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ORIGINAL ARTICLE

Permeability and release properties of cyclodextrin-containing poly(vinyl chloride) and polyethylene films

Éva Fenyvesi · Klára Balogh · István Siró · Judit Orgoványi · Judit M. Sényi · Klára Otta · Lajos Szente

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Abstract In this study poly(vinyl chloride) (PVC) and polyethylene (PE) films with 0%, 1.0%, 1.5% and 2.0% *β*-cyclodextrin (BCD)-content were prepared and their permeation properties were characterized using model flavours like carvone, vanillin and diacetyl. The complex forming carvone and vanillin could penetrate through the films containing cyclodextrin, while diacetyl, which has poor complex forming ability with *β*-cyclodextrin could not.
The effect of CD-concentration on vanillin permeation was found to depend on CD concentration and on the thickness of the films.
The leaching of plasticizers from the polymer matrix to the contacting fluid is a drawback of PVC. The presence of *β*-cyclodextrin in the film results in slower release of plasticizers.

Keywords Active packaging · Leaching of plasticizers · Inclusion complex formation

É. Fenyvesi (✉) · K. Balogh · L. Szente
Cyclolab R&D Laboratory Ltd., Illatos út 7, 1097 Budapest, Hungary
e-mail: fenyvesi.e@cyclolab.hu

K. Balogh · J. Orgoványi · K. Otta
Eötvös Loránd University of Budapest, Institute of Chemistry, Pázmány Péter sétány 1/A, 1117 Budapest, Hungary

I. Siró · J. M. Sényi
Department of Preservation, Corvinus University of Budapest, Faculty of Food Science, Ménesi út 45, 1118 Budapest, Hungary

Introduction

Over the past decade, active, controlled and intelligent packaging have experienced significant growth and change as new products and technologies have replaced the traditional forms of food and beverage packaging. Cyclodextrins (CDs) have their potential in this field of application, too. By mixing CD-complexes of fragrances, dyes, insecticides, UV filters, etc. into molten thermoplastic polymers, improved packaging material: films, laminates, containers, trays, etc. can be produced in which the complexed substances are homogeneously dispersed and only slowly released from the polymer matrix. The application of CDs in smart and active food packaging has been recently reviewed [1].

The advantages of CD application in plastic packaging can be inclusion of by-products of polyethylene generated by heat seal [2], decreased release of impurities and undesired volatile byproducts formed during manufacture of the packaging material into the food or beverages [3], improvement of the barrier function of the packaging material entrapping both the penetrating volatiles, atmospheric pollutants migrating inward as well as the aroma substances, escaping outward [4], odour absorption when ''empty'' CD is used and controlled release of the active component (antimicrobial, antioxidant, etc.) when CD complex is applied. Incorporation of CDs or CD complexes into a plastic packaging material makes it at least partially biodegradable [5].

The aim of the present work was to prepare and characterize CD-containing films produced in pilot scale. As a first step ''empty'' BCD was incorporated into polyvinyl chloride (PVC) and polyethylene (PE) films. In the further studies complexes of antioxidants, antibacterial agents, ripening agents, and other compounds useful for improving the shelf life of the food will be built in the films to be applied for active food packaging. In this study the results with ''empty'' BCD both in PE and in PVC films have been demonstrated.

Experimental

Spray dried BCD, the fine chemical product of CycloLab (Budapest, Hungary) was used.

Vanillin, carvone and diacetyl of food quality were purchased from Sigma-Aldrich.

Manufacture of films

PVC films were prepared by mixing the necessary components (PVC, plasticizer, antifogging and other additives) in MTI 10 fast mixer and extruding the film of 16–20 μm thickness. Two of the additives were studied in detail: epoxydated soy oil, Drapex 392 (Chemtura, USA) used as plasticizer and a non-ionic tenside, Lancrostat (Akzo Nobel, U.K.) used as antistatic agent and viscosity modifier.

PE films were prepared by mixing the antioxidant BCD powder with the LDPE granulates (FB 2320, Borealis, Vienna, Austria) by a simple scroll extruder, and the granules were transformed into films on a blown filmline (Kuhne K36, Kuhne GmbH, Germany).

Permeability studies

Permeability studies were performed using the experimental setup of Fig. 1. The volumes of the donor and acceptor phase were 25 and 50 cm^3, respectively. The donor solution contained 100 mg/cm^3 solute (vanillin, carvone or diacetyl) in 70% ethanol, the acceptor solution was 70% ethanol in water. The acceptor phase was stirred with a magnetic stirrer. The samples withdrawn hourly were measured by UV photometry in case of vanillin and carvone and by gas chromatography in case of diacetyl.

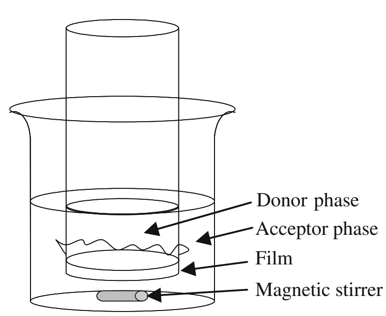

Fig. 1 Experimental setup of the permeability study

Leaching studies

Leaching of the plasticizers was measured similarly using 70% ethanol for both the donor and acceptor phase and measuring the absorbance at 276 nm.

