group contribution method [14,25].

Table 2. Solubility parameters and *RED* values of essential oils, solvents and the *PLA*.

Material	δ_d, $(J/cm^3)^{1/2}$	δ_p, $(J/cm^3)^{1/2}$	δ_h, $(J/cm^3)^{1/2}$	δ_t, $(J/cm^3)^{1/2}$	*RED*
PLA	18.6	9.9	6.0	21.9	-
Lemongrass essential oil	16.4	4.6	5.1	17.8	0.65
Marjoram essential oil	19.5	1.3	3.2	19.8	0.87
Thyme essential oil	21.3	3.2	9.2	23.8	0.89
Peppermint essential oil	25.8	4.6	5.8	26.8	1.43
Fennel essential oil	24.3	3.9	28.0	37.3	2.39
Ethanol	15.1	8.4	18.3	25.2	1.33
Methanol	14.5	11.5	21.4	28.3	1.64
Hexane	14.6	0.0	0.0	14.6	1.31

Based on the solvent solubility parameter, the polymer-solvent affinity is reduced as follows: hexane $\geq$ ethanol > methanol. In the case of essential oils, the solubility is highest in the case of lemongrass essential oil, followed by marjoram, thyme, peppermint, and fennel essential oils. The essential oil in the solvent does not significantly affect the solvents *HSP* and *RED* values. For example, in the case of lemongrass essential oil the solution solubility parameter in ethanol is 25.0, in methanol its 28.0 and in hexane its 14.5.

In pure ethanol, methanol and hexane solvents, the granules are not soluble, but solvent adsorption occurs. The granules absorbed more solvent in alcohols than in hexane. For example, for the granules *S* in methanol the solvent sorption was more than 5%, while in hexane it was 3.7%. Depending on the *HSP* parameter, it can be said that the higher the *RED* value of the solvent the lower the solvent adsorption.

For granules *F* a relation can be observed in both ethanol and methanol solvents between the solvent uptake of *PLA* and the solubility parameter of the relevant essential oil (Figure 7). The higher the *RED* value of the relevant essential oil, the lower the solvent uptake. This was observed primarily in solutions of 1.5 wt.% and 2 wt.% concentrations. For the solvent hexane, similar relation was observed with solutions with a concentration of 1.5 wt.%. However, for a solution with a concentration of 2 wt.%, the amount of solvent adsorbed increases with increasing solubility parameter. This relation is nearly linear for *FHL*, *FHM*, *FHT* and *FHP* samples.

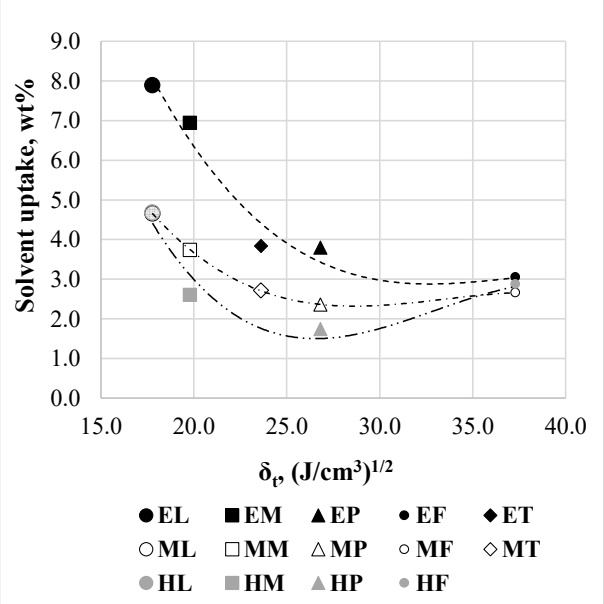


Figure 7. Solvent uptake as a function of the solubility parameter of essential oils in the case of 1.5 wt.% solution concentration with ethanol, methanol and hexane solvent.

