

# Influence of D-limonene absorption on the physical properties of refillable PET

M. S. Tawfik,<sup>a,b\*</sup> F. Devlieghere<sup>a</sup> & A. Huyghebaert<sup>a</sup>

<sup>a</sup>Department of Food Technology and Nutrition, Faculty of Agricultural and Applied Biological Sciences, B-9000 Ghent, Belgium

<sup>b</sup>Department of Food Science and Technology, Faculty of Agriculture, University of Alexandria, El-Shatby, Alexandria, Egypt

(Received 3 February 1997; accepted 28 April 1997)

The absorption of D-limonene into polyethyleneterephthalate (PET) at different initial limonene concentrations and storage temperatures and the effect of this addition on the physical properties of PET were investigated. Strips of PET were immersed in model solutions (160 and 320 ppm limonene) for 45 days at 5, 22 and 37°C. The level of sorbed D-limonene and PET physical properties (tensile strength, modules of elasticity, and % elongation) were monitored as a function of time. Results indicated that the degree of absorption of D-limonene was dependent upon storage temperature and initial limonene concentration. The majority of limonene was absorbed after 30 days at 22 and 37°C, but at 5°C, less absorption was observed. It was found that impact strength and modules of elasticity properties of PET were significantly affected with the level of absorption of D-limonene (at confidence level 0.05), while the elongation was not influenced.

© 1998 Elsevier Science Ltd. All rights reserved

## INTRODUCTION

There has been an increase in recent years in the use of plastics as food packaging materials. In order to reduce the manufactured output of food packaging materials, refillable polyethyleneterephthalate (PET) has become a widely used polymer. In its initial fibre form, its use was restricted to dry foods or in filters. Now with its availability in film, foil and bottle form, its use has increased considerably. The most widely spread application of PET has, however, been in the form of stretch blown bottles for carbonated beverages, where the polymer provides an effective barrier against carbon dioxide losses. In addition, PET is also relatively free of additives and adventitious low molecular weight constituents and so has intrinsic low migration characteristics (Castle *et al.*, 1989). Recently, refillable PET appeared in the market as packaging for orange juice and various soft drinks. Meanwhile, a problem has arisen because flavour compounds are being sorbed into, or are permeating through, the packaging during storage.

D-limonene is the main aroma compound in orange juice where it is required at levels of 120–200 ppm for acceptable flavour and mouthfeel (Kutty *et al.*, 1994). In studies of the interaction between PET and aroma compounds, Nielsen *et al.* (1992) were the first to show that the loss of flavour components is of little significance

for the product, while the residual aromas present in the plastic could cause an off-taste in the next product filled into the same bottle. In a second study, Nielsen (1994) has shown that 1–2% of the total content of myrcene and limonene were absorbed in refillable PET bottles and that the absorption rate was temperature-dependent. However, in the previous two studies there was no information about the effect of migration levels on the physical properties of PET. Hence, it is of major importance to study not only the migration level of the aromas into a specific plastic polymer but also the relation between this migrated material and its effects on the physical properties of the polymer, especially when the material is reusable. Model solutions were used to elucidate the effect of contact surface on components in the product (Mannheim *et al.*, 1987).

It is reported that the thickness and molecular weight of plastic films and the content of plasticizers are the main factors affecting the mechanical properties of plastic. Park *et al.* (1993) showed that tensile strength (TS) of methyl cellulose films was not a function of thickness, but elongation (E) slowly increased as film thickness increased. TS and E of hydroxypropyl cellulose films slowly increased as film thickness increased. TS decreased and E increased for both film types as the concentration of plasticizers was increased. Furthermore, TS and E were affected by the molecular weight of films.

In the literature, there is not much information about the effect of the interaction between foods and

\*To whom correspondence should be addressed.

packaging materials on its physical properties. The effect of limonene sorption rate on the mechanical properties of PET has not been reported before. To date, the work of Hirose *et al.* (1988) is the only published work investigating the effect on limonene absorption on the mechanical properties of sealant polymer films (e.g. low density polyethylene).

The increased use of refillable PET bottles as a packaging for citrus juices has prompted us to investigate the effect of D-limonene adsorption on the mechanical characteristics of refillable PET. The present study was undertaken to assess the migration level of D-limonene in a model solution into PET strips during storage at different temperatures and to evaluate the effects of such additions on the tensile strength, elongation (%) and modulus of elasticity of refillable polyethylene terephthalate (PRBs).

