

Acetaldehyde Scavengers and Their Effects on Thermal Stability and Physical Properties of Poly(ethylene terephthalate)

Brent A. Mrozinski, Elizabeth A. Lofgren, Saleh A. Jabarin

Polymer Institute and Department of Chemical and Environmental Engineering, University of Toledo, Ohio 43606-3390

Received 7 April 2011; accepted 22 September 2011

DOI 10.1002/app.36287

Published online 19 January 2012 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The acetaldehyde (AA) scavenging abilities of poly(ethylene terephthalate) (PET) blends containing various concentrations of anthranilamide, meta-xylenediamine (MXDA), or alpha-cyclodextrin have been evaluated. It was found that higher AA scavenger concentrations generally resulted in greater reductions in detectable AA in terms of both the AA generation rates and residual AA contents. As little as 100 ppm, by weight, of anthranilamide and MXDA were respectively shown to reduce residual AA detected in PET preforms by 46% and 36%. Melt-blending 500 ppm of alpha-cyclodextrin, into PET, reduced preform residual AA concentration by 42%.

The scavengers acted as PET nucleating agents causing more rapid crystallization while heating the blends from the glassy state and when cooling from the melt; however, they caused no changes in the glass transitions, melting characteristics, or oxygen permeation behaviors of the blends. Addition of optimal scavenger concentrations had minimal effects on preform intrinsic viscosity and color changes. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2010–2021, 2012

Key words: poly(ethylene terephthalate) (PET); acetaldehyde; acetaldehyde scavengers

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a packaging material commonly used by the food and beverage industry; therefore, its thermal stability has been studied by many investigators.^{1–13} Some of these studies have placed emphasis on the generation of acetaldehyde (AA). The presence of AA within PET articles is of concern because it has a boiling point at or below room temperature (21°C).¹⁴ This low temperature volatility will allow it to diffuse from the PET into either the atmosphere or any product within the container. Diffusion of AA into most products should be minimized, since the inherent taste/odor of AA is known to affect flavors of some packaged beverages and foods.¹⁵

There are several reported approaches for reducing amounts of AA generated during the melting and processing of PET. One approach is to optimize the processing conditions under which PET containers are manufactured. These variables, which include melting temperature, residence time, and shear rate, have been shown to strongly affect the generation of AA.⁵ A second approach is the use of

PET resins which have been specially tailored to minimize the generation of AA during container manufacturing. These resins are more commonly known as “water grade PET resins”.¹⁶ A third approach is the use of additives known as acetaldehyde scavenging agents.

AA scavengers are designed to interact with any AA that is generated during the processing of PET.¹⁷ These scavengers do not reduce PET degradation or acetaldehyde formation. They can; however, limit the amount of AA that is able to diffuse out of a container and thus reduce any effects upon the packaged contents. Interactions of scavenging agents with AA are postulated to occur according to three different mechanisms, depending upon the molecular structure of the specific scavenger. The first type of scavenging mechanism is a chemical reaction. In this case the AA and the scavenging agent react to form a chemical bond, creating at least one new product. In the second type of scavenging mechanism an inclusion complex is formed. This occurs when AA enters the internal cavity of the scavenging agent and is held in place by hydrogen bonding, resulting in a complex of two distinct molecules connected by means of secondary chemical bonds.¹⁷ The third type of scavenging mechanism includes the conversion of AA into another chemical species through its interaction with a catalyst.^{18–21} Conversion of AA into a different chemical, such as acetic acid, can increase the migrant’s boiling point and

Correspondence to: Saleh A. Jabarin (saleh.jabarin@utoledo.edu).

thus reduce its ability to alter the flavor of the packaged food or beverage.

The development of AA scavengers for PET has been pursued within the industry, with much advancement reported in patent literature.^{19–21} The general purpose of this research is to study specific AA scavengers by determining the relationships among thermal stability as indicated by AA generation, the mechanisms of the chemical reactions, the nature of the scavenging system, and to establish a modeling method to predict the relationships between the scavengers and the process of injection molding PET preforms. In this work (Part I) the purpose is to evaluate and compare anthranilamide, meta-xylenediamine (MXDA), and alpha-cyclodextrin as acetaldehyde scavenging agents and to comprehensively identify the effects of blending various levels each of these additives with PET. This includes characterizing changes in measured AA generation rates, detected residual acetaldehyde in PET resins and preforms, changes in melt viscosity (molecular weight), thermal properties, color, and oxygen permeation. In subsequent papers the mechanism of the scavenging system will be presented and discussed in terms of chemical reactions and AA enclosure (Part II), while an additional paper (Part III), will present a predictive model that relates experimental results to AA contents in multicavity injection molded preforms.

