Barrier Properties of Polymeric Packaging Materials to Major Aroma Volatiles in Herbs

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Abstract. This study determined the main transport coefficients (diffusion, solubility and permeability) of key aroma compounds present in tropical herbs (eucalyptol and estragol) through low–density polyethylene (LDPE), polypropylene (PP), nylon (Nylon), polyethylene terephthalate (PET), metalized–polyethylene terephthalate (MPET) and poly(lactic acid) (PLA) films at 15 and 25 °C. The concentration of aroma compounds permeating through the films were evaluated at various time intervals using a gas chromatograph flame ionization detector (GC–FID). Results showed that the diffusion coefficients of aroma compounds were highest in LDPE whereas the solubility coefficients were highest in PLA at both temperatures. PLA had the highest permeability coefficients for estragol at both temperatures. PP and LDPE had the highest permeability coefficients for eucalyptol at 15 and 25 °C, respectively. MPET had the lowest permeability for both aroma compounds studied. Aroma barrier properties can be used when selecting polymeric packaging materials to prevent aroma loss in various food and consumer products.

1. Introduction

Polymeric materials are widely used in packaging applications. Small molecules from inside and/or outside a package can be transported through polymer films causing changes in the quality of packaged products. Aroma is one of the key quality criteria for many food and consumer products. Aroma transport through packaging materials can result in flavor loss, scalping and/or contamination producing an unacceptable product quality. Therefore, aroma barrier is an important parameter for polymer film selection. However, there is limited information on the aroma barrier properties of many polymeric materials. This is mainly

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because there are many existing aroma compounds and the interactions between aroma compounds and polymers can be very complex. Additionally, the permeation measurement methods and equipment for detecting aroma compounds are more complicated than those for gases such oxygen and carbon dioxide and water vapor.

Various factors have been shown to affect the aroma transport through polymeric materials such as chemical composition of the polymer and the penetrant, morphology of the polymer, concentration of the penetrant, presence of co–permeant, temperature, relative humidity and storage condition, etc. Interaction selectivity is largely determined by hydrophilic and hydrophobic characteristics of polymer and penetrant.

There are a limit number of studies determining the aroma transport through polymeric materials. For example, earlier studies determined the sorption of major flavor compounds present in orange [1] and apple [2] juices by sealant films. The results showed that low–density polyethylene (LDPE) film absorbed the flavor compounds much higher than polyethylene/vinyl alcohol (EVOH) film [1,2]. Whereas another study reported that LDPE and PP absorbed more ester aroma compounds than PET films [3]. Absorption of 10 flavor compounds (linalool, octanol, hexanal, decanal, ethyl 2–methyl butyrate, hexyl acetate, carvone, nonanone, limonene and myrcene) by various packaging materials was also studied in model solutions. The results showed that these compounds were absorbed more in polyolefins (LLDPE and OPP) than polyesters (PC, PET and PEN) [4] indicating a high affinity and interaction between hydrophobic aroma compounds and non–polar polymers such as LDPE. As most previous studies focused on primary aroma compounds in fruits, but not herbs, the aim of this study was to determine the aroma barrier properties of major packaging films (LDPE, PP, PET, M–PET, Nylon and PLA) to key aroma compounds present in tropical herbs, eucalyptol and estragol. The experiments were performed at 15 and 25 °C. This information is useful for the design and selection of polymeric films to prevent loss of herbal aromas from various packaged products.

2.   Materials and Methods

Plastic Films. The following polymer films low–density polyethylene (LDPE, 30 µm), polypropylene (PP, 30 µm), polyethylene terephthalate (PET, 12 µm), metalized PET (MPET, 12 µm), Nylon (Nylon, 15 µm), polylactide (PLA, 30 µm) commonly used for food packaging were used in this study.

Aroma Compounds and Solvents. The aroma compounds used in this study were eucalyptol and estragol. These are the primary compounds present in tropical herbs. The compounds were obtained from Aldrich Chemical Company (St. Louis, MO, USA) with purity in excess of 99%. Dichloromethane with a purity of 99.9% (Mallinckrodt Baker, Inc., Phillipsburg, NJ, USA) was used as an extraction solvent.