In the case of granules *F*, for all the three solvents the relation between the solubility parameter of essential oil and the solvent uptake follows a similar trend, solvent uptake decreases as the polymer-essential oil solubility decreases (Figure 7). This was observed primarily in solutions of 1.5 wt.% and 2 wt.% concentrations. In the case of hexane solvent, similar relation was observed with solutions of 1.5 wt.% concentrations. However, in the case of 2 wt.% concentration solution, the amount of solvent adsorbed increased with increasing solubility parameter.

Figure 7 shows that the lowest effect of the solubility parameter on solvent sorption was observed when methanol was used as a solvent. Compared to methanol, the use of ethanol solvent had a positive effect on the solvent uptake of the granules, as excess solvent uptake was achieved. While the use of hexane was a disadvantage of the solvent sorption, as the excess solvent uptake was less than methanol was used. In particular, there is a discrepancy in the solvent uptake of the granules for essential oils with a solubility parameter below 20.0 $(J/cm^3)^{1/2}$. The relation is not continuous, the individual essential oils may differ from the tendency. The possible reason for this may be the structure or polarity of the main components of the essential oils. Due to the essential oil plasticizing properties, it alters the structural and mechanical properties of the polymer, as a result it can change the polylactic acid solvent sorption properties. The different essential oil components are supposedly change the structure and properties of the polymer to a different extent.

We found a correlation between the amount of essential oil adsorbed and the solubility parameters of essential oils. Considering the *FM2*, *FM1.5* and *FE1.5* samples, the lower the δ_t and *RED* value of the relevant essential oil, the higher the essential oil uptake (Figure 8). On the other hand, for *FE2*, *SM1.5*, *FH1.5* and *SH1.5* samples the relation is opposite. The lower the δ_t and *RED* value of the relevant essential oil, the lower adsorbed amount of the essential oil. In the case of the other samples no relation could be found between the amount of adsorbed essential oil and the solubility parameter of the essential oils.

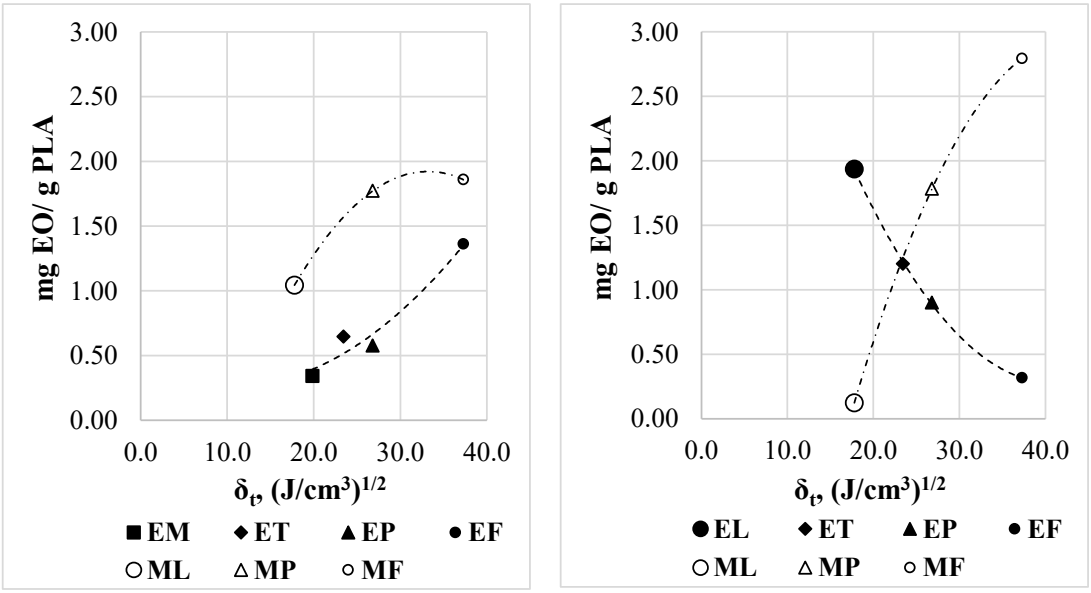


Figure 8. The specific amount of essential oil adsorbed as a function of the solubility parameter of essential oils in the case of sample F in: (**a**) 1.5 wt.% solutions, (**b**) 2 wt.% solutions with ethanol and methanol as a solvent.

