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Sorption of β-carotene from solutions of a food colorant powder into low-density polyethylene and its effect on the adhesion between layers in laminated packaging material

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Solutions of different concentrations of β-carotene (1–100 ppm) were stored in laminated packaging material at 4°C and 25°C for 8 weeks. Sorption of β-carotene into low-density polyethylene was three times higher at 25°C than at 4°C. However, only about 1–2% of the total amount of β-carotene was sorbed at 25°C. The adhesion between the plastic and aluminium layers of the packaging material decreased during the storage, but total delamination never occurred. The effect was more pronounced at the higher temperature and with increasing concentrations. Advancing and receding contact angles of the aluminium surface increased during the experimental period, indicating surface contamination.

INTRODUCTION

Absorption of food constituents into plastic packaging material can have detrimental effects on the quality of the product. Compounds that might be dissolved in polymeric packages include aromas, fatty acids, organic acids and pigments (Koch *et al.*, 1976; Figge, 1980; Halek & Luttmann, 1990; Oerhl *et al.*, 1991; Arora *et al.*, 1991; Ikegami *et al.*, 1991; Charara *et al.*, 1992; Konczal *et al.*, 1992; Nielsen *et al.*, 1992*a*; Paik, 1992). The consequence might be direct loss of food quality, such as aroma loss or decolorisation. In the case of more aggressive components, e.g. acetic acid, being absorbed, damage to the package, for instance delamination, might occur (Schroeder *et al.*, 1990; Olafsson *et al.*, 1993*a*). In that case, the properties of the package can be altered and it might not be able to maintain its protective role towards the product. This can result in reduced shelf-life and decreased quality of the product. Sorption of colorants into the packaging material may also change the appearance of the package, resulting in a reduced acceptance by the consumer.

β-Carotene is a colorant present in many foodstuffs. In addition, it exerts vitamin A activity and belongs to the antioxidative vitamins, on which attention is now focused, not only because of their ability to protect food constituents against oxidation, but also because of their health-protective effects. The β-carotene molecule consists of a long carbon chain with conjugated double bonds, and a terpene-like ring structure at both ends. The sorption of terpenes, especially limonene, into low-density polyethylene (LDPE), the most commonly used polymer for food packages, has been widely studied. Several investigations (Hirose *et al.*, 1988; Halek & Meyers, 1989; Imai *et al.*, 1990; Baner *et al.*, 1991) have reported that limonene can be sorbed into polymeric packaging material to a large extent. The similarity of the molecular structure of terpenes and β-carotene, the long carbon chain of β-carotene and its extreme non-polarity makes it highly possible that it might be dissolved into LDPE. In spite of these molecular similarities, there does not seem to be any reports in the literature on the sorption of β-carotene into polyethylene. Thus, the present study was undertaken with the purpose of investigating the sorption of β-carotene, from solutions, made of a food colorant powder containing 1·3% β-carotene, stored at different temperatures, into the plastic layer of a laminated packaging material, and to establish what effects the storage of these solutions has on the adhesion between the polymer and the aluminium layers of the package.

MATERIALS AND METHODS

Test solutions

A cold-water dispersible powder (BASF, Ludwigshafen, Germany), used as a food colorant, containing 1·3%

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β-carotene, was used for preparing the test solutions. Other ingredients in the powder were corn syrup solids, dextrin, peanut oil, ascorbyl palmitate, tricalcium phosphate, α-tocopherol and lecithin. The powder was dissolved in distilled water while stirring gently. Solutions of four different concentrations, 1, 5, 25 and 100 mg β-carotene/litre, were prepared. The β-carotene content of the powder was determined, using β-carotene of analytical grade (Sigma Chemical Co., St Louis, MO, USA) as reference, by HPLC-analysis.

Food packaging material

The laminated packaging material used in this study was supplied by Tetra Laval AB (Lund, Sweden). It had the following composition: LDPE (15 g/m^2)/paper (210 g/m^2)/LDPE (25 g/m^2)/aluminium foil (7 μm)/LDPE (45 g/m^2). The LDPE had a density of 0·92 g/cm^3. All the polymer layers were extrusion-coated at a temperature of 325°C, without any tie layers. Corona discharge was not applied during the process.