Aroma Permeation Measurements. The aroma permeation of the aroma compounds through the test films in a vapor phase was measured according to the methods described by Peychès–Bach *et al*. (2009) [5]. Test films of 1.1 cm × 1.1 cm were sealed with a Teflon ring directly on the top of a flask containing the pure aroma compound. The exposed film area was $0.785 \times 10^{-4} \, \mathrm{m}^2$. The flask was placed in a permeation diffusion cell, which was flushed by a 20 mL.min^{-1} nitrogen flow at 15 and 25 °C. At sequential time intervals, the amount of aroma compound was carried out on an Agilent model 6820 gas chromatograph (Agilent Technology, Santa Clara, CA, USA) with a flame ionization detector (GC–FID). The aroma sorption of key aroma compounds through the test films in a vapor phase was also measured. At equilibrium, the polymeric films were removed from the aroma bottle and rinsed with distilled water for 2 min and dried. The sample films were placed in 20 mL vials with 5 mL dichloromethane and sealed with a Teflon/silicone rubber septa and screw capped for 24 h and kept in the dark. Quantification of the aroma compounds extracted from the polymer

squares was carried out on GC–FID. The gas chromatograph conditions used were as follows: helium flow at 2.0 mL.min^{-1} and temperature program from 60 to 200 °C at 10 °C. min^{-1}. The column used to separate the compounds was a 30 m long fused silica column (i.d. 0.32 mm) with a film thickness of 0.25 mm (HP5). The concentration and mass uptake of aroma compounds were determined and the experiments were performed in triplicate.

Determination of Diffusion Coefficients (D). Diffusion coefficients were estimated by permeation kinetics [6] as expressed in Eq. 1 by MATLAB software R2011b (The Mathworks Inc., Natick, MA, USA). The root mean square error (RMSE) and the correlation coefficient (R) were used to estimate the goodness of fit and the good correlation, respectively.

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\cdot exp\left[-\frac{(2n+1)^2\pi^2}{L^2}D\cdot t\right].$$

(1)

where M_t and M_∞ are the total amount of diffusing substance during time and infinite time, respectively. L is the film thickness and t is time. The permeation or mass uptake kinetic can be expressed using the following initial and boundary conditions:

$t = 0$; $0 < x < L$; $C = 0$
$t \geq 0$; $x = 0$; $C = C_0 = C_{in}$
$t \geq 0$; $x = L$; $C = C_{eq} = C_{max}$

Determination of Solubility Coefficients (S). Solubility coefficients were obtained from the vapor permeation experiments. Solubility coefficients were determined according to Eq. 2:

$$S = \frac{M_\infty}{vp}$$

(2)

where M_∞ is the corresponding amount during infinite time, v is volume of the sample and p is partial pressure.

Determination of Permeability Coefficients (P). Finally, the permeability coefficients, kg m m^{-2} s^{-1} Pa^{-1}, were calculated using Eq. 3 as follows:

$$P = D*S.$$

(3)

3.   Results and Discussion

Aroma Permeation Study. The concentrations of all the aroma compounds at steady state were highest in LDPE followed by PLA and PP films, respectively. The concentrations of eucalyptol increased rapidly and reached equilibrium at 6 d (Fig. 1) whereas the concentrations of estragol slowly increased and reached equilibrium at 36 d at 25 °C. The concentrations of the aroma compounds permeating through the packaging films showed the similar patterns at 25 °C as at 15 °C. The concentrations of the aroma compounds were highest in LDPE followed by PLA. Eucalyptol and estragol permeated through the films at approximately 20 and 2 fold higher at 25 °C than at 15 °C, respectively showing that the permeation of the aroma compounds through the packaging films increased with increasing temperatures. Permeation is a temperature active process due to the dependence on free

