Influence of Apple Flavor Absorption on Physical and Mechanical Properties of Poly(ethylene terephthalate) Films

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ABSTRACT: Poly(ethylene terephthalate) (PET) films (280-μm film thickness), which are used in food packaging, were immersed into 160- and 320-ppm apple flavor solution for 14, 28, and 56 days at 5, 25, and 40°C, respectively. At the end of this period, the changes in the PET films were investigated by measuring the mechanical and physical properties. The mechanical properties were determined by examining changes in the Young's modulus. The changes in the physical properties were investigated by Fourier transform IR spectroscopy and scanning electron microscopy (SEM). The formation of microcracks in the structure of PET films was observed by SEM. According to the results of those investigations, the apple flavor affects PET films, even at very low concentrations and temperatures. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1802–1807, 2006

Key words: poly(ethylene terephthalate); mechanical properties; scanning electron microscopy; Fourier transform IR

INTRODUCTION

Plastics are used extensively in the packaging industry because of their excellent physical, mechanical, and chemical properties. Plastics are easy to find, versatile, and easy to process.[1] Therefore, the production and application of these materials has been increasingly important in the last decade.[2] Poly(ethylene terephthalate) (PET) has become one of the most important engineering thermoplastics[3] because of its toughness, clarity, capability of being oriented, and reasonable cost, as well as in the development of high-speed bottle processing technology. It is used in the manufacturing of synthetic fibers, soft drink bottles, photographic films, audio- and videotapes, and films for food packaging; it is even utilized as electrical insulating materials for capacitors. Because of these properties of PET materials, their utilization has increased substantially in packaging and storage of flavored beverages such as orange, lemon, and apple juice. Whether there is an interaction between the packaged food and the plastic materials during storage has always been a problem. The environmental conditions such as the temperature, moisture, light, pressure,[4] and radiation[5,6] play an important role in these interactions. These phenomena effect the physical and chemical structure properties of packaging materials. It is well known that changes in the structure of the material particularly affect the barrier characteristics of the material; barrier properties are closely related to the diffusion, gas permeability, and sorption of food molecules. There are few studies in the literature about the examination of changes in the physical and chemical properties of PET. In general, most of the studies are carried out either on the examination of the changes in the food packaged by some plastic material,[7,8] or on the relationship between the barrier[9] characteristics and the diffusion/sorption[10] phenomena. In order to develop new materials or improve the existing ones, their physical and mechanical characteristics should be explored extensively.

For this purpose we chose PET films, which are a prominent type of commercial plastics, and apple aroma, which is a substance used in the beverage industry, in our study. The variations taking place in PET films as a result of the interactions between the two materials were investigated.

The methods employed in the present study include examination of the physical properties (macromolecular structure and microcracks) and mechanical properties (Young's modulus).

EXPERIMENTAL

Standard solutions

Standard solutions at 160- and 320-ppm concentrations were prepared with apple flavor (natural food–beverage ingredients, article 767) and distilled water at room temperature. The apple flavor was supplied by Kent Company.

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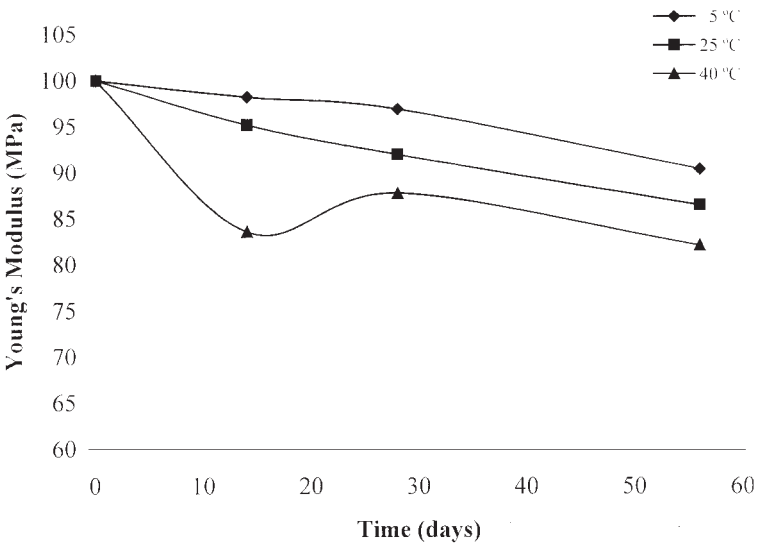

Figure 1 Changes in the Young's modulus of PET films in standard solution without and with apple flavor (160 ppm) at different temperatures.