## MATERIALS AND METHODS

### Model solutions

The model solutions used in this study were two concentrations of 160 and 320 ppm D-limonene (Aldrich Co., Bornem, Belgium), containing 200 ppm of a mixture of antioxidants, BHA and BHT (1:1 v/v), 200 ppm antibacterial agent, sodium azide (Sigma Chemical Co.), to prevent oxidative and microbial changes during storage (Hirose *et al.*, 1988), 800 ppm commercial citric emulsifier and 600 ppm Arabic gum (Aldrich Co., Bornem, Belgium).

The solutions were homogenized by using a Schatten Homogenizer (Diegem, Belgium) in two steps under pressures of 2.07 and 1.38 MPa, respectively. Control treatments were conducted using the model solution without limonene.

### Sample preparation

Newly manufactured PET bottles were used. The flat parts of PET bottles were cut into strips of 5 cm × 10 cm, the strips were linked with glass rods to keep them separated during immersion. Three strips per 300 ml solution were placed in sterilized glass jars, sealed and stored in the dark at 5, 22 and 37°C for 15, 30 and 45 days; nitrogen was flushed into the bottles to remove air from head space, before sealing them. The ratio of film area to solution volume was 0.5 (cm<sup>2</sup> ml<sup>-1</sup>).

### Limonene in plastic

To determine the amount of D-limonene in the plastic material, the plastic was cut into small pieces after the solution was removed and the plastic pieces were rinsed with distilled water. The plastic pieces were then placed in a distillation flask and 100 ml isopropanol was added so that the sample was completely immersed. The

sample/isopropanol mixture was allowed to rest for approximately 24 h. Several extraction times were used to determine recoveries of D-limonene from the plastic stock. Distilled water (100 ml) was then added and the sample distilled to determine the amount of D-limonene in the plastic (Hirose *et al.*, 1988).

### D-limonene

The bromide–bromate titration method (Scott and Veldhuis, 1966) was employed for D-limonene determination.

### Mechanical properties

Tensile strength, modulus of elasticity and percentage of elongation were measured by the Hounsfield Test Equipment (Department of Organic Chemistry of the Faculty of Science, University of Ghent, Belgium) with a cross head speed of 10 mm min<sup>-1</sup>. The test was conducted with 10 mm wide samples with 40 mm length. Sample films were cut into strips in the machine and cross (or transverse) directions of plastic. The procedure used was adopted from ASTM Standards D882-83 (1984). Eight specimens were tested to obtain an average value.

### Statistical analysis

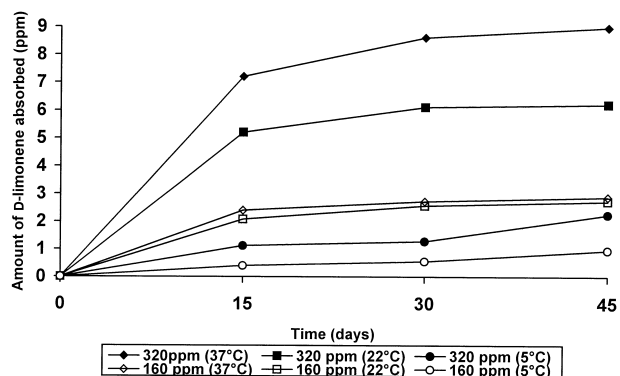
Each treatment was carried out in duplicate. Four analyses each were taken for the test samples at each specific time interval. Mean values and standard deviations were calculated at each time interval and analyzed by SPSS version 6 (SPSS Inc., Chicago, IL) for analysis of variance, *F*-ratio test (at confidence level 0.05) and multiple regression analysis.

## RESULTS AND DISCUSSION

No significant changes in the pH, colour or total bacterial count were observed in the solution during storage time due to the addition of antioxidant and antimicrobial agents.

### Sorption of D-limonene into PET

In general, the absorption level of D-limonene from the model solutions into PET strips ranged from 1.12 to 8.90 ppm. It is postulated that the sorption of D-limonene into PET during storage time depends on the initial concentration of the limonene, as well as storage temperature (Fig. 1). After 15 days, the PET immersed in a model solution containing 320 ppm limonene and stored at 37°C had absorbed seven-times more D-limonene than that stored at 5°C, but only four-times more after 45 days. However, at the lower concentration (160 ppm) of limonene the absorption ratio was 6:1 and



**Fig. 1.** Absorption of D-limonene into PET strips in the model solutions containing 320 and 160 ppm limonene at different temperatures (37, 22 and 5°C) during 45 days.

