QUANTIFICATION AND CONTROL OF CONTAMINANTS IN RECYCLED HDPE

Myer Ezrin, E. Dale Wyatt, Gary Lavigne, and Andrew Garton
Institute of Materials Science, University of Connecticut
Storrs, CT 06269-3136

Introduction

The goal of expanding the use of recycled plastics from post consumer packaging containers, for food applications, is the reason for studies being cofunded by the American Plastics Council and the US EPA Pollution Prevention R & D Center at this university. The research is being conducted along two lines: Phase (1) - analysis of composition of volatile compounds in commercial recycled HDPE from dairy and other beverage sources; Phase (2) - the kinetics of absorption and removal of model compounds simulating possible contaminants. Analysis of potentially hazardous contaminants in recycled washed resin is being done by headspace GC/MS.[1,2] Qualitative identification of compounds evolved with heat is done by mass spectroscopy. Quantitative analysis is made for compounds considered potentially hazardous or unacceptable for any reason. The initial work is focused on recycled HDPE from well defined sources such as milk, juice and water containers ("dairy containers"). Headspace GC/MS is suitable for analysis of relatively volatile compounds, and for materials of much lower volatility. BHT antioxidant, for example, is being analyzed quantitatively. Analytical methods being used for the absorption and removal phase of the work include infrared spectroscopy (IR) and headspace GC/MS.

PHASE 1
Headspace GC/MS analysis of commercial recycled dairy resin

As many as 100 or more compounds are detected in recycled HDPE, some of which are present in virgin PE. The capillary GC column used is SGE-BPX5, 25 meters, 1μ film thickness, 0.22 mm ID, which provides good resolution for compounds over a wide range of volatility. The GC temperature program is 35-300°C at 5°C per minute. The headspace temperature is controlled so as to drive out the volatiles in several minutes, without degrading the polymer or additives and creating volatiles not present in the samples as received. For qualitative purposes, this presents no problem because relatively low temperatures and short times can be used to obtain a peak for each compound present.

For accurate quantitative analysis, however, the temperature and time are much more critical. Various combinations have been evaluated to obtain approximately 90-100% of each compound in one or two heating periods of up to 10 minutes each. For the relatively volatile aromatics (benzene, toluene and xylenes), their strong affinity for PE necessitates temperatures of 300-325°C and times of 10-60 minutes to evolve close to all the compounds. The question then arises if any of the compounds are being generated by the headspace conditions from decomposition of polymers and additives. It is unlikely that decomposition of PE will generate benzene, toluene and xylenes. It is

certain that the aromatics are present in both virgin and recycled HDPE as received because they can be detected at 150°C headspace temperature. Considerably more aromatics of the order of 5-10 times as much are present in the recycled polymer.

For quantitative analysis of other compounds, like BHT, temperature of 300-325°C appears to give quantitative results in 10-20 minutes or less. At this writing, quantitative values determined, especially for aromatics, must be considered tentative. They do, however, furnish approximate levels of concentration which will be made more accurate with further development of the headspace method and by use of an independent method (see 2.1 below).

For the most precise measure of GC peak area of very low levels of aromatics of virgin HDPE, selected ion data collection by the mass spectrometer is used. Another variable that may affect quantitative results is sample weight. The apparatus will accommodate up to about 40-50 mg polymer. While lower weights are desirable because of more complete evolution of volatiles in a given time, they may not be as representative of the whole lot as a larger sample. Quantitative analysis of small samples can be improved by performing an adequate number of multiple runs.

Grinding of recycled pellets to small particle size preparatory to analysis causes loss of some volatile compounds as surface area is increased. For this reason we conducted analyses on portions of up to 10 pellets as received, obtained with a razor blade.

Analysis of commercial recycled HDPE dairy resin from two resin suppliers has given similar results: (1) low levels of aromatics, (2) fragrance and taste materials such as pinenes and limonenes, (3) BHT antioxidant, (4) many aliphatic hydrocarbons, some of which are also seen in virgin resin, and (5) other miscellaneous compounds. For the limited number of samples analyzed so far, the contents of aromatics and BHT are in Table 1.