Results

Varying the conditions of manufacturing, films with acceptable mechanical properties were obtained using both PE and PVC as raw materials. In case of PE applying a lubricant was necessary to avoid the segregation of the BCD powder and the PE granules. As lubricant paraffin oil was used. The microscopic photos in Fig. 2 show that BCD is more or less evenly distributed within the film, but it is in aggregated state.

Leaching studies

PE granules without further additives were used for manufacture of the films. A negligible leaching of paraffin oil was observed by UV measurements without significant difference between the CD-containing and the control films.

In case of PVC films leaching of the additives monitored by the UV absorbance at 276 nm was reduced significantly in the presence of BCD (Fig. 3). Both the epoxydated soy oil (Drapex) used as plasticizer and the non-ionic tenside, Lankrostat used as antistatic agent and viscosity modifier show absorbance at 276 nm and both form complexes with BCD resulting in increased solubility. The solubility of Drapex was unmeasurable in water (no clear solution could be obtained without CD), while a 1.2 mg/cm^3 concentration was measured in the presence of 1.5% BCD in the solution indicating the complex formation. In case of Lankrostat an emulsion was obtained. We could not crack the emulsion either by centrifuging or by salting, therefore the solubilising effect of BCD could not be proved by the traditional phase solubility method. To prove the interaction between the CD cavity and this non-ionic tenside the solubility isotherm in RAMEB solution was recorded. A_L type isotherm was obtained with 22 mg/cm^3 solubility at 10% RAMEB concentration (Fig. 4) proving that there is an affinity between Lankrostat and the BCD cavity. These solubility studies suggest that the reduced

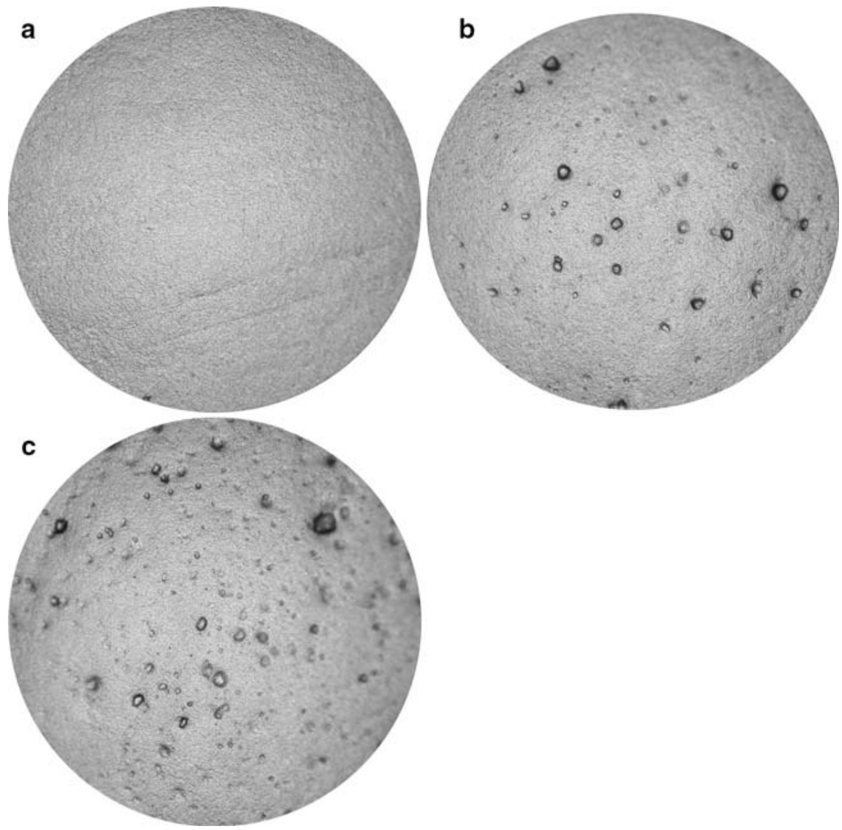

Fig. 2 Microscopic photos of the films extruded from low-density polyethylene with 0% (a), 1% (b) and 2% (c) BCD (magnification 320×)

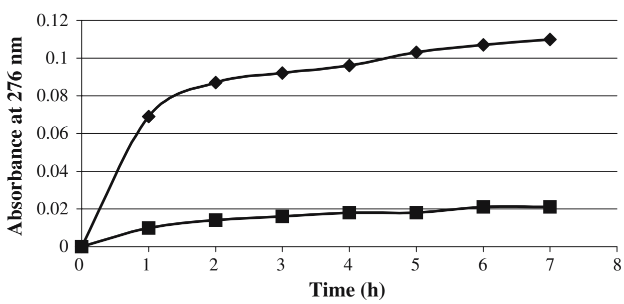

Fig. 3 Leaching of the plasticizer (monitored by the UV absorbance at 276 nm) from BCD-containing (■) and control (◆) films

