High-Performance Liquid Chromatographic Determination of Migrating Poly(ethylene terephthalate) Oligomers in Corn Oil

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A high-performance liquid chromatographic (HPLC) method has been developed for determining poly(ethylene terephthalate) (PET) oligomers in corn oil. The oligomers are extracted from corn oil with hexane–acetonitrile, the extract is evaporated almost to dryness, and the concentrate is diluted with dimethylacetamide for separation and quantitation of the oligomers by HPLC. Recovery studies were performed using bis(2-hydroxyethyl) terephthalate (BHET) and the PET cyclic trimer. The mean recoveries from corn oil were 96.2 and 98.4% for BHET and the PET cyclic trimer, respectively. This method was also used to measure the migration of PET cyclic oligomers from PET susceptor food trays, PET-coated paperboard food trays, and crystallized PET food trays under microwave-use conditions. Oligomers beginning with the cyclic trimer through the cyclic octamer were found to migrate.

The use of poly(ethylene terephthalate) (PET) as a food-packaging polymer has grown substantially over the last few years. Until recently its largest application by volume was in blow-molded carbonated-beverage bottles. However, it is now being widely used in microwave susceptor and dual-ovenable containers by the frozen food industry for reheating, cooking, and crisping of food in microwave or convection ovens. Because of the wide temperature range over which these packaging materials are being used [i.e., 25 to ≥400 °F (−3.8 to ≥+204 °C), which is well above the glass transition temperature of PET], residual reactants and polymeric compounds in these containers have a much greater potential for migrating into food contained therein. Chemicals migrating from packaging materials are regulated by the Food and Drug Administration (*CFR*, 1987). The regulations require the development of appropriate migration data for the determination of probable consumer exposure.

Migration data are typically generated by conducting extraction studies of packaging materials with food-simulating solvents. For packaging applications at room temperature or below, food-simulating solvents such as water or solutions of ethanol–water are placed in contact with the container material at an exaggerated temperature (120 °F or 49 °C) for an extended period of time (10 days). Following this exposure, the solvents are analyzed for chemicals that have migrated. For high-temperature applications, which require testing at temperatures of 400 °F and higher, water and water–ethanol by themselves are not appropriate food simulants because their boiling points are exceeded. A high-boiling vegetable oil or oil emulsion is more appropriate. This study employs corn oil as a high-temperature fatty-food simulant for the characterization of PET oligomer migration from dual-ovenable and microwavable trays under conditions of use.

Generally, potential migrants from PET food packaging consist of initial reactants including monomers, reaction byproducts, and oligomers of low molecular weight. These compounds have been determined in a number of PET resins and packaging materials (Begley and Hollifield, 1989), including dual-ovenable trays, microwavable trays, and microwave susceptor food packaging. Although several methods exist for characterizing PET (Zaborsky, 1977; Hudgins et al., 1978; Jabarin and Balduff, 1982; Tice, 1988; Begley and Hollifield, 1989), they are generally designed to determine molecular weight distributions, prepolymer components, and resin residuals and are not applicable to the determination of PET oligomers in foods or food simulants.

This paper describes a method for the analysis of corn oil for bis(2-hydroxyethyl) terephthalate (BHET) and the homologous series of cyclic oligomers from the trimer to the nonamer. The method consists of liquid–liquid partitioning of the corn oil in hexane with acetonitrile, a concentration step, and analysis by high-performance liquid chromatography (HPLC) with ultraviolet detection. We have found this method particularly helpful in monitoring the migration of PET oligomers from microwave susceptors and dual-ovenable trays under conditions of use. Food trays made of crystallized PET (CPET), PET-coated paperboard, and aluminized-PET-coated paperboard (susceptor tray) were studied.

EXPERIMENTAL SECTION

HPLC Apparatus and Operating Conditions. The HPLC system consisted of a Hewlett-Packard Model 1090 solvent delivery system (Hewlett-Packard, Palo Alto, CA) equipped with a Rheodyne Model 7010 20-μL sample injector (Rheodyne, Inc., Cotati, CA) and Rheodyne Model 7125 sample injector with a Brownlee C_8 30 × 4.6 mm, 5-μm guard column (Brownlee Laboratories, Inc., Santa Clara, CA) as the sample loop, a Waters Model 480 Lambda Max variable-wavelength detector (Waters Associates, Milford, MA) operated at 254 nm, and a Nelson Analytical Model 3000 chromatography data system (Nelson Analytical, Cupertino, CA) run on an IBM AT computer. The HPLC column was 5-μm Microsorb C_8, 250 × 4.6 mm (Rainin Instrument Co., Woburn, MA). HPLC mobile phases: solvent A, water–acetonitrile–acetic acid (85:15:0.25); solvent B, acetonitrile–water (85:15). Linear gradient programmed as follows at flow rate of 1.5 mL/min: from 5 to 60% B in 8 min; from 60 to 70% B in 8 min; from 70 to 100% B in 7 min; 100% B for 11 min; from 100 to 5% B in 1 min.

