Investigation of the adsorption/desorption properties of polymer-based sorbents

PhD THESES

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1. Background, Objectives

Plastics are used in all areas of everyday life. The diversity of polymers and the versatility of their properties are used to produce a wide range of products that bring medical and technological advances, energy savings and other societal benefits. However, the environmental impact of fossil-based polymers has led to the growing importance of biodegradable and degradable plastics in industry. Nowadays, bio-based alternatives exist for almost all fossil-based conventional plastics and applications. These bioplastics have similar properties to conventional plastics, with the advantage of a lower carbon footprint.

Both for fossil-based polymers and for biopolymers, the interactions between the polymer and its environment affect its applicability. For example, in the case of packaging materials, exposure to the environment or the material being packaged may result in a change in the mechanical properties of the polymer (tensile strength, elongation at break), permeability, solubility, and degradation. Regarding the transport processes between material systems, adsorption and diffusion are the most important processes, so it is important to investigate the adsorption and diffusion properties of polymers in this respect.

In my work I have investigated the adsorption properties of a biopolymer, polylactic acid (PLA). I investigated the adsorption properties of PLA particles, granules and microparticles of different sizes, structures and compositions with different additives by using essential oils extracted from plants (*Melissa officinalis*, *Foeniculum vulgare*, *Thymus vulgaris*The interactions between the polymer and the essential oil change the mechanical and physico-chemical properties of the particles. Therefore, I have investigated the relationship between the adsorption properties and the Hansen's solubility parameters that characterise the solubility of the polymer, and how solvent and essential oil adsorption affect the thermal properties of the granules and microparticles.

2. Experimentals and evaluation methods

2.1. Investigation the properties of granules

I investigated the essential oil and solvent adsorption properties of different types of PLA granules produced for different applications, such as 3D printer monofilaments and biaxially oriented films. I determined how the solvent uptake of granules changes by the adsorption of essential oils of different composition such as lemongrass, marjoram, thyme, peppermint and fennel essential oils and how the solvent adsorption properties are related to the Hansen's solubility parameter of the polymer (δ_t is the total solubility parameter) and its coefficients (e.g. δ_p is the polarity parameter of the Hansen's solubility parameter).

For the adsorption studies, the granules were immersed in essential oil solutions of given concentrations (1.0 m/m%, 1.5 m/m% and 2.0 m/m%) for 1 day. The particles were separated from the solutions by filtration and the composition of the filtrate was analysed by gas chromatography.

2.2. Investigation the properties of microparticles

I investigated the adsorption properties of PLA microparticles prepared by solvent evaporation emulsion method. I have investigated the essential oil (lemongrass, thyme and fennel essential oils) uptake of microparticles prepared from different types of granules using essential oil solutions of different concentrations (0.25 mg/ml, 0.50 mg/ml and 1.00 mg/ml). I also investigated the effect of particle size (50, 100 and 200 μm) and the internal structure and porosity of the particles on the essential oil uptake of PLA microparticles. In this context, I investigated the relationship between the adsorption properties and the solubility parameter.

Microparticles were prepared by solvent evaporation emulsion methods. The microparticles were prepared by adding PLA solution to 1 wt.% aqueous PVA solution. PLA solutions were prepared at concentrations of 2.5 m/m%, 5.0 m/m% or 7.5 m/m% using dichloromethane or chloroform solvents.

The adsorption properties of the microparticles were investigated by the immersion method in essential oil solutions of given concentrations (0.25 mg/ml, 0.50 mg/ml and 1.00 mg/ml) for 1 day. The particles were separated from the solutions by filtration, and UV-Vis spectrophotometry was used to determine the concentration of essential oil in the filtrate by recording the absorbance spectra of the samples between 200 and 800 nm.

2.3. Investigations in supercritical fluid

I have also investigated the essential oil (lemongrass, thyme and fennel essential oils) adsorption properties of PLA microparticles in a supercritical fluid (supercritical carbon dioxide, $scCO_2$) at pressures of 100 bar, 150 bar and 200 bar for samples of different particle size and porosity.

I used a supercritical chromatograph (Jasco) to study the adsorption properties of the polymer. The measurements were carried out at 100 bar, 150 bar and 200 bar and at 40 °C. Supercritical carbon dioxide and absolute ethanol cosolvent were used as solvents. The solvent flow was set at 0.5 ml/min, to which 5 v/v% cosolvent was added. The prepared PLA particles were placed in a chromatography column (4.6×120 mm) and 10 µl of 0.5 mg/ml ethanol essential oil solution was injected onto the column. The essential oil was detected by UV-Vis detection.

2.4. Determination of thermal properties

I have investigated the thermal properties of both granules and microparticles. I have investigated how the glass transition temperature, melting point, cold crystallization properties and degree of crystallinity of the particles vary with the particle composition, size and structure and how these thermal properties are altered by essential oil adsorption.

Differential scanning calorimetry (*DSC*) was used to determine the thermal properties of polymer particles using a NETZSCH DSC 214 Polyma. The measurements were carried out at a N_2 flow rate of 60 ml/min for two heating-cooling cycles between 20-200°C at a heating and cooling rate of 10 °C/min.

2.5. Determination of the Hansen's solubility parameter

To determine the Hansen solubility parameter of essential oils, I used the Hoftyzer-Van Krevele method. The Hoftyzer-Van Krevele method was used to estimate the solubility parameters of the main components of essential oils, based on the structural formula of the essential oil component.