Experiment specimens

The PET films with a thickness of 280 μm were cut down to 100 × 150 mm. These films were provided by Farmomak Company. The specimens were placed in closed glass vessels with 160- and 320-ppm apple flavor solution. They were kept at 5, 25, and 40°C for 14, 28, and 56 days, respectively.

Methods

Mechanical properties

The Young's modulus was determined by a mechanical tensile tester (Zwick model 1455) under a crosshead speed of 50 mm min^{-1} at room temperature according to ISO 527 1–3.[11,12] The films had gauge dimensions of 25 × 6 mm (length/width). The results of the measurements were determined as the average value of five experiment samples.

Fourier transform IR (FTIR) spectral analysis

The microstructure changes were measured by a Watson 1000 FTIR apparatus. Spectra were acquired for 100 scans between 400 and 4000 cm^{-1} at a resolution of 16 cm^{-1}. The maximum absorbance groups (between 3300 and 3600 cm^{-1}) were detected. The optical density of these groups was calculated from Beer's Law,[13]

$$A = \log\frac{I_0}{I}$$

where I_0 is the intensity of the incident IR beam at a wavenumber at which characteristic IR absorption occurs and I is the intensity of the incident IR beam following absorption.

Scanning electron microscopy (SEM)

A JEOL JMS 5410 LV scanning electron microscope was used to investigate the morphology of PET films. The film surfaces were sputter coated with gold.

RESULTS AND DISCUSSION

Young's modulus

The effect of apple flavor on the PET films was investigated in relation to the concentration, temperature,

TABLE I
Changes in Mechanical Properties of PET Films (280-μm Thickness) Without and with 160- and 320-ppm Standard Solution and with Distilled Water at End of 56 Days

	Young's modulus (MPa)						
Temperature (°C)	160 ppm			320 ppm			Distilled water
	14 days	28 days	56 days	14 days	28 days	56 days	56 days
Pure film[a]	2443.70	2443.70	2443.70	2443.70	2443.70	2443.70	2443.70
5	2399.81	2368.17	2208.52	2328.90	2266.07	1790.20	2278.64
25	2326.11	2248.09	2112.56	2420.96	2295.98	2026.25	2251.38
40	2042.68	2144.83	2006.03	2042.62	1931.98	1925.19	2058.23

[a] The pure film was kept in the room temperature without exposure of chemicals.

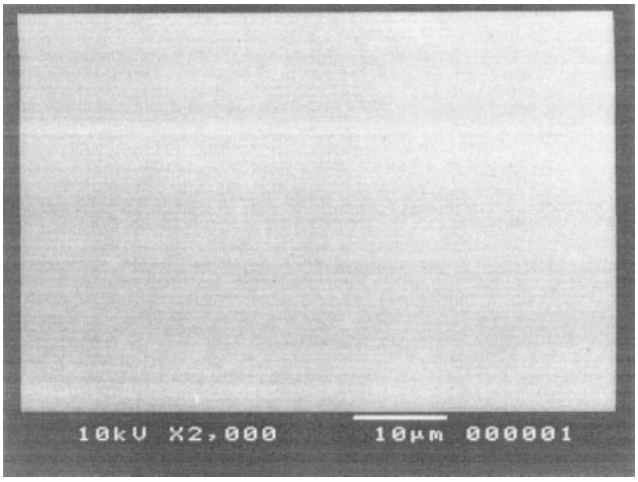

Figure 2 A scanning electron micrograph of pure PET film.