Test packaging

The packaging material was formed into envelopes of an approximate size of 13 × 15 cm and filled with 35 ml of the test solutions. Sixty envelopes of each of the four different β-carotene concentrations were prepared. Half of them were stored at 4°C, and the other half at 25°C. Envelopes containing distilled water were prepared in a similar manner and used as blanks.

High-performance liquid chromatography (HPLC) analysis

HPLC analysis was performed using the method for determination of carotenoids described by Broich *et al.* (1983). The HPLC equipment was composed of a Varian (Sunnyvale, CA, USA) 2510 HPLC pump, a Varian 2550 variable wavelength detector and a Supelcosil LC-18 (Supelco Inc., Bellefonte, PA, USA) stainless steel column (25 cm × 4·6 mm) packed with ODS C18 of 5 μm particle size. The mobile solvent used was a mixture of methanol/acetonitrile/chloroform (47 : 47 : 6). All solvents were of spectrograde quality and were supplied by Merck (Darmstadt, Germany). Detection was at 456 nm.

Sorption measurements

The inner LDPE layer from the side of the envelope that had faced down during the storage was peeled off for analysis of the β-carotene sorption into the plastic. The entire polymer layer, approximately 0·5 g, was accurately weighed and was extracted by 2 × 10 ml tetrahydrofuran (THF, Merck) for 2 × 24 h. The absorbances of the collected extracts were measured at a wavelength of 456 nm on a Varian DMS 100 S UV–Vis spectrophotometer. Three replicate extractions and analyses were made for each sample.

Adhesion tests

The adhesion was measured using a JJ Tensile Testing Machine, model T 30 K with recorder, model A 128 (JJ Lloyd Instruments, Southampton, UK). The test was a 180° peel test and performed, as earlier described (Olafsson *et al.*, 1993*b*), with a crosshead speed of 50 mm/min using a 100 N load cell. Three strips from two packages each were analysed, which meant six replicate analyses for each sample.

Contact angle measurement

A 15 mm strip of the packaging material was cut out and the plastic layer peeled off. By means of a motor-driven micro-syringe 5–10 μl Millipore® water was pumped out onto the surface of the aluminium layer. The advancing contact angle was registered by a camera. The motor was then reversed and the water drawn back into the syringe until the edges of the water droplet moved, and the receding contact angle was registered. The angles were evaluated from the photographs taken. Six measurements were performed for each sample.

RESULTS AND DISCUSSION

The test solutions were prepared using a food colorant powder instead of pure β-carotene for two reasons. Pure β-carotene could not be dissolved in water, but the powder had been modified in a way that made it cold water-dispersible. Furthermore, the powder was used for food applications, and thereby it was of interest to evaluate its effects on food packaging material.

HPLC analysis of the food colorant powder indicated that it contained only one compound, β-carotene, that absorbed light at the chosen wavelength, 456 nm. This wavelength was selected after obtaining an absorption spectrum of pure β-carotene solution by scanning from 350 to 550 nm. The β-carotene concentration of the powder was determined by comparing its absorption with that of pure β-carotene. Repeated analyses showed that the powder had a β-carotene content of 1·3%. The content of the other ingredients of the food colorant powder were not determined.

An antioxidant, α-tocopherol, was present in the powder to prevent β-carotene, which is very sensitive to oxygen, from being oxidised. During the filling and sealing of the envelopes, care was taken to minimise the headspace, and thereby the oxygen present in the packages. The test solutions were continously analysed for β-carotene content during the entire period of the study. The stability of the solutions was found to be satisfactory; less than 10% of the β-carotene had been degraded at 25°C after 56 days of storage.

Solutions of four different concentrations were prepared; 1, 5, 25 and 100 mg β-carotene/litre. These concentrations were chosen after considering the β-carotene contents of different foodstuffs, e.g. carrot juice 26 mg/litre, and orange juice 0·70 mg/litre (Souci *et al.*, 1981).

Sorption

The sorption of β-carotene into LDPE was determined by extracting the polymer with THF twice, and measuring the absorbance of the pooled collected extracts. Further extractions of the plastic resulted in no absorption at 456 nm, indicating that two extractions were enough to remove all sorbed β-carotene from the LDPE.