These are preliminary values for a limited number of samples from two suppliers (#1, #2) and are not necessarily representative of recycled resin in general. The primary purpose of this paper is mainly to report on the analytical methodology being used.

The values in the table were obtained using a single 10 min. headspace period at 325°C, and 3-5 mg sample. Calibration was done with BHT over a range of concentrations. For the aromatics, calibration was made with toluene, and assumed to apply also to benzene and xylenes. In subsequent analyses, direct calibration will also be made with benzene and xylenes. GC peak areas were measured using selected ion data collection with mass 78 for benzene, 91 for toluene and xylenes, and 205 for BHT. These are the strongest peaks in each case. The limit of detection is <1 ppb.

By using a single 10 minute heating period at 325°C, the values for BHT are close to the total amount. For the aromatics, however, that released in a single 10 min. period is about half of the total given by multiple periods up to 60 min. The actual contents of aromatics may be as much as twice the levels in the table. Thus, the average content of toluene in recycled HDPE may be as high as 1500 ppb (1.5 ppm).

1.   M. Ezrin and G. Lavigne, "Failure Analysis Using Gas Chromatography/Mass Spectroscopy", ANTEC Conf. Proceedings, 1991, 2230.
2.   M. Ezrin and G. Lavigne, "Application of Direct Dynamic Headspace GC/MS to Plastics Compositional and Failure Analysis", ANTEC Conf. Proceedings, 1992, 1717.

Typical chromatograms for volatiles are in Figures 1-3. In each case, the figure is only a portion of the overall chromatogram. Figure 1 is for the low-boiling region of a recycled HDPE dairy grade resin. Headspace temperature was 200°C for 20 minutes. Virgin and recycled resin contain benzene, toluene and xylenes, toluene having the largest peak of the three. Other low boiling compounds in the recycled resin, not present in virgin resin, are 2-butanal, 2-butanone (MEK), 3-methylfuran and others not identified. Fig. 2 is for the portion of the chromatogram of the same recycled resin as Fig. 1, using 250° C headspace temp. for 20 minutes, which includes BHT antioxidant. For quantitative purposes, 325° C is used. Figure 3 is the corresponding curve for virgin resin, showing the substantial absence of BHT.

Fig. 4 is for virgin and recycled resin using 250°C headspace temperature, 20 minutes, over the full range of GC retention time. In all four figures, the first 10 or 20 minutes of retention time is the headspace period, when the volatiles are cryofocused at the head of the column with liquid nitrogen.

The fact that as many as 100 compounds can be detected by GC needs to be put in perspective. The total weight % of such material appears to be of the order 0.1% (1000 ppm) or less and is being determined separately. A large portion of the volatiles are aliphatic hydrocarbons which are also present in virgin resin and may not be any more hazardous then the PE polymer. The actual contents of material which may be of concern, such as aromatics and BHT are in the low ppm range. When further diluted as they may be extracted into foods, the final contents in food products would be in the low ppb range.

Discussion of headspace GC/MS as an appropriate method of analysis

The advantages of this method are high sensitivity, good resolution between compounds, quantitative determination of composition, and identification of compounds by mass spectroscopy. Identification can be further established by means of reference compounds and their GC retention times. Another advantage of mass spectroscopy is that detectability of low levels of compounds that are not detected by monitoring total ions can be greatly enhanced by single ion monitoring and even further by selected ion data collection. In effect, heat is used to "extract" the volatiles for analysis by GC/MS. Extraction with solvent is a more conventional method, followed by injection of the extract into a GC or LC (liquid chromatograph). Solvent extraction suffers from serious disadvantages for analysis of low levels of compounds in recycled plastics. For example, sensitivity compared to heat extraction (headspace) is far less due to the dilution effect of solvent.