and time. Figure 1 shows the changes in the Young's modulus of PET films as a function of the storage time at different temperatures (5, 25, and 40°C) and at a concentration of 160 ppm. Similar results were found for the apple flavor at a concentration of 320 ppm at the same temperatures. The Young's modulus data of concentrations of 160 and 320 ppm are presented in Table I. As seen in Figure 1, the Young's modulus decreases as time elapses. However, we found that the Young's modulus decreases when the temperature rises. These processes were also examined for distilled water. The events of absorption and diffusion of water by different commercial plastic materials are examined in many studies in the literature.[14–16] However, the effect of water or different chemical substances on the physical and mechanical structure of materials was not searched intensively. As a result of our investigations, a small change was observed in the Young's modulus of PET films with distilled water. The results

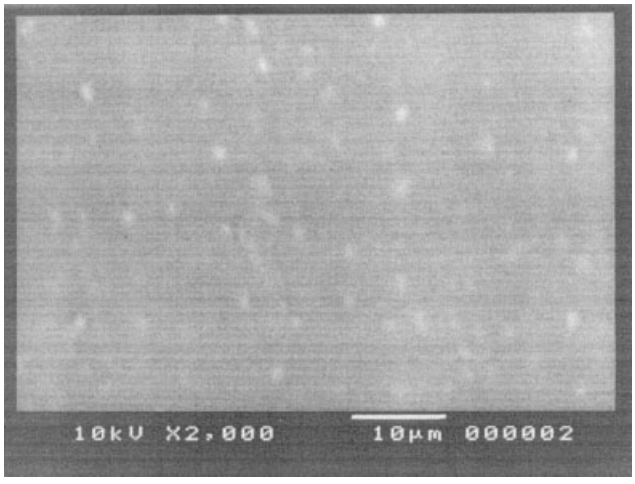

Figure 3 A scanning electron micrograph of PET film in the distilled water at the end of 56 days at 40°C.

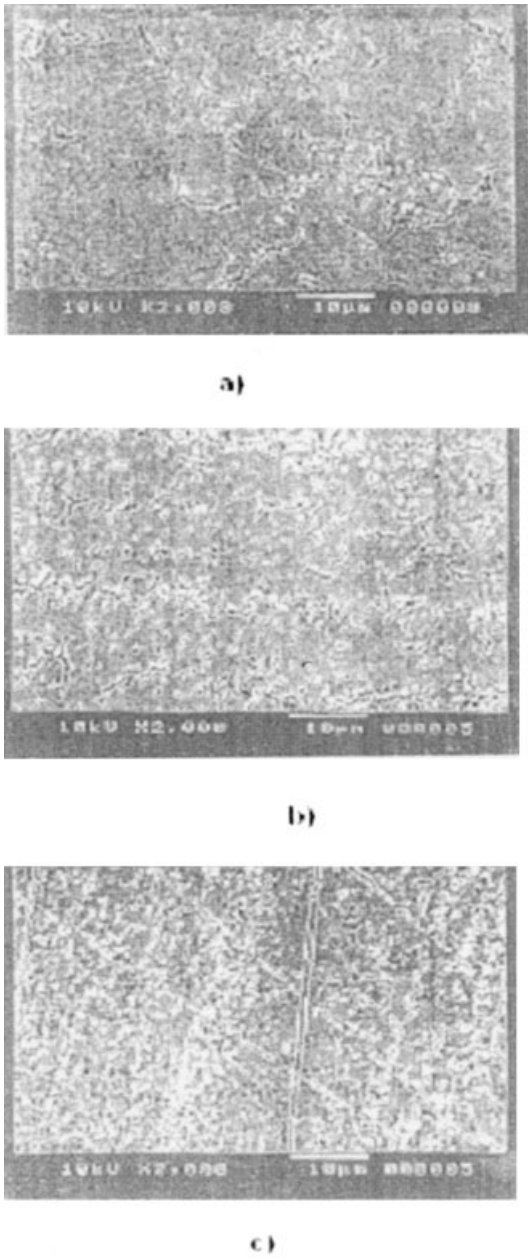

Figure 4 Scanning electron micrographs of PET films in the 160-ppm model solution at the end of 56 days (a) at 5, (b) 25, and (c) 40 °C.

are presented in Table I. FTIR measurements supported the Young's modulus results.