The results, based on triplicate analyses, from the sorption measurements are displayed in Table 1. As can be seen from the table, the relative standard deviations were quite large, especially for the solutions with low concentrations of β-carotene. One reason for the big differences between replicate analyses was the very non-uniform sorption. The β-carotene was sorbed into defined parts of the polymer; spots of the plastic layer were intensely yellow-coloured, while other areas, to the eye, seemed unaffected. As a consequence, the samples were somewhat heterogeneous, which resulted in relatively large deviations between repeated analyses. This has to be taken into account, and care must be taken when evaluating the experiment. However, some trends could be detected in the results, and some conclusions could be drawn.

A steady increase in the β-carotene content in the plastic layer of the packaging material could be seen during the 8 weeks of storage, indicating that equilibrium was not reached after 56 days. Approximately 30–40% of the total amount of β-carotene sorbed from the 100 mg/litre solution during the entire study was sorbed already after 1 day of storage.

Envelopes stored at 25°C sorbed significantly larger amounts of β-carotene than packages stored at 4°C, at almost all studied concentrations and times. The only exception being solutions containing 1 mg β-carotene/litre, which lost approximately the same amount of β-carotene to the polymer at both temperatures. At this low concentration very small amounts of the colorant were dissolved in the plastic layer, and it is hard to discriminate between these low values. After 1 and 3 days of storage the packages with 100 mg/litre solution sorbed about double amounts at 25°C compared with packages stored at 4°C. However, from 7 days and to the end of the study, the sorption was approximately three-fold at 25°C compared with at 4°C. A similar pattern can be seen in the sorption of β-carotene from solutions with 25 mg/litre into LDPE. There could be at least two reasons for the higher sorption at 25°C compared with that at 4°C. First, the equilibrium constant might be different at the two temperatures, resulting in a larger degree of sorption at 25°C than at 4°C. Another explanation might be that the diffusion process was more rapid at the higher temperature. As a consequence, the equilibrium would be reached quicker. If this was the case the differences at the two temperatures would level out during a longer period of storage.

Larger shares of the total amount of β-carotene present in the solutions were sorbed from the solutions with lower concentrations. At 25°C, 1·7% of the total amount of the colorant in the 1 mg/litre solution was dissolved in the polymer, while only 1·0% of the 100 mg/litre solution was lost to the plastic layer.

The amount of β-carotene and limonene sorbed into LDPE seem to differ markedly, in spite of chemical similarities between these two compounds. Limonene has been reported to, within a few weeks, be sorbed into LDPE to 40–90% of the total amounts from both model solutions and fruit juices (Kwapong & Hotchkiss, 1987; Hirose *et al.*, 1988; Halek & Meyers, 1989). In this experiment, the sorption of β-carotene was, after 8 weeks storage, only 1–2% of the total content in the solution. The degree of sorption is a function of the solubility of the sorbate in both the solvent and the polymer. Emulsifying agents in the colorant powder might have increased the affinity of β-carotene for the solution, which could explain the relatively low extent of sorption. In an actual foodstuff, larger amounts of β-carotene might be sorbed into the packaging polymer.

The sorption of the other ingredients of the powder was not measured. However, it is likely that, for instance, α-tocopherol and peanut oil compounds were dissolved in the LDPE. Other investigations (DeLassus & Strandburg, 1991; Nielsen *et al.*, 1992*b*) have reported that a combination of sorbates can have both enhancing and suppressing effects on the sorption of the individual compounds into plastic packaging material. Therefore, it is hard to speculate on the possible synergistic effects in this case.