3.4. Thermal Characteristic of the PLA Granules

Differential scanning calorimetry (*DSC*) was performed in order to know the thermal characteristics of the samples. We investigated how the thermal properties of the granules used differed from each other and how the solvent uptake affected the properties. The

glass transition (T_g), cold crystallization (T_{cc}) and melting temperature (T_m) of the *PLA* granules were determined from the second heating of the *DSC* measurement (Table 3). The degree of crystallinity (X_c%) was calculated from the melting enthalpy (ΔH_m) and the cold crystallization enthalpy (ΔH_{cc}), considering an ideal melting enthalpy ($\Delta H_m{}^0$) of 94 kJ/kg [28,29].

$$X_c\% = [(\Delta H_m - \Delta H_{cc})/\Delta H_m{}^0] \times 100, \quad (1)$$

Table 3. Thermal characteristic of the samples.

Sample	T_g, °C	T_{cc}, °C	T_m, °C	ΔH_{cc}, J/g	ΔH_m, J/g	X_c, %
F	61.5	113.9	177.6	16.28	27.91	12.4
S	60.7	117.0	152.0	1.23	2.13	1.0
FEL	61.8	130.8	177.1	14.56	15.07	0.5
FEM	61.4	123.8	176.2	14.56	25.09	11.2
FET	61.6	129.8	177.0	17.35	19.68	2.5
FEP	61.5	130.1	175.8	14.91	16.31	1.5
FEF	61.9	128.6	177.6	23.61	28.95	5.7
SEL	60.0	-	151.1	-	0.39	0.4
SET	60.3	118.4	150.8	0.78	1.14	0.4
SEF	60.4	117.3	150.5	1.36	3.50	2.3

The *F* granules exhibited an exothermic, cold crystallization peak at 114 °C and an endothermic, melting peak at 178 °C. The *S* granules also exhibited two peaks but with lower T_m and peak intensity (Figure 9). The *F* granules has a higher crystallinity degree (12.4%) than the *S* granules (1.0%). Probably this the reason of the difference in the solvent adsorption properties.

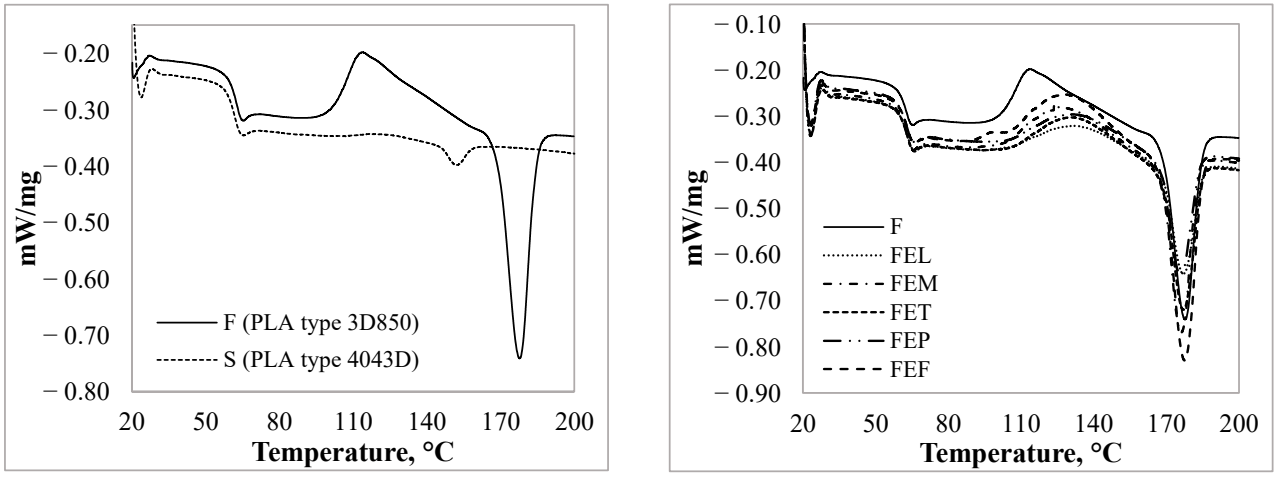


Figure 9. *DSC* thermograms of the samples: (**a**) DSC curves of the two *PLA* granules, (**b**) *DSC* curves of 3D850 *PLA* granules after adsorption.