Morphology

The influence of the morphology on the mechanical properties of PET films was discussed, because the size and number of microcracks affected the Young's modulus. The PET films were stored for 56 days with standard 160- and 320-ppm concentration solutions. After exposure of the standard solution, the samples were washed with distilled water and kept in a thermostatically controlled oven for a short time period.

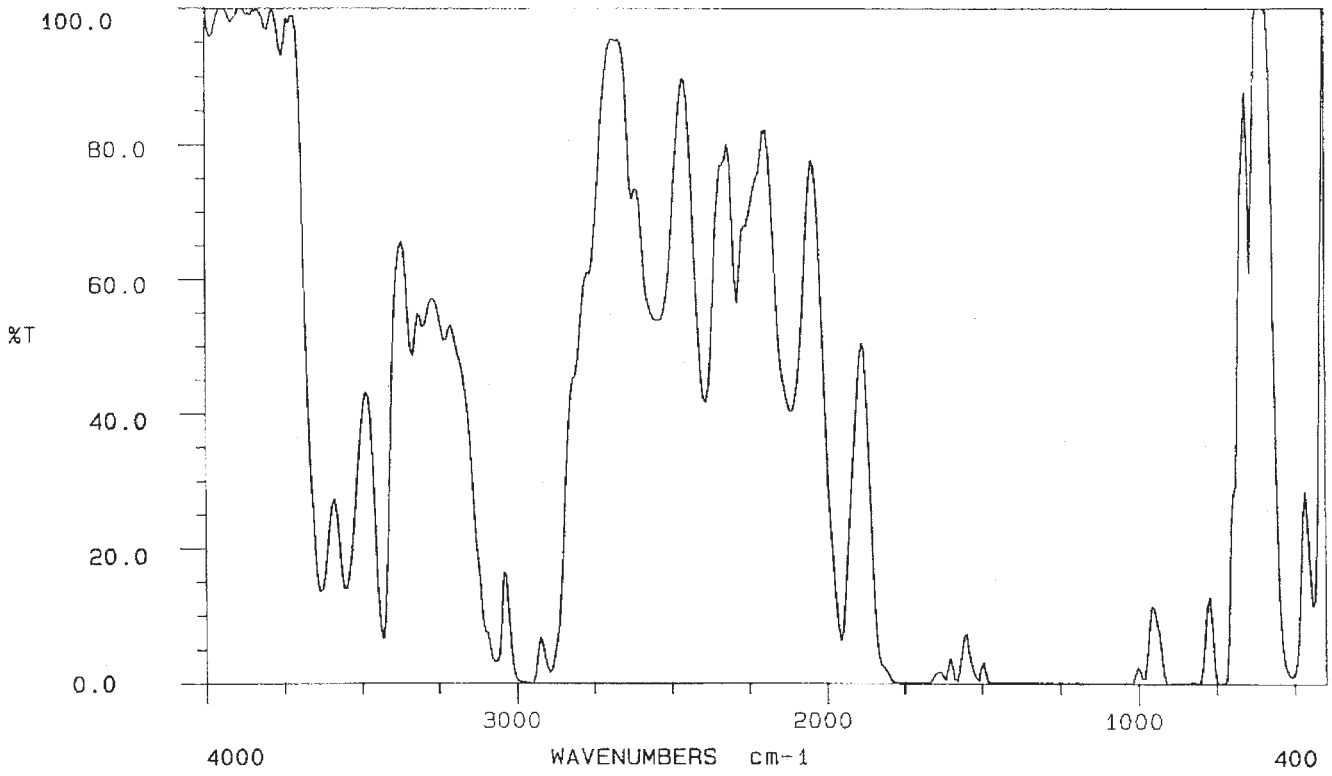

Figure 5 FTIR spectra of the pure PET film.