Concentrator. A Kuderna-Danish evaporative concentrator with 10-mL collection tube, 125-mL flask, and three-ball condenser column (Kontes Glass Co., Vineland, NJ) was used for solvent evaporation.

Reagents. All solvents were distilled in glass and were purchased from Burdick & Jackson Laboratories, Inc. (Muskegon, MI). Water was distilled and then purified by a Milli-Q water purification system (Millipore Corp., Bedford, MA). The PET cyclic trimer, cyclic tris(ethylene terephthalate), was a gift from Eastman Chemical Products, Inc. (Kingsport, TN). *N,N*-Dimethylacetamide (practical) was purchased from Eastman Kodak

Table I. Recovery of Bis(2-hydroxyethyl) Terephthalate (BHET) and Poly(ethylene terephthalate) (PET) Cyclic Trimer

compd added	added, μg/g of oil	recd, μg/g of oil	% rec
BHET	0.476	0.475	99.8
	0.476	0.459	96.4
	0.476	0.448	94.1
	0.476	0.449	94.3
mean			96.2
PET cyclic trimer	0.523	0.494	94.5
	0.523	0.461	88.1
	0.523	0.503	96.2
	0.523	0.604	115
mean			98.4

Co. (Rochester, NY); BHET was purchased from Polysciences, Inc. (Warrington, PA); acetic acid (glacial) was purchased from J. T. Baker Chemical Co. (Phillipsburg, NJ); Mazola brand corn oil was from Best Foods (Englewood Cliffs, NJ).

Extraction. Approximately 3.0 g of corn oil was accurately weighed into a 50-mL beaker. A 25-mL portion of hexane was added, and the mixture was stirred and transferred to a 125-mL separatory funnel. The beaker was rinsed with a second 25-mL portion of hexane, and the rinsings were transferred to the same separatory funnel. The corn oil–hexane mixture was extracted with two 25-mL portions of acetonitrile. The acetonitrile extracts were combined, transferred to a Kuderna-Danish evaporative concentrator, and evaporated almost to dryness on a steam bath. The concentrate was diluted to 2.0 mL with dimethylacetamide.

Quantitation. External standards of BHET and the PET cyclic trimer were used for calibration. Calibrations employed linear regression analysis of integrated peak areas of at least five standard solutions ranging in concentration from 0.4 to 70 μg/mL. All standard solutions were prepared in dimethylacetamide.

Recoveries. Recovery experiments were performed by spiking 15 g of corn oil with 0.75 mL of a standard solution containing BHET and the PET cyclic trimer in chloroform, each at an approximate concentration of 10 μg/mL. Four aliquots of the spiked corn oil containing each analyte at an approximate concentration of 0.5 μg/g of oil were extracted and subsequently analyzed by HPLC. Recovery results are summarized in Table I.

Analysis of Microwavable Trays. Glass beads (2–4 mm in diameter) were placed in each rectangular tray to cover the bottom surface. (The glass beads served as an inert load on the tray.) Corn oil was then placed in the tray to just cover the glass beads. The ratio of the mass of the corn oil to the bottom surface area was held constant (1.2 g/in.^{2} or 0.186 g/cm^2) for all trays. Because the exposure of the oil to the surface of the side walls was slight, it was ignored in this study. After the corn oil was placed in the tray, the tray was microwaved for 3.0 min on high power in a microwave oven (577 W, measured by heating 1000 g of water). Then 3.0 g of corn oil was removed from the tray and analyzed for migrants. A simulated blank or control was prepared for analysis by microwaving a comparable weight of corn oil in a glass Petri dish with a susceptor placed beneath the dish. The corn oil blank had the same ratio of mass to bottom surface area as the PET trays. The trays and tray material used in this study were obtained from commercial suppliers. The CPET and the PET-coated paperboard trays were tested in their commercial forms; the susceptor trays were constructed manually from flat stock.