3:1 after 15 and 45 days. In agreement with the present study, Nielsen (1994) showed that there were relative differences between sorption levels of PET bottles containing a soft drink type orange (60 mg limonene litre<sup>-1</sup>) stored at 25°C and those at 4°C with ratio 7:1 after 1 week, decreasing to 3:1 after 12 weeks. This indicates that the diffusion process is temperature-dependent, as could be expected with a slower rate at lower temperature. A similar effect of temperature on absorption was reported by Kwapong and Hotchkiss (1987).

After 45 days at the three storage temperatures (37, 22 and 5°C), there were significant differences (at  $P < 0.05$ ) of the absorption of limonene between the two initial concentrations tested. This indicated that absorption rate was dependent on the initial concentration of the aroma compounds as well as the effect of storage temperature. The effect of the initial concentration on the absorption level was significant (at  $P < 0.05$ ). It has been reported that 1 g of PET stored in orange juice with a content of 177 mg litre<sup>-1</sup> limonene at 22°C absorbs 30 µg limonene (Imai *et al.*, 1990). The sorption was 9.9 µg limonene per gram of PET bottle storage at 25°C and the orange juice contained approx three times less limonene than in the previous study (Nielsen, 1994).

The equilibrium sorption levels were reached within 30 days at 37 and 22°C at the two concentrations tested (Fig. 1). However, at 5°C, stabilization was not achieved even after 45 days. It was shown (Nielsen, 1994) that the equilibrium sorption of PET is not achieved during 12 weeks of storage at 25°C. Approximately half of the total amount of sorption occurred within the first week of storage. These differences between the two studies can be explained by the differences in the initial limonene concentration (160 and 320 ppm compared with 60 ppm) and thickness of the polymers (50 µm compared with 73–100 µm). Nevertheless, Nielsen *et al.* (1992) stated that the equilibrium sorption levels of apple aromas into different food packaging polymers (including the PET) in thin films of 12–50 µm were achieved within a week.

Kutty *et al.* (1994) reported that freshly squeezed juice contains 200–400 ppm D-limonene, which was in

the range applied in the presented study. Hence, in accordance with the presented results, between 0.2 and 2.8% of the limonene content in the liquid, whether it is soft drink or pure orange juice, will be sorbed into the PET over a 45-day period. This is, however, dependent upon the temperature of storage and initial limonene concentration used. A sorption percentage of 1.4% of the total limonene in the soft drink into PET bottles was detected by Nielsen (1994). Nevertheless, no other reports were found in the literature about the absorption percentage of limonene in fresh orange juice in refillable PET bottles. The present study suggests a strong likelihood of changes in the organoleptic properties of fresh orange juice when packed into refilled PET bottles. This damage will increase with unsuitable storage conditions. In addition, caustic washing could not remove more than half of the sorbed amounts (Nielsen, 1994).

#### Effect of D-limonene absorption on the physical properties of PET strips

To determine the mechanical properties, four replicates from each different set with limonene and without limonene, and two sets for every treatment were assayed and the mean values are presented in Tables 1 and 2.

#### Tensile strength (TS)

Figure 2 shows the effect of immersing PET strips in model solutions with (320 ppm) or without limonene on the TS (MC). The present results showed that, even in the absence of D-limonene, the tensile strength ( $T/T_0 \times 100$ ) of the PET was decreased significantly (at  $P < 0.05$ ) during contact with the solution. The addition of limonene enhanced the decrease in the tensile strength independent of the limonene concentration (Fig. 3). In the model solution containing 320 ppm limonene, the tensile strength, in machine direction (MD) or in cross direction (CD), decreased significantly ( $P < 0.05$ ) with time at the three temperatures tested (Table 1). However, at the lower concentration of limonene (160 ppm), the decrease in tensile strength (CD) was in accordance with absorption rate (Table 2). Hirose *et al.* (1988) studied sorption of D-limonene (in orange juice) into sealant polymer films and the effect of this sorption on the mechanical properties. They reported that the tensile strength decreased with an increase of the absorption level of limonene into the polymer, but this decrease was also dependent on the polymer type. The maximum decrease was noticed with surlyn sodium salt (sealant film) (53% (MD) - 63% (CD)). There have been no published studies investigating the effect of the absorption of the aroma compounds on the physical properties of PET.

In the present study, the maximum decrease of elongation was 6.7% (MD) to 6.5% (CD) after 45 days in the model solution, with 320 ppm limonene stored at 37°C.