As indicated above, in accurate quantitative analysis of compounds that are difficult to remove from the host polymer with heat alone, a compromise headspace temperature is used between that which will remove most of the compound in a reasonable number of minutes, but which is not so high as to cause formation of decomposition products. Another disadvantage is that not all compounds are sufficiently volatile to be analyzed in this way. (e.g., Irganox 1010, DSTDP and calcium).

An alternate method of analysis is SFE and SFC (supercritical fluid extraction and chromatography), which use carbon dioxide for extraction and as the carrier in SFC at considerably lower temperature than in headspace GC/MS. Another option is to couple SFE and GC/MS. Possibly the aromatics can be extracted more readily and completely by SFE than by heat alone (headspace).

PHASE 2
Absorption and Removal of Model Compounds

A major concern in the processing and use of recycled plastics is the variable, and unknown, nature of the feedstock. Post-consumer and post-industrial-user waste may have been used for a variety of applications not originally intended by the manufacturer. For example, a consumer may purchase a HDPE milk jug, drink the milk, and then use the jug for the storage of waste motor oil before returning the jug and oil to their appropriate recycling bins. Instances as this may result in only a low percentage of contaminated milk jugs in the total recycling stream; however, this low percentage causes sufficient concern to prevent FDA approval of recycled post-consumer packaging containers for food grade applications.

A further problem arises when the contaminated feedstock is reprocessed, as was seen in phase one of this research. Previous studies have been concerned with the migration of monomer or processing agents from a plastic container to its contents, often food.[3] The FDA has prescribed allowable levels for monomer and processing agent content in food.[4] This type of study must be expanded to include consumer induced contamination in conjucntion with the addition of reprocessing aids.

In this phase of the research, small sections of HDPE milk jugs are "spiked" with compounds which model common household chemicals. By analyzing single contaminants in a worst case scenario of complete saturation of contaminant in HDPE, the kinetics of absorption and more importantly the kinetics of desorption by several methods can be more easily understood. With understanding of this process come the ability of the reprocessing group to more completely remove these potentially harmful substances from the recycled container.

Experimental

Compounds to be used as contaminants were chosen with the following criteria: likelihood of being found in the waste stream, relative toxicity, ease of analysis, and chemical structure. The contaminants selected for the initial sorption experiments were ethylene glycol, methyl salicylate, 2,4-dichlorophenol, and methyl stearate. They model the following common chemicals, respectively; antifreeze, oil-based household cleaners, pesticides, and brake fluid or lubricating oils. These compounds represent polar compounds, aromatics, halogens, and relatively long chain aliphatics. 2,4 - dichlorophenol and methyl stearate are solids at room temperature and therefore were dissolved in 10% by weight solutions of mixed xylenes. Xylene was also studied alone as a contaminant to determine its influence on the desorption of the solutions.

Samples were cut from HDPE jugs which were previously cleaned by hand in hot water and laboratory detergent. The average sample size was 1 x 5 cm with an average thickness of 0.4 mm. Samples were then immersed in approximately 25 ml of either of the neat contaminants or either of the solutions of contaminant in xylene for a period of 1, 4, 8,

3.   S.-S. Chang, C. M. Guttman, et al., "Theoretical and Computational Aspects of Migration of Package Components to Food, in "Food Packaging and Interactions," ACS Symposium Series 365, 1987.
4.   Plastics Recycling Task Force, Food & Drug Administration, "Points to Consider for the Use of Recycled Plastics in Food Packaging: Chemistry Considerations," May, 1992.

or 16 days. After removal, the samples were blotted dry, weighed, and analyzed with a Mattson Cygnus 100 FTIR spectrometer in the transmission mode. Each sample was then left in open air to give the contaminant an opportunity for desorption. Weight measurements and FTIR observations were completed each day to monitor the desorption of the contaminant with time for a period of 7 days.

In order to quantify the desorption process by FTIR, peaks characteristic of the contaminant and of the HDPE milk jug were determined and ratioed. Figure 5 is an example of the desorption of methyl salicylate with time (0, 1 and 7 days) as measured with FTIR. The extinction coefficients were calculated by FTIR liquid cell measurements using several dilute solutions of each contaminant in heptane. The sample thickness was an average of several thicknesses measured along the length of each sample. Concentration was then calculated using the familiar Beer's law.