After the adsorption measurements the extent of the aforementioned peaks was decreased (Table 3), due to the sorption of the essential oil solutions, but the T_m of the resultant granules remained almost unchanged (176.8 ± 0.7 °C) and the T_g also remained unchanged (61.6 ± 0.2 °C). The T_{cc} of the samples increased, with more than 10 °C compared to the reference but the ΔH_{cc} did not changed significantly (15.5 ± 1.2 J/g) except for *FEF* (23.6 J/g). Based on the results, it can be concluded that int the case of lemongrass, peppermint and thyme essential oils the higher the solvent uptake of the granules from the essential oil-containing solution, the lower the degree of crystallinity will be. Compared to

the *F* sample the degree of crystallinity of *FEL*, *FEP* and *FET* samples decreased by 11.9%, 10.9% and 9.9% respectively. The *FEM* sample forms an exception because the degree of crystallinity of the sample didn't change significantly (decreased by 1.2%) even though the granules had the second highest rate of essential oil uptake in the case of the marjoram essential oil. The deviation of the degree of crystallinity of the samples from the reference may be related to the polarity of the essential oils. The higher the δ_p parameter of the essential oil, the greater the X_c% deviation from the reference.

4. Conclusions

The aim of our work was to investigate a method for determining the solvent sorption capacity of polylactic acid (*PLA*) and to investigate how different additives, such as essential oils, affect the solvent sorption properties of the polymer. We used two types of polymer granules with different degrees of crystallinity and different purity. The solvent adsorption of the two granules was different in the pure solvents. The solvent sorption of 4043D granules was 46.4% higher in ethanol, 50.7% higher in methanol and 54.0% higher in hexane than that of 3D850 granules. This could be due to the fact that the 3D850 granules according to are purer (94% *PLA*), more resistant to temperature and more crystallized (X_c is 12.4%), while 4043D is amorphous (X_c is 1.0%) and less pure (89% *PLA*). In the presence of essential oil, the solvent uptake of the two granules changed inversely. While one granule solvent uptake decreased on average by 2–3%, the other increased by a similar amount. In the case of granules *F*, solvent sorption increases in the presence of essential oil, which is directly proportional to the amount of amount of the adsorbed essential oil for 4 of the 5 essential oils. The specific essential oil uptake was highest in solutions with a concentration of 2.00 mg/mL, about 2.00 mg *EO*/g *PLA*. In alcoholic solutions we observed a relation between the solvent uptake of *PLA* and the solubility parameter of the relevant essential oil. The solvent uptake of 3D850 type granules depends on the *RED* value and the solubility of the components, but for the 4043D granules it does not depend on them. For some samples, we found a correlation between the solvent uptake and the δ_t of essential oils and also between the essential oil uptake and the δ_t of essential oils. They follow different trends. The relation between the data in not continuous, the individual essential oils may differ from the tendency.

The adsorption of essential oils resulted in changes in the adsorption properties of the polymer and small changes in the thermal properties of the *PLA* granules. Based on the results, it can be concluded that in the case of lemongrass, peppermint and thyme essential oils the higher the solvent uptake of the granules from the essential oil-containing solution, the lower the degree of crystallinity will be. The change in the X_c% was 11.8%, 9.9% and 6.7% respectively. However, the T_g and T_m did not change significantly (61.6 $\pm$ 0.2 °C and 176.8 $\pm$ 0.7 °C, respectively).

The correlations found as a function of solubility parameter may be suitable for model-based prediction of polymer properties in similar material systems. By predicting the adsorption properties of the polymer, we can make progress towards increasing the applicability of polymers.

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