**Table 1. Changes in the physical properties of PET strips during 45 days of storage in model solution containing 320 ppm limonene at different temperatures<sup>a</sup>**

Temperature (°C)	Time (days)	Tensile strength (MPa)		Elasticity modulus (MPa)		Elongation (%)	
		(MD)	(CD)	(MD)	(CD)	(MD)	(CD)
37	0	130.6 (0.2)	161.0 (0.4)	828.0 (0.6)	1066.0 (0.5)	12.1 (0.1)	12.5 (0.2)
	15	124.9 (0.01)	152.8 (0.01)	811.7 (0.2)	1004.4 (0.6)	12.3 (0.05)	12.9 (0.6)
	30	123.9 (0.1)	151.7 (0.1)	803.5 (0.2)	985.4 (0.5)	12.6 (0.2)	13.3 (0.04)
	45	121.8 (0.02)	150.5 (0.2)	797.1 (0.8)	879.6 (0.6)	12.4 (0.1)	13.3 (0.6)
22	15	125.3 (0.6)	153.2 (0.3)	813.8 (0.9)	1005.8 (0.4)	12.2 (0.1)	13.0 (0.7)
	30	124.3 (0.5)	152.8 (0.1)	806.2 (0.2)	1002.6 (0.7)	12.1 (0.02)	12.7 (0.5)
	45	123.4 (0.9)	150.8 (0.05)	799.5 (0.3)	979.9 (0.6)	12.1 (0.2)	12.6 (0.05)
5	15	130.6 (0.3)	154.3 (0.4)	822.1 (0.2)	1006.3 (0.1)	12.1 (0.01)	12.5 (0.05)
	30	128.9 (0.3)	153.8 (0.1)	810.2 (0.2)	1005.7 (0.7)	12.2 (0.03)	12.9 (0.5)
	45	127.3 (0.9)	153.0 (0.2)	801.6 (0.6)	989.8 (0.3)	12.0 (0.5)	12.7 (0.4)

MD, machine direction; CD, cross direction.

<sup>a</sup>Means of two separate experiments with four observations each. Values in parentheses represent the standard deviation.

**Table 2. Changes in the physical properties of PET strips during 45 days of storage in model solution containing 160 ppm limonene at different temperatures<sup>a</sup>**

Temperature (°C)	Time (days)	Tensile strength (MPa)		Elasticity modulus (MPa)		Elongation (%)	
		(MD)	(CD)	(MD)	(CD)	(MD)	(CD)
37	0	130.6 (0.2)	161.0 (0.4)	828.0 (0.6)	1066.0 (0.5)	12.1 (0.1)	12.5 (0.2)
	15	126.1 (0.7)	153.3 (0.4)	812.5 (0.7)	1004.6 (0.6)	12.3 (0.5)	12.9 (0.05)
	30	124.1 (0.4)	153.0 (0.1)	804.5 (0.3)	1004.2 (0.5)	12.5 (0.2)	12.8 (0.2)
	45	123.5 (0.7)	152.9 (0.1)	803.4 (0.5)	990.5 (0.4)	12.2 (0.07)	12.8 (0.03)
22	15	126.5 (0.8)	153.6 (0.4)	812.8 (0.4)	1004.6 (0.1)	12.4 (0.05)	12.8 (0.2)
	30	124.9 (0.1)	153.1 (0.2)	807.2 (0.3)	1004.2 (0.1)	12.3 (0.2)	12.7 (0.2)
	45	124.4 (0.06)	153.0 (0.2)	804.9 (0.9)	991.4 (0.2)	12.2 (0.01)	12.7 (0.4)
5	15	130.2 (0.6)	154.5 (0.2)	818.1 (0.8)	1016.4 (0.4)	12.1 (0.5)	12.6 (0.06)
	30	129.3 (0.04)	154.3 (0.08)	815.7 (0.2)	1005.4 (0.1)	12.2 (0.01)	12.7 (0.4)
	45	127.3 (0.4)	153.5 (0.2)	809.1 (0.3)	995.6 (0.4)	11.9 (0.6)	12.7 (0.2)

MD, machine direction; CD, cross direction.

<sup>a</sup>Means of two separate experiments with four observations each. Values in parentheses represent the standard deviation.

This case also represented the maximum absorption level (8.9 ppm).

Linear regression showed a good correlation between sorption of limonene (320 ppm) into PET and the loss of its physical properties at different temperatures. An example is represented in Fig. 4, which shows the effect of sorption level on the tensile strength ( $r^2=0.81$ ) in the machine direction (MD).