RESULTS AND DISCUSSION

Corn oil was chosen as the fatty food for these studies to simulate some of the convenience foods, e.g., popcorn, that are packaged for microwave ovens. Corn oil has a very high boiling point, and unlike solutions of ethanol–water, which are often recommended as food simulants for migration testing, it does not appear to react with

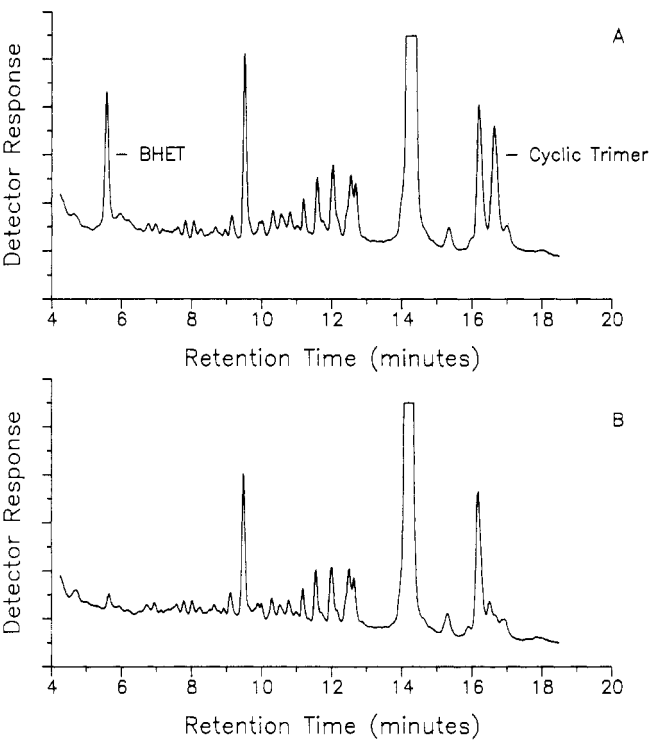

Figure 1. Chromatograms obtained from analysis of (A) corn oil extract spiked with BHET at 47.6 ng/g and the cyclic trimer at 52.3 ng/g and (B) corn oil blank extract.

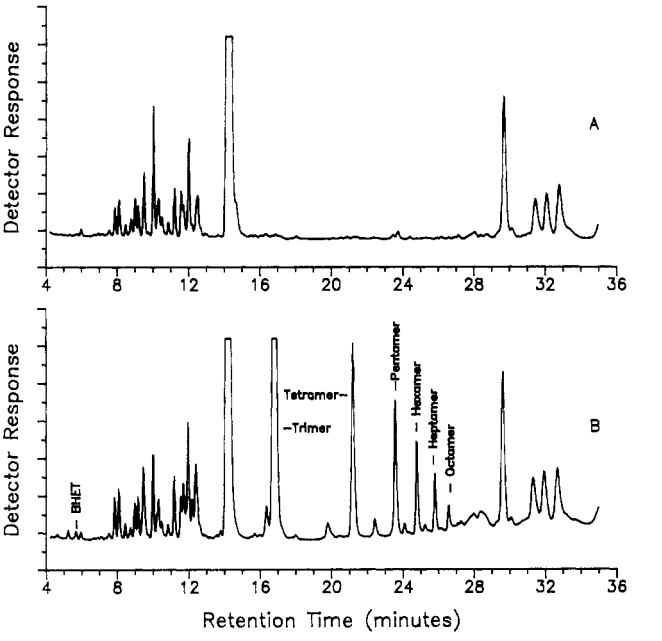

Figure 2. Chromatograms of extracts from corn oil that was microwaved for 3.0 min in contact with (A) glass Petri dish with susceptor film underneath the dish and (B) PET susceptor tray.

PET or its oligomers. Ethanol food simulants tend to undergo transesterification and hydrolysis reactions with PET and its oligomers and, therefore, are not appropriate for testing this polymer.

In this study nonspecific ultraviolet responses were measured. Although it was recognized that the absorptivities of the various terephthaloyl moieties are slightly different, the absorptivities of the most probable species were used for quantitation. A similar approach was used in the HPLC determination of PET polymeric oligomers by Zaborsky (1977). The absorptivities of BHET and the cyclic trimer were used in this study for quanti-