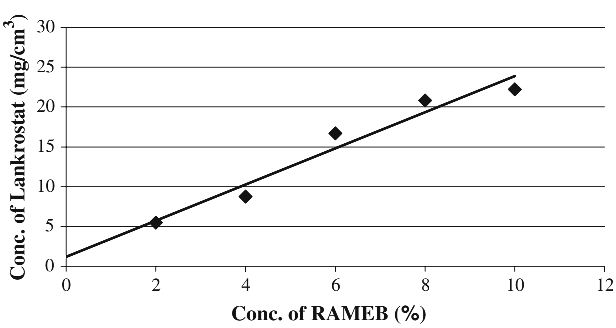

Fig. 4 Phase solubility diagram of Lankrostat plasticizer in RAMEB solutions

leaching of additives from PVC films containing BCD is due to the complex formation of these additives with BCD.

Permeability studies

For the permeability studies three aroma substances were selected as model compounds: vanillin and carvone, the latter is the component of caraway and dill and diacetyl, the buttery flavour. It is well known that BCD has high affinity to carvone [7, 8], and low affinity to diacetyl [9].

The experimental PVC films were impermeable for these aroma substances (Fig. 5a, b, c). Incorporating BCD into the films vanillin and carvone (the compounds able to form inclusion complexes) can penetrate through the film, while diacetyl, which is too small for BCD, cannot. These preliminary results suggest that BCD is ‘‘active’’ within the film; it possesses the inclusion complex forming ability.

Increasing the BCD concentration the amount of vanillin penetrated through the films is increased (Tables 1 and 2) in case of both PE and PVC films. The PE films are more permeable for vanillin than the PVC films. The effect of CD-concentration was found to

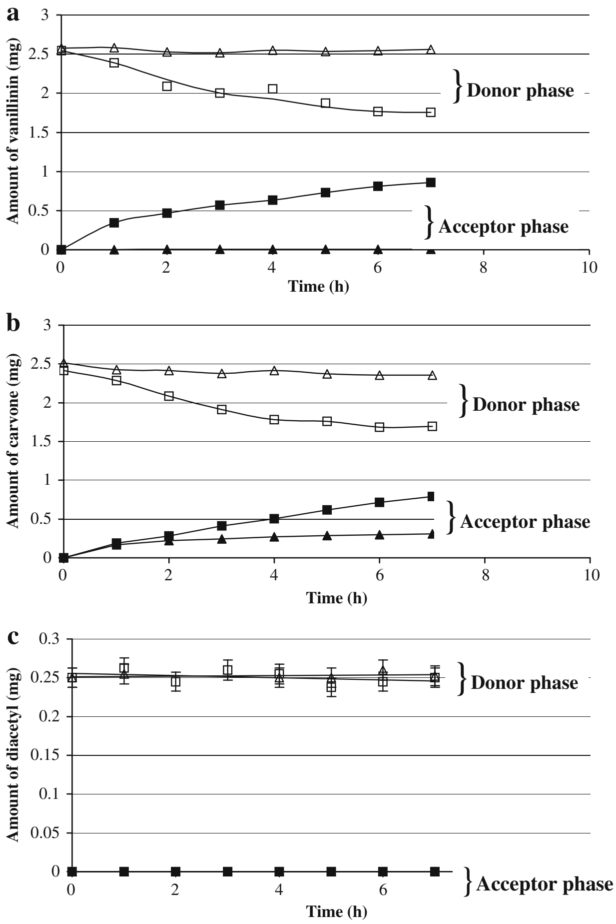

Fig. 5 Permeability of vanillin (**a**), carvone (**b**) and diacetyl (**c**) through the control (■, □) and the BCD (2%)-containing (▲, △) PVC films

Table 1 Effect of film thickness and CD-concentration on the permeability of the BCD-containing PVC films

CD conc. (%)	Vanillin in the acceptor phase in % of the initial amount in donor phase	
	Film thickness (mm)	
	0.010 ± 0.03	0.015 ± 0.03
0	0.02	0.06
1	0.18	0.08
2	0.40	0.10

Table 2 Effect of CD-concentration on the permeability of the BCD-containing PE films (film thickness is 0.04 ± 0.01 mm)

CD conc. (%)	Vanillin in the acceptor phase in % of the initial amount in donor phase
0	1.6 ± 0.4
1	1.1 + 0.3
2	6.0 ± 2.2

depend on the film thickness being more pronounced in case of PVC films of lower thickness (Table 1).

Conclusions

The microscopic investigations indicate that CD is located within the film in the form of aggregates.

The presence of β-cyclodextrin in the film effectively hindered the leaching of the plastic additives, which can be an important advantage of CD-containing films.

The preliminary permeability studies on the experimental PVC films containing ''empty'' β-cyclodextrin suggest that the CD cavities within the film are able to form inclusion complexes enabling the penetration of substances, which otherwise do not penetrate through the film.

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