EXPERIMENTAL

Materials

The acetaldehyde (AA) scavenging capabilities of three materials were evaluated. Anthranilamide was purchased from Sigma-Aldrich; meta-xylenediamine (MXDA) was donated by Mitsubishi Gas Chemical America; and alpha-cyclodextrin was supplied by the Wacker Chemical Corporation. The poly(ethylene terephthalate) (PET) resin used in these evaluations was Voridian CB12. This carbonated soft drink (CSD) grade resin, produced by Eastman Chemical, is an IPA modified (2 wt %) copolyester with an initial intrinsic viscosity (I.V.) of 0.84 dL/g and a peak melting temperature of 255°C. This copolymer will henceforth be referred to as PET.

Processing conditions

The melt-blending of the AA scavengers into PET resin was performed by means of a Werner and Pfleiderer ZSK-30 twin-screw extruder, operating at 300 revolutions per minute (rpm) and 280°C. During blending, nitrogen gas was purged into the throat of the extruder to displace any oxygen, creating an inert environment for PET melting and processing. A vacuum pump was attached to the barrel of the

extruder and was used to remove any volatile chemicals generated during PET processing.

Experimental samples were prepared by melt-blending each of the three scavenging agents with the PET resin. For each of these agents, an AA scavenger/PET blend or “master-batch” sample was initially extruded. Additional concentrations of each AA scavenger/PET blend system were then made by diluting the appropriate “master-batch” blend. For these blends, a specific amount of the “master-batch” sample was re-extruded with a known amount of virgin PET. For comparative purposes, pure PET control samples were prepared under equivalent extrusion conditions.

Prior to extrusion, all PET samples were dried for 8 h at 150°C in a Conair Franklin desiccant hopper/dryer or a small vacuum oven. This step was taken to limit the presence of moisture and thus minimize the effect of hydrolytic degradation during extrusion. To further prevent hydrolytic degradation the solid anthranilamide and alpha-cyclodextrin scavengers were dried under vacuum at 80°C for 8 h before being extruded with PET. The MXDA is a viscous liquid at room temperature. It was, therefore, pumped into the twin-screw extruder at a predetermined rate without additional treatment.

Weight loss experiments were conducted for each extruded scavenger/PET blend system in order to investigate the relative volatilities of the scavengers from the blends. For these evaluations, the scavengers were each combined with PET through twin-screw extrusion blending to obtain 1 wt % samples. Three portions of each blend, as well as control (virgin) PET samples, were weighed into aluminum pans and held in an oven at 300°C for 6 h. After being cooled to room temperature, they were reweighed. No measurable weight-loss was observed among these samples, indicating that scavenger concentrations would remain constant during processing. In addition to the gravimetric measurements, an attempt was made to quantify scavenger concentrations with ¹H-NMR. Levels present in the blends were too low to give accurate results; however, even when using a 600 MHz instrument.

Injection molded preforms, designed for 2-L bottles, were prepared with an Arburg 320S machine. This single cavity injection molder has a 55-ton capacity and a reciprocating screw. The injection pressure was set at 1500 bar and the cooling time was 10 s. The processing temperature was controlled to be 280°C, with a nozzle temperature of 290°C. While processing PET, temperatures at least 20°C above the final melting temperature are generally required in order to completely melt highly crystalline solid state polymerized resin.

In preparation for injection molding, two concentrations of each AA scavenger were prepared.

Specified amounts of each previously extruded, melt-blended, pelletized, AA scavenger/PET "master batch" blend were dry-blended with virgin PET. Each dry-blended sample was then dried overnight, at 150°C, in a Conair Franklin hopper/drier. After drying, a transfer pipe from the Conair Franklin drier was attached to the throat of the injection molder for automated resin loading. A PET resin control sample was also prepared by a similar process.