Table II. Migration of Oligomers from Metallized Poly(ethylene terephthalate) (PET) into Corn Oil[a]

oligomer	oligomer content,[b] mg/in.^{2} PET	oligomer concn in replicate oil extr (n = 4),[c] mg/in.^{2} PET				av oligomer migration	
						mg/in.^{2} PET	% oligomer content[b]
trimer	0.138	0.1070	0.1270	0.1290	0.1170	0.1200	86.9
trimer ether	0.004	0.0016	0.0023	0.0017	0.0016	0.0018	45.0
tetramer	0.039	0.0170	0.0169	0.0209	0.0191	0.0185	47.4
tetramer ether	0.003	0.0018	0.0013	0.0017	0.0019	0.0017	56.7
pentamer	0.019	0.0130	0.0093	0.0118	0.0102	0.0111	58.4
pentamer ether	0.002	0.0003	0.0005	0.0007	0.0006	0.0005	25.0
hexamer	0.014	0.0091	0.0055	0.0072	0.0060	0.0070	50.0
hexamer ether	0.001	0.0009	0.0004	0.0004	0.0005	0.0005	50.0
heptamer	0.010	0.0057	0.0028	0.0039	0.0016	0.0035	35.0
octamer	0.006	0.0027	0.0017	0.0024	0.0018	0.0022	36.7
BHET[d]	0.0002	0.0003	0.0003	0.0003	0.0003	0.0003	150
total	0.236	0.159	0.168	0.180	0.161	0.167	70.8

[a] Corn oil (1.2 g/in.^{2} or 0.186 g/cm^2) and glass beads heated for 3 min in each PET susceptor tray in a 577-W microwave oven. [b] Oligomer content in susceptor based on method described by Hudgins et al. (1978). [c] Values represent oligomer concentrations migrating to corn oil from four individual trays made from the same lot of susceptor material. [d] BHET = bis(2-hydroxyethyl) terephthalate.

tation, which included the calculation of recoveries. The absorptivity of the cyclic trimer was used to estimate the concentrations of the oligomers of higher molecular weight in the absence of specific standards.

Figure 1 shows that BHET and the cyclic trimer in the partitioned extract are well separated from each other and from the background in spiked corn oil. In the chromatograms of the corn oil extracts (Figure 1A,B), the 7- to 15-min retention time region contains eluate peaks that are due primarily to corn oil components and oxidation products. The chromatograms of the blank and the susceptor extract in Figure 2 parts A and B, respectively, indicate that the oxidation products in the extracts do not significantly interfere with the separation of the PET oligomers.

Data for the recovery of BHET and the cyclic trimer from corn oil are given in Table I. Recoveries were calculated by blank subtraction and external standards. Mean recoveries of BHET and the cyclic trimer added to corn oil were 96.2 and 98.4%, respectively, for spiking levels of 0.476 and 0.523 μg/g. Although the data in Table I illustrate that the method has acceptable precision, the actual levels of migrating cyclic trimer and higher PET oligomers from susceptors were much higher than the levels of the compounds used in the recovery studies. Because of the lack of standards, no recoveries of the cyclic oligomers of higher molecular weight were conducted.

At the temperatures achieved by the corn oil during microwave heating, all of the cyclic oligomers in the PET polymer migrated to some extent. Figure 2 shows chromatograms of an extract of a corn oil blank and an extract of corn oil that had been heated in a susceptor tray. Two regions in the chromatogram indicate whether terephthaloyl compounds have migrated into the corn oil. The first region, which represents retention times from 4 to 7 min, contains peaks of compounds such as terephthalic acid, monohydroxyethyleneterephthalic acid, and BHET. The second region, which represents retention times from 15 to 28 min, contains peaks of oligomers of higher molecular weight (e.g., the cyclic trimer peak at 16.5 min). Peaks of the principal migrating PET oligomers are found in this second chromatographic region and appear to be those of the cyclic oligomers reported by Hudgins et al. (1978) in their characterization of PET oligomers. Thus, it appears that cyclic oligomers from the trimer to the octamer migrate from PET susceptor film into corn oil under the microwave conditions used in this study. In the absence of standards, the characteristic pattern of a homologous series shown in Figure 2B is evidence for the migration of these higher oligomers. Also, molecular weights obtained by HPLC–mass spectrometric analysis for compounds responsible for several of these peaks are consistent with those of cyclic oligomers from the trimer to the pentamer.

Table II lists the results from the analysis of corn oil that was heated in contact with a susceptor for 3 min in a microwave oven. The chromatograms indicate that the major migrants were the cyclic trimer and compounds believed to be successively higher members of the homologous series of cyclic oligomers through the octamer. Collectively these compounds represent about 2% of the film weight. It is estimated that about 65–70% of these oligomers migrated during the 3-min microwave heating period. Oligomer migration from PET susceptor films approached 100% during 5–6 min of microwave heating. The quantities of migrants that elute earlier than the cyclic trimer are insignificant compared with those of the trimer and the oligomers of higher molecular weight, as shown by the chromatograms in Figure 2 and the much lower BHET migration value of 0.3 μg/in.^{2} (0.046 μg/cm^2). Under the current experimental conditions, analysis of a susceptor film that produces a cyclic trimer migration of 0.12 mg/in.^{2} or 0.019 mg/cm^2 (the cyclic trimer migration value for the susceptor) is equivalent to the analysis of an oil extract that has a cyclic trimer concentration of approximately 100 ppm. The level at which the recovery experiments were performed was substantially lower than 100 ppm because of the limited availability of reference materials.