### Elasticity modulus

Plastic film elasticity, in model solution with no D-limonene, did not alter significantly whereas it did in the presence of 320 ppm of D-limonene (Fig. 5). It is concluded that, in the absence of limonene, there were no significant differences between the elasticity modulus of PET at different temperatures during storage.

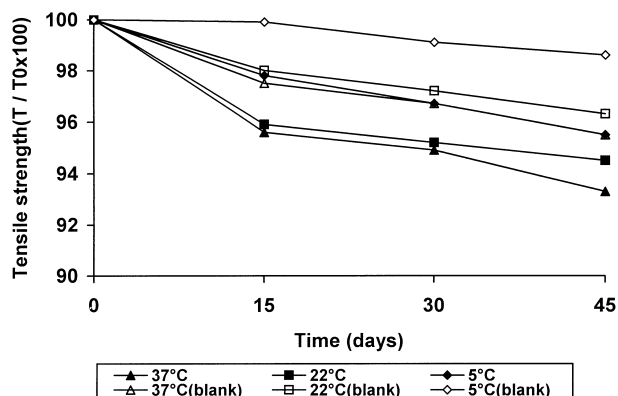


Fig. 2. Tensile strength (MD) of PET strips affected by immersing in model solutions without or with (320 ppm) limonene at different temperatures.

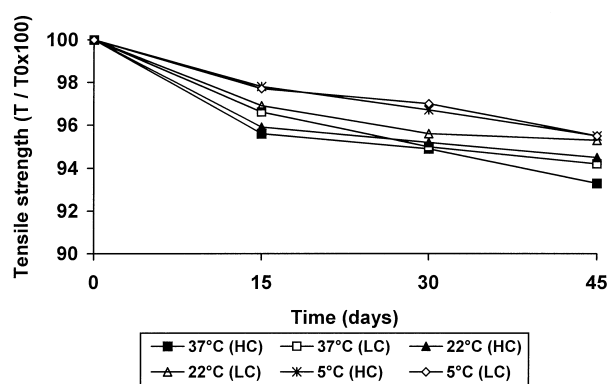


Fig. 3. Effect of limonene concentration on the tensile strength (MD) of PET strips at different temperatures. Two levels of limonene were used, 320 ppm (high concentration, HC) and 160 ppm (low concentration, LC).

The effects of storage of PET strips in limonene solutions at different temperatures on modulus of elasticity are shown in Tables 1 and 2. The results show that the elasticity always decreased significantly (at  $P < 0.05$ ), with both tested limonene concentrations, at different temperatures and different sampling times. This suggests that, in PET, the decrease in elasticity will continue even when the absorption rate of limonene reaches equilibrium or increases slightly. In the study by Hirose *et al.* (1988), D-limonene absorption significantly affected the modulus of elasticity of LDPE and Surlyn (sodium type) but, for the Surlyn film (zinc type), the modulus of elasticity in both MD and CD was not affected significantly by absorption of D-limonene. This effect of the absorbed limonene on the elasticity will limit the number of uses of refillable PET bottles. Refillable PET bottles (PRBs) contain approximately twice as much resin to increase the wall thickness (Feron *et al.*, 1994).

#### Percentage of elongation

Tables 1 and 2 show that the elongation percentages of the PET strips were increased but not significantly (at

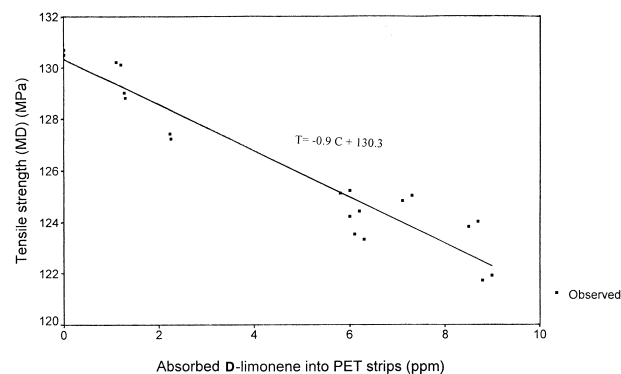


Fig. 4. Predicting relationship between absorbed D-limonene into PET strips and its tensile strength (MD). The strips immersed in model solution contained 320 ppm limonene and were stored at different temperatures.

