



Material characterisation

Aroma scalping characteristics of polybutylene succinate based films



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ABSTRACT

The removal of aroma compounds from packaged food items - aroma scalping - can be primarily controlled by the choice of packaging materials. Although the utilization of biodegradable polymers as packaging materials can greatly contribute to the sustainability of the packaging industry, only limited data on their aroma scalping properties are available. In this work, the aroma scalping characteristics of a series of films made from biodegradable polybutylene succinate (PBS) and polybutylene succinate-co-addipate (PBSA) for common aroma compounds in foods (ethyl acetate, ethyl butyrate, ethyl hexanoate, hexan-1-ol, heptanal and (R)-(+)-limonene) are reported. The aroma scalping characteristics of a film made from poorly biodegradable low density polyethylene (LDPE) are reported for comparison.

The aroma scalping characteristics, namely sorption and diffusion coefficients, of the tested aroma compounds were determined at 23 °C by means of sorption microgravimetry, and the permeability coefficients were estimated using the solution-diffusion model. The permeability coefficients for the films made from PBS, PBSA and LDPE were comparable for the more polar compounds: hexan-1-ol, ethyl acetate and ethyl butyrate. Conversely, the permeability coefficients of the less polar aroma compounds (ethyl hexanoate, heptanal and (R)-(+)-limonene) in PBS and PBSA-based films were by one to two orders of magnitude lower than those of the LDPE. In addition, a new mathematical model was proposed for the kinetics of the transient sorption of aroma compounds of low volatility ($p^{\text{sat}} < 1$ kPa).

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1. Introduction

Invariability of the flavour of packaged food items is one of the important issues for food producers because flavour changes influence consumer acceptance of food products. The undesired changes of flavour result from a number of factors [1]: i) from aroma scalping, i.e. the sorption and transport of aroma compounds through the package, ii) from the release of off-odours from the packaging material [2], and iii) from the chemical reactions (oxidation, hydrolysis etc.) that occur in the food item itself. Above all, aroma scalping is considered to be the key process controlling flavour changes in packaged products.

Concurrent with the need to characterize the aroma scalping properties of packaging materials is the need to utilize

biodegradable polymers in food and beverage packaging [3]. A comprehensive review of biodegradable polymers and their applicability can be found elsewhere [4]. One promising alternative to the widely used, but poorly biodegradable polyethylene (LDPE) and polypropylene (PP) is polybutylene succinate (PBS), which not only has similar mechanical and thermal properties [4–6], but is also biodegradable [4]. Above all, the bio-based PBS can be produced from renewable feedstock [7,8].

Whereas aroma scalping characteristics (i.e. sorption, diffusion and permeation coefficients) have been reported for LDPE and PP for a considerable set of aroma compounds [9–13], the characteristics of PBS have not yet been reported. Therefore, we report the aroma scalping characteristics for a film made from PBS, for three films made from PBS–PBSA (polybutylene succinate-co-addipate) layers, and for a film made from LDPE for comparison purposes. We did so for a comprehensive set of aroma compounds which simulates a wide range of physico-chemical properties of common aroma compounds in foods: ethyl acetate, ethyl butyrate, ethyl

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hexanoate, hexan-1-ol, heptanal and (*R*)-(+)-limonene.

The extent of the flavour changes caused by aroma scalping depends on a number of factors: the basic characteristics of the aroma compounds in the food (concentration, polarity, etc.); the structure and parameters of the polymer (polarity, glass transition temperature, crystallinity, etc.); the food characteristics (pH, humidity, etc.); and the storage conditions (temperature, relative humidity of the atmosphere, etc.) [1,14]. For simplicity, only the influences of the chemical structure and the properties of the polymers and aroma compounds are studied in this work at a temperature of 23 °C, which represents the average room temperature.

1.1. Transport characteristics

The aroma scalping properties of different polymers can be compared according to their sorption, diffusion and permeation coefficients [14–16]. The permeation coefficient is a measure of barrier properties and can be calculated [17–19] from the other two coefficients using the solution-diffusion model:

$$P = DS, \quad (1)$$

where the sorption coefficient can be obtained from the partial pressure of the aroma compound above the polymer and its equilibrium concentration in the polymer in the following form:

$$S = \frac{c}{p}. \quad (2)$$

The concentration of the compound in the polymer generally depends on both its partial pressure and the physical state of the polymer. This dependence of concentration on partial pressure at a constant temperature (i.e. the sorption isotherm) can often be parameterized by two common models: the Flory–Huggins [20] and Dual mode [21,22] sorption models (DMS). The Flory–Huggins model parameterizes the linear and type III [23] isotherms, and can be written in the following form:

$$\ln(a) = \ln(\phi) + (1 - \phi) + \chi(1 - \phi)^2, \quad (3)$$

where χ is the Flory–Huggins interaction parameter, a is the vapour activity of the compound sorbed in the polymer, $a = p/p^{\text{sat}}$, and ϕ is the volume fraction of the compound in the polymer. The Flory–Huggins interaction parameter exceeds 0.5 for solvents in which the polymer is insoluble; the lower the value, the more mutually soluble are the compound and polymer [24]. While the Flory–Huggins model is derived from the lattice model of the polymer–compound solution, the DMS model is derived by combining the linear Henry-like dissolution term and Langmuir's case I adsorption [25] term. The DMS model, which parameterizes linear and type I–II [23] isotherms, has the following form:

$$c = k_D p + \frac{C_H b p}{1 + b p}, \quad (4)$$

where k_D is Henry's law solubility constant; C_H is the capacity constant and b is the affinity constant of Langmuir's case I model.

To determine the transport properties of polymeric films, sorption and permeation tests are generally used [17,26]. Permeation tests enable the direct measurement of the permeability coefficient and, with the suitable setup, also of the diffusion coefficient from the permeation transient [13,15,16,19]; the solubility coefficient is then calculated using Eq. (1). Similar to the permeation tests, the sorption tests enable the direct

measurement of the sorption isotherm and, thus, sorption coefficient; see Eq. (2). The measurement of the sorption transient [13,19,27] enables the evaluation of the diffusion coefficient and, consequently, to calculate the permeability coefficient using Eq. (1). A cross validation of both tests can be found in the literature [13,19,28].

In this study, the sorption tests were used in a setup in which the vapour of the measured aroma compound was released into an evacuated chamber with the degassed polymeric film; the equilibrium and transient sorption uptakes were measured microgravimetrically. In such a general setup, the diffusion coefficient D can be determined from the sorption transient using the equation

$$\frac{m_\tau}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{i=0}^{\infty} \frac{1}{(2i+1)^2} \exp\left[-\frac{(2i+1)^2 \pi^2 D \tau}{L^2}\right], \quad (5)$$

where m_τ is the mass uptake at time τ , m_∞ is the mass uptake in sorption equilibrium, and L is the thickness of the tested film. The above equation was derived [17] from Fick's 2nd law for the instantaneous pressure change of a sorbing compound above a homogeneous thin film made of a dense polymer. This model was also used in this work for the modelling of transient sorption in two-layered films, whose layers have similar properties and chemical structure. Hence, an effective diffusion coefficient that averages the diffusivities of both layers was obtained. Because the real pressure dependence can differ from the instantaneous increase, an analysis is given in Appendix A1.

2. Experimental

2.1. Materials and chemicals

The tested films were made by means of extrusion (co-extrusion) from PBS (FZ91PD, Mitsubishi Chemicals), PBSA (AD92WD, Mitsubishi Chemicals) and LDPE (density 0.929 g cm⁻³). These films had the following structures: PBS (single layer, thickness 9 ± 1 μm, film A), PBS and PBSA (two layers, thickness 44 ± 2 μm, film B), PBS and PBS with 10% of PBSA (two layers, total thickness 47 ± 2 μm, film C), PBSA and PBS with 10% of PBSA and with 10% of talc (two layers, thickness 47 ± 2 μm, film D), LDPE (single layer, thickness 27 ± 1 μm). Based on the literature data [29,30], the density of the films A–D was 1.26 g cm⁻³. Density of the LDPE film was measured by the flotation method [31] using ethanol (p.a., Penta), demineralized re-boiled water (0.5 μS cm⁻¹) and an Anton Paar density meter (DMA 4100 M). The characterized aroma compounds were used as obtained from the producers, the physical properties were taken from literature; see Table 1.

To further characterize the properties of the film made from pure PBS (film A), the XRD pattern and heating and cooling DSC scans were measured. The XRD pattern was measured at room

Table 1
Properties of the characterized aroma compounds at 23 °C.

Compound	$p^{\text{sat}}/\text{kPa}$	$\rho/(\text{g}\cdot\text{cm}^{-3})$	Purity, supplier
Ethyl acetate [33]	11.3	0.896	99.7+%, Penta
Ethyl butyrate [34]	1.61	0.876	99%, Aldrich
Ethyl hexanoate [35,36]	0.177	0.868	99+%, Aldrich
Heptanal [33]	0.540	0.831	95%, Aldrich
1-Hexanol [33]	0.0821	0.817	99+%, Sigma–Aldrich
(<i>R</i>)-(+)-Limonene [33,37,38]	0.177	0.842	97%, Sigma

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