3. Theses

I. I have investigated the solvent and essential oil adsorption properties of polylactic acid granules. I have found that there is a 50% difference between the solvent adsorption of the two granules depending on the properties (type, composition and crystallinity) of granules, which varies in the opposite direction due to the adsorption of essential oil. The solvent uptake of one granule (type 4043D) decreased by an average of 2.2 m/m%, while that of the other (type 3D850 granules) increased by by an average of 1.6 m/m%. For the more crystalline 3D850 granules, the solvent adsorption increases in the presence of essential oil, which is directly proportional to the amount of essential oil adsorbed in the case of lemongrass, thyme, peppermint and fennel essential oils. The solvent uptake and essential oil uptake of granules can be related to the total solubility parameter (δ_t) of essential oils. The higher the δ_t value of the essential oil, the lower the solvent uptake.

II. I have investigated the adsorption properties of essential oil microparticles prepared from different granules as a function of essential oil concentration I have found that the uptake of essential oils in ethanol solutions is mainly caused by differences in particle properties, such as the degree of crystallinity or the material quality of the granules (purity or L:D isomer ratio), and not by the type of essential oils present in the solutions. When methanol solvent is used, the type of essential oil is also a determining factor. The specific amount of essential oil adsorbed was different for each essential oil (1.2-0.8 mg EO/g PLA) and decreased with decreasing essential oil concentration. The specific amount of essential oil adsorbed depends mainly on the polarity of the essential oils and can be related to the polarity parameter of the Hansen solubility parameter (δ_p). The closer the δ_p of the essential oil is to the δp of PLA, the higher the specific amount of essential oil adsorbed.

III. I have investigated the effect of particle size, as well as structure and porosity as a function of the preparation parameters, on the adsorption properties of essential oil in PLA microparticles. I have found that the specific amount of essential oil adsorbed did not change significantly with the variation in particle size, but it was affected by the type of essential oils. Particles prepared with dichloromethane solvent have a higher essential oil absorption than those prepared with chloroform. The solvent uptake and

essential oil uptake of the particles also increase with increasing particle porosity. In all cases, I found that the specific amount of essential oil adsorbed is mainly a function of the polarity of the essential oils. The amount of essential oil adsorbed can be related to the parameter δp of the essential oils. For particles prepared using dichloromethane solvent, the closer the δp of the essential oil is to the δp of PLA, the higher the specific amount of essential oil adsorbed by the particles.

IV. I have investigated the adsorption properties of PLA microparticles in a supercritical fluid. I found that in supercritical carbon dioxide, PLA microparticles retain the essential oils. The reduction in pressure and particle size is beneficial for the retention and separation of essential oils. Reducing pressure and particle size increases the retention of essential oils on the particles. For thymus essential oil, separation can be achieved on 50 µm particles. The retention is determined by the polarity of the essential oil. As the parameter δ_p of essential oils decreases, the rate of essential oil retention increases.

V. I have investigated the thermal properties of PLA particles. I found that the thermal properties of PLA microparticles are influenced more by the type of solvent used in the production method than by the PLA particle size. By *DSC* measurements, I confirmed that the thermal properties of the microparticles were not permanently altered by the adsorption of essential oils, neither by adsorption from liquid nor by adsorption from supercritical fluid. However, based on the results of the first heating step, I found that the adsorption of essential oils and the interaction with the $scCO_2$-ethanol solvent affect the thermal properties of PLA. *DSC* measurements have confirmed that the adsorption of essential oils and the interaction with the $scCO_2$-ethanol solvent affect the thermal properties of PLA. Compared to the reference samples, the glass transition temperature of the particles decreases by an average of 8°C and the degree of crystallinity of the particles can increase by up to 5%.

4. Publications

Articles

1. Virág, L.; Bocsi, R.; Pethő, D. Adsorption Properties of Essential Oils on Polylactic Acid Microparticles of Different Sizes. Materials 2022, 15, 6602. https://doi.org/10.3390/ma15196602
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3. Virág, L.; Bocsi, R.; Pethő, D. Study on adsorption of essential oils on polylactic acid microparticles. Hungarian Journal of Industy and Chemistry 2022, 50(2), 43-49. DOI: 10.33927/hjic-2022-17

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1. Virág Lilla, Bocsi Róbert, Pethő Dóra, Kén-hidrogén adszorpciója módosított felületű szén alapú szorbenssel, PhD hallgatók anyagtudományi napja XIIX, 2018. november, Veszprém, Magyarország
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6. Virág Lilla, Bocsi Róbert, Pethő Dóra, Illóolajok hatása politejsav szemcsehalmaz oldószer felvételére, Műszaki Kémiai Napok, 2021. április, Online konferencia
7. Virág Lilla, Bocsi Róbert, Pethő Dóra, Illóolajok adszorpciós tulajdonságainak a vizsgálata politejsav szemcséken, PhD hallgatók anyagtudományi napja XXI, 2021. november, Veszprém, Magyarország
8. Virág Lilla, Bocsi Róbert, Pethő Dóra, Illóolajok hatása politejsav szemcsehalmazok illóolaj adszorpciós tulajdonságaira, 50. Műszaki Kémiai Napok Jubileumi Konferencia, 2022. április, Veszprém, Magyarország