Mass desorption is depicted in Figure 6 as percent change in mass. This is a ratio of the change in mass to the initial mass before absorption.

Results and Discussion

The ethylene glycol samples showed little to no absorption within the accuracy of the analysis techniques. This was likely due to the high polarity of the ethylene glycol with respect to the HDPE. No further measurements will be made with the ethylene glycol as a contaminant.

The remaining three contaminant systems were found to reach an equilibrium sorption within the first 24 to 96 hours of immersion in contaminant by mass uptake measurements and headspace GC. Figures 6 and 7 represent typical desorptions for each of the three contaminants. In the case of desorption monitoring by mass loss, the amount of xylene desorbing from the solutions can not be separated from the total mass loss. For this reason, FTIR is a particularly useful technique for monitoring the change in concentration of the contaminant with time. Characteristic peaks can be found to represent the xylene and contaminant separately. Monitoring of each peak allows for the effect of one on the other to be determined, as well as the concentration of the contaminant alone to be calculated. FTIR also provides a rapid method of analysis so that inaccuracy with respect to time fluctuations is reduced.

To further explore the effect of xylene on the desorption, it was considered as a contaminant. HDPE samples immersed in xylene were found to lose the majority of any mass gained within a period of two days. This appears to be the case also with the xylene in conjunction with methyl stearate. The long aliphatic chain present in the methyl stearate, as might be expected, favors the HDPE rather than staying in solution with the xylene.

Future Work

Preliminary work has been performed to determine the effect of temperature on desorption rates. Work is also under way to model the washing procedure of industry and to determine the amount of

contaminant which is being removed in a simple wash. This area will be expanded to include complete reprocessing of small batches of laboratory "spiked" samples.

The types and numbers of chemicals used for the "spiking" procedure will also be expanded to better represent the large number of compounds which may be present as contaminants. Combinations of contaminants will also be studied to attempt to better model the large and varied chemicals already identified as a potential hazard from phase one of the research.

The ultimate goal of the work is to determine categories of chemicals which are difficult to remove under current washing procedures and to offer suggestions for changes in current industry procedures which could enhance contaminant removal during washing and reprocessing.

Table 1

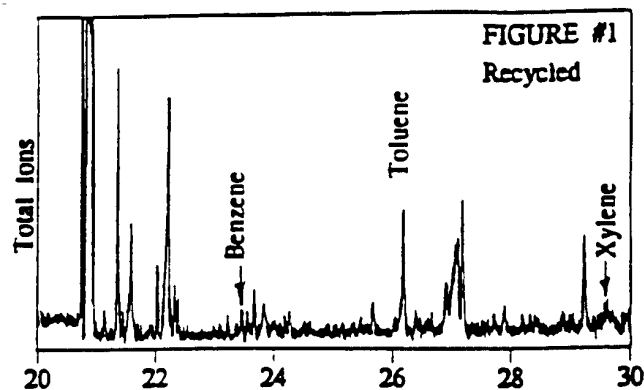| | Parts per billion (ppb) | | | ppm |
	Benzene	Toluene	Xylenes	BHT
Virgin				
#1	58, 38	88, 85	38, 36	0.3
#2	62, 70	94, 99	85, 92	0.6
avg.	57	92	63	0.45
Recycled				
#1	220, 210	700, 700	625, 540	33.5
#2	355, 345	900, 750	550, 400	15
avg.	283	763	529	24