Table 1. Sorption of β-carotene (μg/g plastic) from solutions of different concentrations (1, 5, 25 and 100 mg β-carotene/litre) stored at 4°C and 25°C into the LDPE layer of a laminated packaging material (mean ± SD, *n* = 3)

Sample solution	Storage time (days)					
	1	3	7	14	28	56
1 mg/litre, 4°C	0	0	0.1 ± 0.1	0.1 ± 0.1	0.2 ± 0.1	0.5 ± 0.1
5 mg/litre, 4°C	0	0	0.1 ± 0.1	0.1 ± 0.1	0.4 ± 0.1	0.6 ± 0.2
25 mg/litre, 4°C	0.5 ± 0.1	2.6 ± 0.3	2.5 ± 0.2	2.7 ± 0.4	3.1 ± 0.1	4.5 ± 0.3
100 mg/litre, 4°C	4.7 ± 0.5	5.3 ± 1.2	5.7 ± 0.4	5.8 ± 0.3	6.7 ± 0.3	10.8 ± 0.7
1 mg/litre, 25°C	0	0	0.1 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.6 ± 0.1
5 mg/litre, 25°C	0	0.4 ± 0.1	1.6 ± 0.2	1.3 ± 0.1	1.9 ± 0.5	1.7 ± 0.3
25 mg/litre, 25°C	1.5 ± 0.3	2.3 ± 0.5	5.3 ± 0.5	6.5 ± 0.7	9.8 ± 1.9	12.1 ± 2.7
100 mg/litre, 25°C	10.1 ± 2.1	10.2 ± 0.5	14.2 ± 2.8	16.3 ± 1.9	24.2 ± 2.3	34.5 ± 5.4

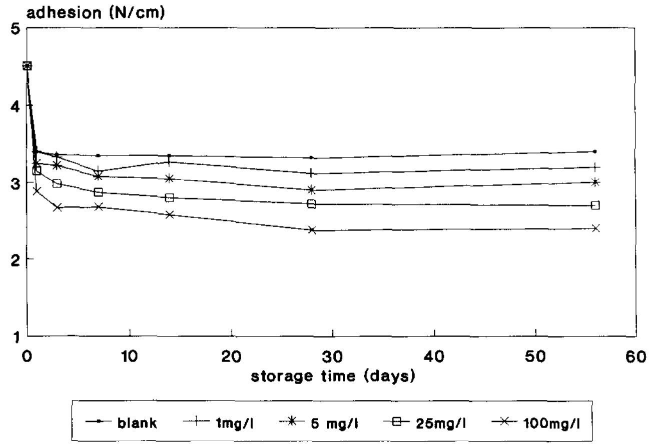

Fig. 1. Adhesion (N/cm) between LDPE layer and aluminium foil of laminates stored at 4°C in different solutions.

Adhesion

The adhesion between the LDPE and aluminium layers was measured by a peel test as earlier described. The results from these measurements are summarised in Figs 1 and 2. Each sample was measured by analysing three strips of the laminated packaging material from each of two envelopes, making a total of six replicate analyses. The analyses showed a good repeatability with a relative standard deviation of less than 10%. This indicates that the unevenly distributed sorption into the packages did not result in the adhesion between the two layers varying at different places of the laminate.

Untreated packaging material had an adhesion between the polymer and aluminium layers of 4·4 N/cm. A blank with distilled water stored in envelopes caused a decrease of the adhesion by about 25%, already after 1 day of storage. The adhesion was then constant at that level during the entire experimental period. This was the case at both studied temperatures.

At 4°C there were no significant differences between the adhesion values of envelopes containing solutions of 1 and 5 mg β-carotene/litre and the packages with pure water. Packages with 25 mg/litre solution had a slow but constant drop of the adhesion during the storage. After 56 days the adhesion was about 60% of its initial value. The decrease of the adhesion in the packages storing the most concentrated solution was even larger, the adhesion being slightly over half the initial value at the end of the study.

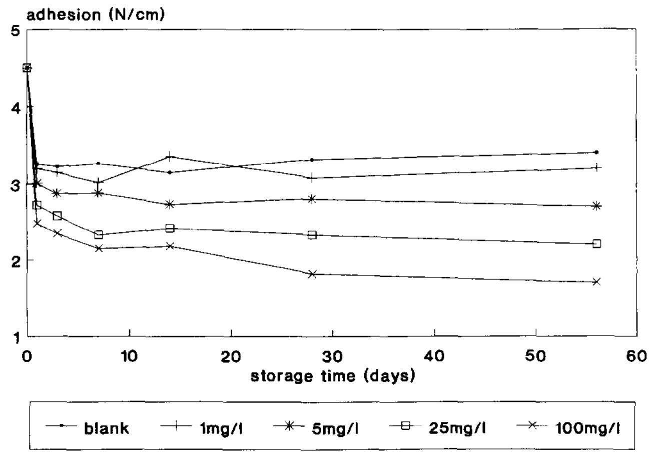

Fig. 2. Adhesion (N/cm) between LDPE layer and aluminium foil of laminates stored at 25°C in different solutions.