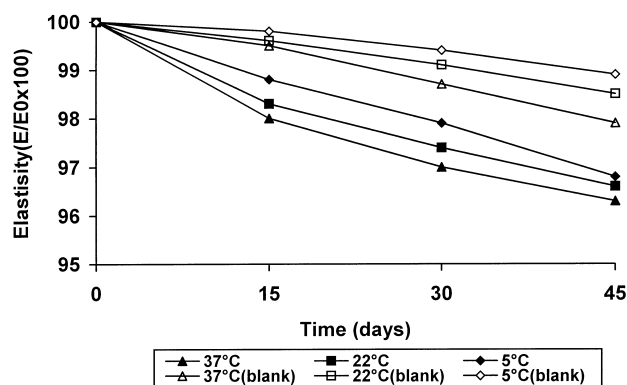


Fig. 5. Changes in the elasticity of PET strips immersed in model solution without and with limonene (320 ppm) at different temperatures.

$P < 0.05$ ), either in the absence or presence of limonene. Hirose *et al.* (1988) showed that percent elongation of LDPE (MD) at break increased due to absorption. They stated that the significant increase in the percentage of elongation may be explained by the absorbent acting as a plasticizer to allow the chains to slide past one another. Elongation of LDPE (CD) tended to decrease, though the difference was not significant. Moreover, the absorption of D-limonene by the Surlyn films did not affect their elongation.

#### CONCLUSION

From the present study, it can be concluded that absorption of limonene into refilled PET will not exceed 2.8% of the total D-limonene. However, this might affect the final product taste (off-flavour) and the absorption will be enhanced by increasing the initial concentration of the limonene in the packed product and the storage temperature. In addition, the physical properties of PET will be influenced in a negative way by absorption of limonene. Tensile strength and elasticity modules are influenced significantly by the absorption

of limonene into PET. A long storage time was used here to examine the validity of the first-order reaction for limonene absorption and its effect on the physical properties of PET. Attention should now be turned towards a modification of the polymer (such as increased crystallinity, to avoid absorption of high concentrations of aroma compounds (Nielsen, 1994).

#### ACKNOWLEDGEMENTS

We wish to thank Professor E. Schacht, and his group, Lab. of organic chemistry, Faculty of Sciences, University of Ghent for their technical support and fruitful discussion during this study. M. S. Tawfik is indebted to the Egyptian Ministry of Education and University of Alexandria.

#### REFERENCES

- Castle, L., Mayo, A., Crews, C. and Gilbert, J. (1989) Migration of poly(ethyleneterephthalate) (PET) oligomers from PET plastics into foods during microwave and conventional cooking and into bottled beverages. *Journal of Food Protection* **52**, 337–342.
- Feron, V. J., Jetten, J., Kruijf, N. and Berg, F. (1994) Polyethylene terephthalate bottles (PRB's): A health and safety assessment. *Food Additives and Contamination* **11**, 571–594.
- Hirose, K., Harte, B. R., Giacini, J. R., Miltz, J. and Stine, C. (1988) Sorption of d-limonene by sealant films and effect on mechanical properties. In *Food and Packaging Interaction*. ACS Symposium Series 365, American Chemical Society, Washington DC.
- Imai, T., Harte, B. R. and Giacini, J. R. (1990) Partition distribution of aroma volatiles from orange juice into selected polymeric sealant films. *Journal of Food Science* **55**, 158–161.
- Kutty, V., Braddock, R. J. and Sadler, G. D. (1994) Oxidation of d-limonene in presence of low density polyethylene. *Journal of Food Science* **59**, 402–405.
- Kwapong, O. Y. and Hotchkiss, J. H. (1987) Comparative sorption of aroma compounds by polyethylene and monomer food-contact plastics. *Journal of Food Science* **52**, 761–763, 785.
- Mannheim, C. H., Miltz, J. and Letzter, A. (1987) Interaction between polyethylene laminated cartons and aseptically packed citrus juices. *Journal of Food Science* **52**, 737–740.
- Nielsen, T. J. (1994) Limonene and myrcene sorption into refillable polyethyleneterephthalate bottles, and washing effects on removal of sorbed compounds. *Journal of Food Science* **59**, 227–230.
- Nielsen, T. J., Jagerstad, I. M., Oste, R. E. and Wesslen, B. O. (1992) Comparative sorption of low molecular aroma compounds into commonly used food packaging polymer films. *Journal of Food Science* **57**, 490–492.
- Park, H. J., Weller, C. L. and Vergano, P. F. (1993) Permeability and mechanical properties of cellulose-based edible films. *Journal of Food Science* **58**, 361–370.
- Scott, W. C. and Veldhuis, M. K. (1966) Rapid estimation of recoverable oil in citrus juices by bromate titration. *Journal Association Official of Analytical Chemistry* **49**, 628–633.