Before and after storage, the surface of the PET films was sputter coated with gold. Surface photographs are given in Figures 2–4. SEM was used for this purpose. Figure 2 shows an SEM photograph of pure PET film. Figures 3 and 4 display the change in the size and number of microcracks on the PET film surfaces at 40°C with distilled water and at different temperatures (5, 25, and 40°C) with a concentration of 160 ppm for 56 days, respectively. These two figures were examined and compared by using the reference photograph in Figure 2. As a result of examining the SEM photographs, we observed that the size and number of microcracks on the PET film surfaces was increased with increasing temperature and concentration.

TABLE II
Band Assignments for IR Spectrum of Pure PET

Wavenumber (cm^{-1})	Assignment
3535	Absorbed moisture O—H stretching of diethylene glycol end group
3060	Aromatic C—H stretching
2960, 2880	Aliphatic C—H stretching
1950	Aromatic summation band
1720	Carbonyl C═O stretching
1615, 1450, 1430	Aromatic skeletal stretching bands
1465	—CH_2— deformation band
3061	Carbonyl C═O stretching of ester group
1175, 1120, 1020	Bands in skeletal ring region indicative of aromatic substitution pattern and indicates 1,4-Substitution
980	O—CH_2 stretching of ethylene glycol segment in PET
850	C—H deformation of two adjacent coupled hydrogens on aromatic ring
730	Associated with out of plane deformation of two carbonyl substituents on aromatic ring

Band assignments from Holland and Hay.[17]

FTIR spectral analysis

The changes in the structure of PET films in the apple flavor for different storage periods (14, 28, and 56 days) and temperatures (5, 25, and 40°C) were exam-

TABLE III
Change of Optical Density of Peaks of 3500–3650 and 3250–3350 cm^{-1} of IR Spectra of PET Films (280-μm Thickness) in 160-ppm Apple Flavor Solution at Different Temperatures at End of 56 Days

	Temp. (°C)	14 days	28 days	56 days
3500–3650 cm^{-1}	5	42.45	54.40	56.21
	25	44.94	64.88	67.77
	40	49.95	73.23	75.58
3250–3350 cm^{-1}	5	8.71	8.39	7.09
	25	8.84	7.46	6.36
	40	8.39	8.05	7.25

TABLE IV
Change of Optical Density of Peaks of 3500–3650 and 3250–3350 cm^{-1} of IR Spectra of PET Films (280-μm Thickness) in 320-ppm Apple Flavor Solution at Different Temperatures at End of 56 Days

	Temp. (°C)	14 days	28 days	56 days
3500–3650 cm^{-1}	5	43.75	73.63	56.98
	25	50.35	64.62	71.60
	40	48.30	50.42	74.03
3250–3350 cm^{-1}	5	7.53	7.63	8.37
	25	8.26	7.50	7.45
	40	8.84	7.68	7.03

ined by IR spectra and compared with the mechanical properties. The IR spectrum of pure PET film is shown in Figure 5 and assignments are provided in Table II.[17]

Most of the peak positions were found to be unshifted. However, we observed changes in the absorbance or transmittance of specific chemical groups within a 3350–3600 cm^{-1} region after bond deformation. The increase of positions in this region influences the structure of the material. It is believed that the peak positions increase as a result of the reaction of the polymer surface with atmospheric oxygen and water.[18] The optical density of these groups in the spectra were calculated from Beer's law and the results calculated were presented in Tables III and IV. The structure of the PET film is not extensively degraded, as seen by the FTIR transmission in Figure 6. However, note that the optical density for those bands increases with increasing time in the 160- and 320-ppm standard solutions displayed in Figure 7 and at different temperatures. The increase in the moisture absorbed peak at 3550 cm^{-1} causes the Young's modulus to decrease by the conversion of microcracks on the PET film surfaces into macrocracks. These processes were examined for distilled water and compared with the results of apple flavor. The analysis of the IR absorption spectra in Table V proves that, during the exposure of samples to distilled water, some small changes take place within the 3350–3600 cm^{-1} region. A comparison of the results shows that the change in the Young's modulus of PET films was effected not only by the amount of apple flavor but also by pure water, especially at 40°C and after 56 days.