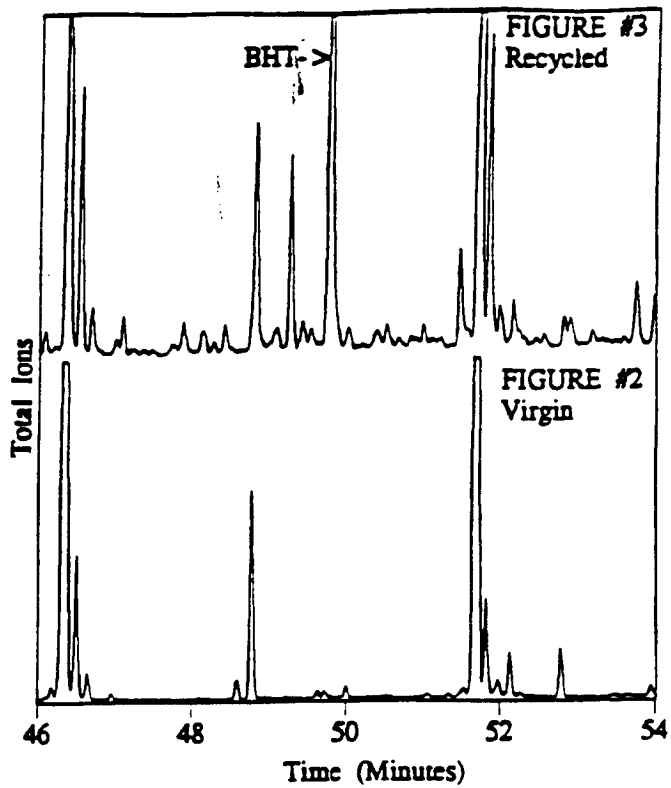Fig. 1. Low retention time portion of GC of recycled HDPE. X-axis: minutes.

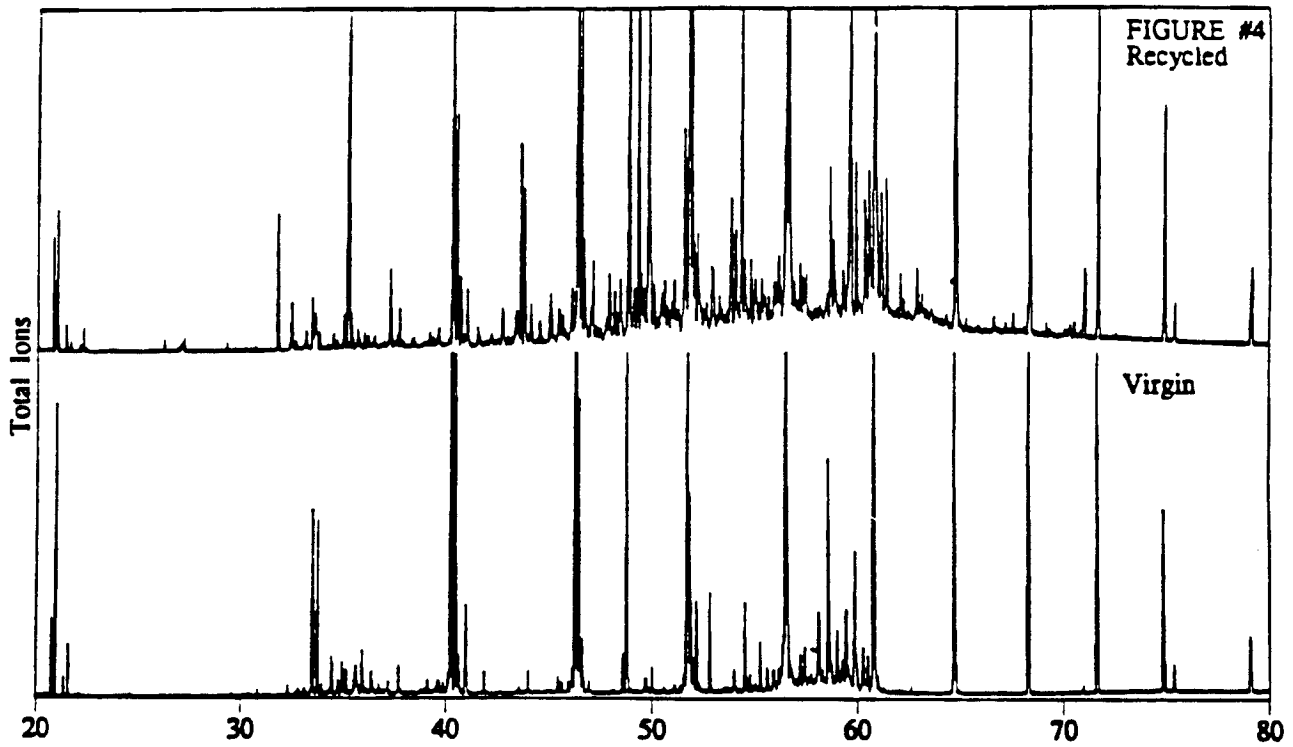Fig. 2.3. GC of virgin and recycled HDPE showing BHT.