Packages stored at 25°C behaved in a similar manner, with higher concentrated solutions having a larger effect on the adhesion, and the adhesion dropping slowly during the storage. The decrease, however, was greater at this temperature than at 4°C. The adhesion in envelopes containing a solution of 100 mg β-carotene/litre decreased to less than 40% of the initial value during the 56 days of storage.

Yet again, components of the food colorant powder other than β-carotene might have affected the adhesion between the two layers. Earlier studies (Koch *et al.*, 1976; Bieber *et al.*, 1985) have shown that fats and oils were sorbed by polyolefins. It is of general knowledge in the food packaging industry that this can cause problems with the adhesion in laminated packages.

Contact angle

Contact angle measurements are made to determine the wettability of a surface (Johnson & Dettre, 1969). It gives information about surface energetics, surface roughness and surface heterogeneity. When $\theta = 0$, the liquid spreads freely over the surface, completely wetting it. This occurs when the molecular attraction between the liquid and solid molecules is greater than that between similar liquid molecules (Fowkes, 1967). The angles are determined by applying a droplet of a liquid, often pure water, on the surface of interest. Two different angles, the advancing and the receding, can be measured. The advancing angle is the largest angle that can be formed by the liquid on the surface, and it is roughly a measure of the surface itself. The receding angle is the smallest possible angle, and it gives information about any contamination of the surface.

The contact angle measurements were performed at days 28 and 56 of storage and are presented in Table 2. As can be seen from the results there was an increase of the contact angles during the storage. At 4°C the effect was not that pronounced but packages containing the most concentrated solution had larger contact angles after 56 days of storage than untreated packaging material had. For packages stored at 25°C the change was more marked. The more concentrated solutions the packages contained, the larger the increase of the contact angles. The 100 mg/litre solution caused an increase of the advancing angle from 96° for untreated material to 105° after 56 days. The receding angle was affected even more by this solution, increasing from 71 to 89°. This indicates that constituents of the powder, probably including β-carotene, had permeated through the LDPE layer and contaminated the aluminium surface. The surface then became more hydrophobic and

Table 2. The advancing and receding contact angles for a water droplet on the aluminium foil of laminated packaging material; solutions of different β-carotene concentrations (1, 5, 25 and 100 mg/litre) were stored in the packages at 4°C and 25°C (means, n = 6)

Sample	Storage time (days)			
	28		56	
	Advancing angle	Receding angle	Advancing angle	Receding angle
Untreated	96	71	96	71
Water, 4°C	96	69	96	70
1 mg/litre, 4°C	95	70	96	67
5 mg/litre, 4°C	96	69	96	67
25 mg/litre, 4°C	98	70	99	72
100 mg/litre, 4°C	98	73	101	75
Water, 25°C	96	68	98	70
1 mg/litre, 25°C	94	72	99	68
5 mg/litre, 25°C	97	73	102	74
25 mg/litre, 25°C	101	82	102	81
100 mg/litre, 25°C	100	84	105	89

the contact angles, especially the receding angle, increased. It is, however, not possible to state if this contaminant was β-carotene, or any other powder ingredient.

CONCLUSIONS

Small amounts of β-carotene, 1–2% of the total content, dissolved in the plastic layer of a laminated packaging material during 8 weeks of storage at 4°C and 25°C. The sorption did not result in any significant loss of the colour of the product. The package itself, however, was discoloured and became intensely yellow-coloured, with possible consequences for the consumer acceptance. Furthermore, the sorption decreased the adhesion between the plastic and aluminium layers of the packaging material to almost half the initial value. It is, however, not possible to state if the sorption of β-carotene alone caused the decrease in adhesion or if other components of the food colorant also participated. The sorption, and the concomitant adhesion drop might have negative effects on the properties of the package, which in turn could lead to loss of food quality at a later stage.

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