Figure 3 shows histograms representing micrograms of cyclic trimer migrated per square inch of PET for the three types of microwaved food trays analyzed. The histograms illustrate that the within-product-type differences are reasonable, 20–50%, but that the between-product-type differences can be as large as 80-fold (CPET vs susceptor). The large migration difference between susceptor and nonsusceptor trays (CPET and paperboard) is mainly a result of temperature difference (about 212 °F or 100 °C); that is, because the susceptor tray gets much hotter than the CPET tray, the oligomers in the former migrate into the corn oil at a greatly increased rate. The migration difference between the CPET and the paperboard trays is a function of polymer crystallinity, if it is assumed that both tray types reach the same temperature in the microwave oven. Generally, the higher the polymer crystallinity, the lower the expected migration. Therefore, the CPET tray, which has the highest crystallinity, had the lowest migration. Much of the within-product-type reproducibility can be attributed to the

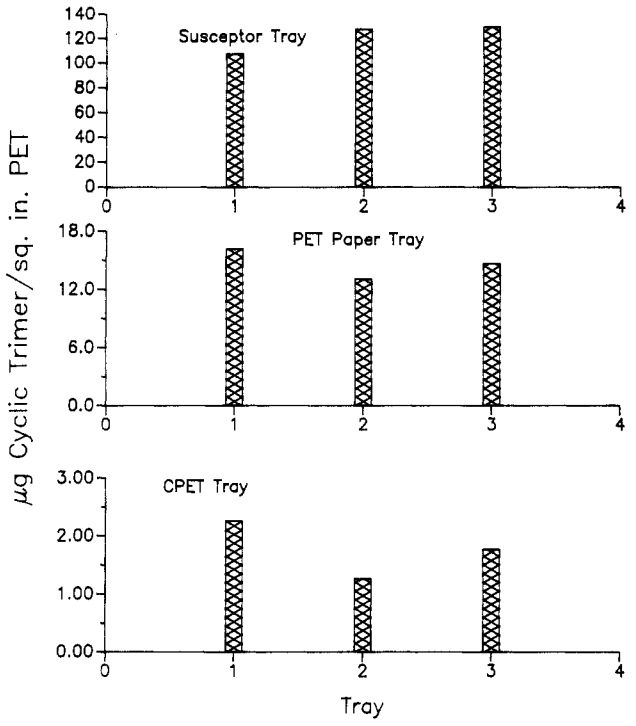

Figure 3. Histograms of migrating cyclic trimer from three types of PET food trays (three trays/type) microwaved for 3 min after addition of corn oil (1.2 g/in.^{2} or 0.186 g/cm^2).

method precision of 12% (relative standard deviation of the percent recovery) plus the variability in the tray material and tray deformation caused by the rapid heat generated. Tray deformation may result in pooling of the corn oil at one side of the tray, thereby affecting the effective extraction surface area. Ways to improve the reproducibility of these extractions are under investigation.

The HPLC method described here has been particularly useful for conducting high-temperature migration studies to evaluate PET packaging items designed for microwave and conventional oven use. It has been used to identify PET oligomers and measure their migration into corn oil under high-temperature conditions of use. Since the method employs ultraviolet spectrometric detection, it is not applicable to nonterephthaloyl moieties, such as ethylene glycol, that may be present in PET. However, it has been shown to be quantitative for BHET and the cyclic trimer. On the basis of our experience, we believe that the cyclic trimer absorptivity coefficient is a reasonable approximation to use in calculating the concentrations of the higher terephthaloyl moieties.

ACKNOWLEDGMENT

We express our thanks to the following companies for supplying materials for this method development study: Eastman Chemical Products, Kingsport, TN; James River Corp., Neenah, WI; Mullinix Packages, Inc., Fort Wayne, IN; Manville Forest Products, West Monroe, LA; ITW High Performance Plastics Division, Glenview, IL.

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Received for review October 26, 1988. Revised manuscript received May 23, 1989. Accepted June 30, 1989.