volume and glass transition temperature of the films. The effect of temperature on the permeation was different depending the aroma/polymer systems [7].
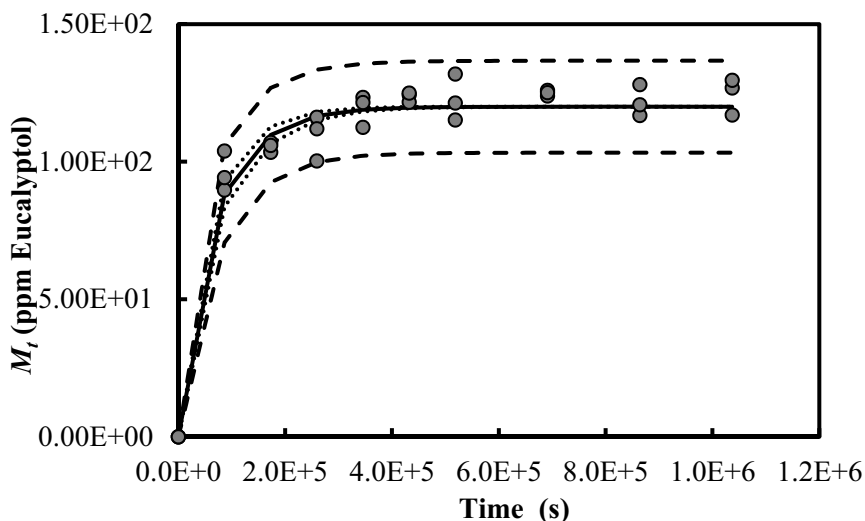

Fig. 1 Diffusion of eucalyptol through LDPE film in the dynamic system at 25 °C.

Determination of Diffusion Coefficients. Tables 1 and 2 show the diffusion coefficients of the aroma compounds through different films in the dynamic system. The diffusion coefficients of the aroma compounds could be determined using Eq. 1 for all film types, but for eucalyptol and Nylon, PET and MPET at 15 °C since these values have higher RMSE values at a 95% confidence. In such cases, the diffusion process of small molecules occurs in the glassy state, which is much more complex than that in the rubbery state. This sorption behavior is generally described by a dual−mode sorption model combining the Henry's law and Langmuir isotherm for glassy polymers [8]. Similarly, the transport of ethyl acetate in PLA film followed the dual sorption model [9]. The results suggest that the dual-mode sorption behavior involved not only the penetrant activity but also the interaction in the glassy polymers.

The diffusion coefficients of the aroma compounds through the test films were highest in LDPE films and lowest in MPET films at both temperature conditions. The results supported the effects of glass transition temperature (T_g) of the packaging films on the diffusion of the aroma compounds as described earlier. As the T_g values of LDPE (−80 °C) and PP (−9 °C) films were lower than the storage temperature (15 and 25 °C), the transports of aroma compounds occurred in a rubbery state. Generally, the diffusion of small molecules in rubbery polymers follows Fick's laws [8]. On the contrary, the T_g values of PET (79 °C), MPET (70 °C) and PLA (55 °C) films were higher than storage temperature; therefore, the diffusion of small molecules took place in a glassy state, of which was more complex than that in a rubbery state. For PLA film, as the storage temperature of 25 °C was closer to its T_g (55 °C), the polymer chain tended to be more relax, hence diffusion increased [10,11]. This can partially explain the higher diffusion coefficients of the aroma compounds in the PLA film than those in PET and MPET films.

Determination of Solubility Coefficients. The amount of aroma compounds sorbed in the films were determined after storage at 15 and 25 °C for 42 and 22 d, respectively. The sorption of the aroma compounds was highest in PLA, except that of eucalyptol which was highest in PP at 15 °C. Solubility coefficients were determined from the amount of aroma sorbed into the films at equilibrium. Solubility coefficients for aroma compounds of the test

films are shown in Tables 1 and 2. The results showed the similar trends with the amount of the aroma sorbed in the films. The solubility coefficients of all the aroma compounds were highest in PLA. It demonstrated that the plasticization of PLA by the aroma compounds occurred at very low vapor activities [12].