Fig. 4. GC of virgin and recycled HDPE over full range of retention time. X axis: minutes.
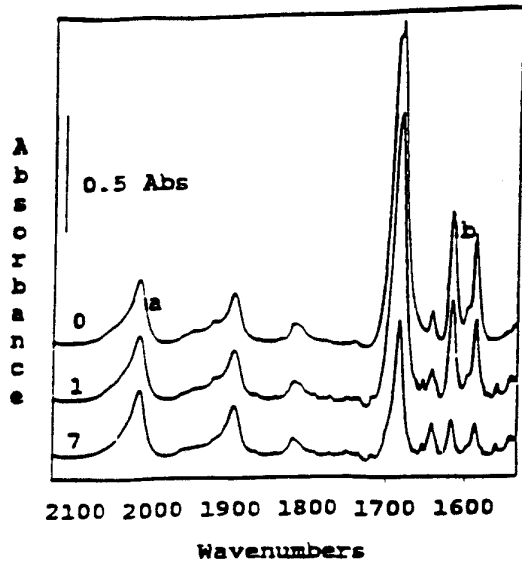
Figure 5: FTIR spectra of reference (a) and characteristic (b)
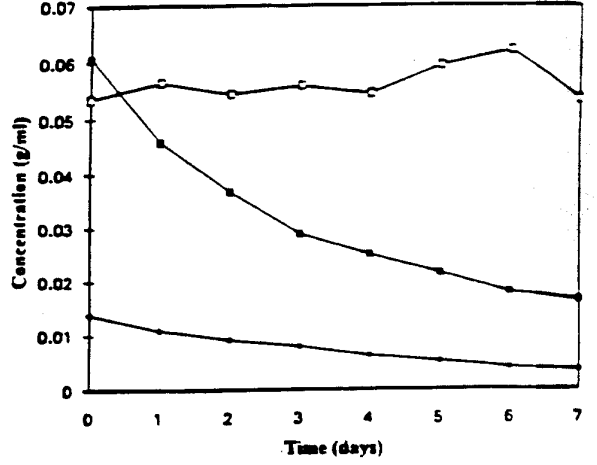peaks for methyl salicylate desorption from a HDPE milk jug.

Figure 7: Open air desorption of contaminants as measured by
FTIR spectroscopy. —■— Methyl Salicylate —□— Methyl
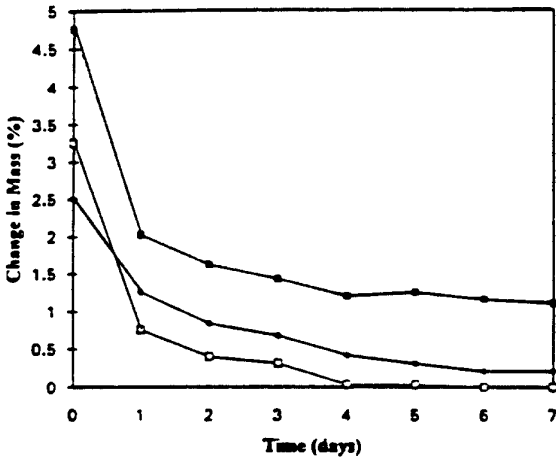Stearate —◆— 2,4-Dichlorophenol

Figure 6: Open air desorption of contaminants as measured by
mass change. —■— Methyl Stearate —□—2,4-Dichlorophenol
—◆— Methyl Salicylate