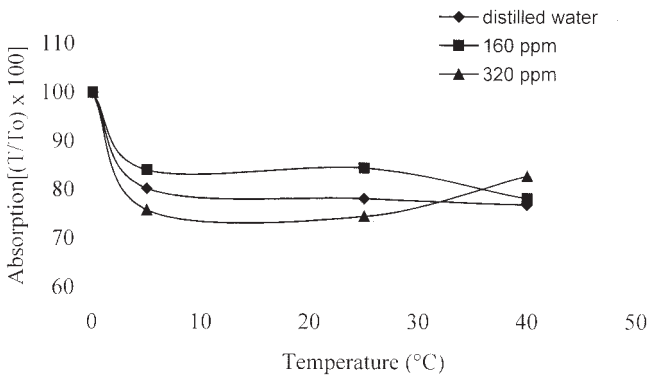

Figure 7 The change of the optical density of the peaks at 3500–3600 cm^{-1} of the IR spectra of PET films with 280-μm thickness in the 160- and 320-ppm apple flavor solution and distilled water at different temperatures at the end of 56 days.

CONCLUSIONS

The results of the effect of apple flavor on PET films were presented comprehensively.

1. There was a 10% decrease in the Young's modulus at low concentration (160 ppm) and at low temperature (5°C) at the end of 56 days.

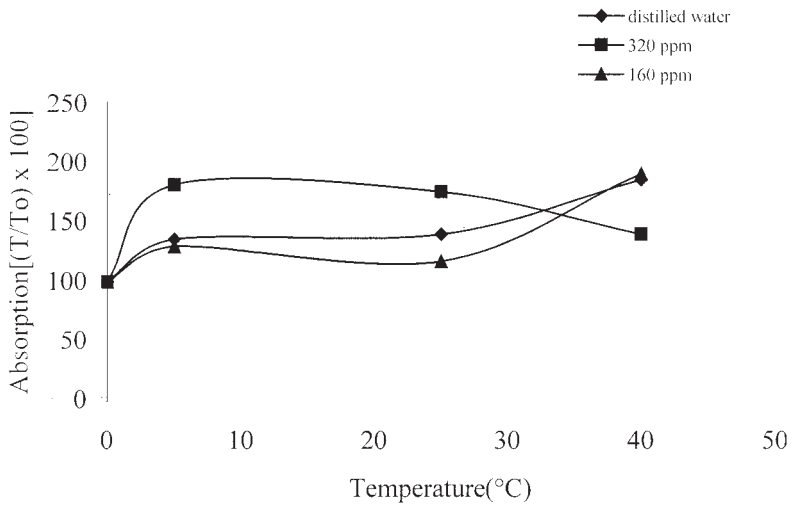

Figure 6 The change of the optical density of the peaks at 3250–3350 cm^{-1} of the IR spectra of PET films with 280-μm thickness in the 160- and 320-ppm apple flavor solution and distilled water at different temperatures at the end of 56 days.

TABLE V
Change of Optical Density of Peaks of 3500–3650 and 3250–3350 cm^{-1} of IR Spectra of PET Films (280-μm Thickness) in Distilled Water at Different Temperatures at End of 56 Days

Temp. (°C)	3500–3650 cm^{-1}	3250–3350 cm^{-1}
5	55.28	7.58
25	56.97	7.24
40	73.67	7.05

2. As the concentration of apple flavor increased twofold at 5°C, the degradation at the end of 56 days was more than double.
3. Even pure water had an effect on PET films, and the change was slightly lower than low concentration apple flavor.
4. As the temperature increased to 40°C, the effect of apple flavor at low concentration increased roughly twofold. This effect was further increased by increasing the concentration.
5. Although a greater effect of apple flavor at high temperature was expected, this effect could be predicted to decrease because the apple flavor solution spoiled.

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