The solubility coefficients of all aroma compounds at 15 °C were quite similar to that at 25 °C. The temperature effect on aroma sorption seems to be more important for Nylon, PET, MPET and PLA, compared to PE and PP at the experimental temperature, which might be due to the T_g value of the glassy polymers closely to the storage temperatures. The aroma was easier absorbed because of the more polymer chains relaxation, causing the increasing free volume [4].

TABLE 1 TRANSPORT COEFFICIENTS OF AROMA COMPOUNDS FOR VARIOUS
POLYMERIC FILMS AT 15 °C.

Packaging	D [m^2.s^{-1}]		S [kg.m^{-3}.Pa^{-1}]		P [kg.m.m^{-2}.s^{-1}Pa^{-1}]	
Films	Eucalyptol	Estragol	Eucalyptol	Estragol	Eucalyptol	Estragol
LDPE	1.93E−17	ND	8.88E−06	1.65E−04	1.71E−22	ND
PP	1.43E−17	4.15E−17	4.50E−04	1.04E−03	6.42E−21	4.33E−20
Nylon	ND	3.03E−18	6.05E−05	7.07E−04	ND	2.14E−21
PET	ND	2.67E−18	nd	6.43E−04	nd	1.72E−21
MPET	ND	2.64E−18	nd	5.01E−04	nd	1.33E−21
PLA	1.82E−17	1.21E−17	4.02E−06	2.21E−02	7.30E−23	2.66E−19

ND: not determined (RMSE values were higher than the experimental error within a 95% confidence.)

nd: not detected

TABLE 2 TRANSPORT COEFFICIENTS OF AROMA COMPOUNDS FOR VARIOUS
POLYMERIC FILMS AT 25 °C.

Packaging	D [m^2.s^{-1}]		S [kg.m^{-3}.Pa^{-1}]		P [kg.m.m^{-2}.s^{-1}Pa^{-1}]	
Films	Eucalyptol	Estragol	Eucalyptol	Estragol	Eucalyptol	Estragol
LDPE	2.22E−15	1.14E−16	5.68E−05	1.71E−04	1.26E−19	1.95E−20
PP	1.88E−16	8.76E−17	2.71E−04	1.04E−03	5.10E−20	9.15E−20
Nylon	4.60E−17	2.06E−17	5.22E−05	4.53E−04	2.40E−21	9.33E−21
PET	3.89E−17	1.06E−17	9.53E−06	5.67E−04	3.71E−22	6.02E−21
MPET	3.35E−17	1.20E−17	5.01E−06	4.77E−04	1.68E−22	5.72E−21
PLA	2.57E−16	4.79E−17	3.58E−04	1.23E−02	9.19E−20	5.89E−19

Determination of Permeability Coefficients. The permeability coefficients for aroma compounds of the packaging films at 15 and 25 °C are shown in Tables 1 and 2. PLA had the highest permeability coefficients for estragol at both temperature, while PP and LDPE had the highest permeability coefficients for eucalyptol at 15 and 25 °C, respectively. The permeability for eucalyptol and estragol was lowest in MPET followed by PET at both storage temperatures. This was attributed to the combined solubility and diffusion effect, which are the processes involving permeability. The permeability coefficients of all aroma compounds were higher at 25 °C than that at 15 °C, suggesting that it is temperature dependent. The goodness of the correlation was tested according to the Pearson correlation coefficients (r). The results showed that the solubility coefficients were highly correlated

with the permeability coefficients of eucalyptol ($r = 0.81^{**}$) and estragol ($r = 0.98^{**}$) ($p \leq 0.01$). The correlation results suggest that solubility is the primary determining factor for permeability.

4. Conclusion

The diffusion coefficients of aroma compounds were highest in LDPE whereas the solubility coefficients were highest in PLA at 15 and 25 °C. PP and LDPE had the highest permeability coefficients for eucalyptol at 15 and 25 °C, respectively, while PLA had the highest permeability coefficients for estragol at both storage temperatures. MPET followed by PET had the lowest permeability for all the aroma compounds studied. The affinity between the aroma compounds and the polymer films were shown to be critical factors for permeability.

5. Acknowledgements

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