For each sample set, the first 10 preforms were discarded; allowing the machine to reach a steady-state until sample collecting began. Once the machine reached steady-state, 20 samples were collected and immediately placed in a freezer. This was to prevent any acetaldehyde from diffusing from the PET preforms. The remaining preforms were set aside to be stretch-blow-molded into 2-L bottles.

The prepared preforms were blow molded into 2-L bottles through a process that heated each PET preform (10–20°C) above its glass transition temperature (T_g). Temperature control was provided by exposure to the infrared radiation of 12 quartz lamps, each rated at 1600 watts; with peak filament temperatures of 2200 K at 240 V. Heater zone profile, stretch rod pressure, and blow pressure conditions were optimized to yield the best bottle appearance.

Characterization

In order to determine apparent AA generation rates at melting temperatures and simulate heating conditions that would occur during processing, PET and the various scavenger blends were evaluated in a manner previously described by Kim and Jabarin.⁴ Measurements were made with a Perkin-Elmer automatic thermal desorption system (ATD 400) coupled to a Perkin-Elmer auto system XL gas chromatograph (GC), equipped with a flame ionization detector (FID) and utilizing a 30 m × 0.32 mm ID Stabilwax®-DA (carbowax) capillary column. The GC column was maintained at 60°C and the FID at 300°C. The system utilized helium as a purge gas and was calibrated with a standard solution of known AA concentration, treated in a manner similar to that of the samples. Concentrations of AA were calculated as µg AA/g PET or ppm.

Resin samples were vacuum dried overnight at 120°C before evaluation. For each determination, two pellets (with a combined weight of 0.03 ± 0.01 g) were placed in a cylindrical Teflon sample chamber in which they were separated by quartz wool. This packed tube was placed in a metal sample tube and heated in the ATD 400 for times from 9 to 17 min, at temperatures of 280, 290, or 300°C. Three measurements were performed for each material at each experimental condition. AA generation rates (k)

were established at these temperatures and used for determination of activation energies (E_A) by means of the Arrhenius equation.

$$k = A \times e^{\left(\frac{-E_A}{RT}\right)} \quad (1)$$

Detected levels of residual acetaldehyde in resin and preform samples were measured using a Perkin-Elmer TurboMatrix 40 (TM 40) headspace sampler coupled with the previously described Perkin-Elmer AutoSystem XL gas chromatograph. All samples were stored in a freezer and ground under liquid nitrogen to prevent volatilization of the AA prior to analysis. A Tekmar grinder was used to prepare the ground material that was separated using sieves to provide 20 mesh particles for analysis. Ground PET samples of 0.3 ± 0.1 g were weighed to five decimal places in glass sample vials, which were immediately capped and sealed. Each sample was heated in the (TM 40) for 60 min at 150°C and 18 psi in order to volatilize the residual AA present within the sample for analysis by GC. Measurements were performed in triplicate.

Melt viscosity measurements were performed with a Rheometric Scientific (RDA III) viscoelastic tester using parallel plate geometry, a frequency sweep from 1 to 100 rad/s, and a gap between the plates of 1 mm. Samples were vacuum dried at 140°C for 8 h before being evaluated at a temperature of 280°C in the presence of a nitrogen purge to avoid oxidation. Melt viscosity values taken at 10 rad/s were converted to PET equivalent intrinsic viscosity (I.V.) values according to the method described by Tharmapuram and Jabarin.²²

Pellet color changes resulting from processing and/or the AA scavengers were analyzed by means of a Hunter Lab Color/Difference Meter D25-2, calibrated using standard color plates. Response from the instrument yields lightness (L), red [+]/green [–] (a), and yellow [+]/blue [–] (b) values for each sample. These values were then converted to Y , $X\%$, and $Z\%$ values; and used to calculate a yellowness index (YI) according to ASTM D 1925.²³

$$YI = \frac{(125 \times (X\% - Z\%))}{Y} \quad (2)$$

Thermal properties of the PET and the various scavenger blends were monitored with a Perkin Elmer (DSC-7) differential scanning calorimeter, calibrated with indium and zinc standards. Samples of about 10 mg were heated and cooled at 10°C per minute, in a nitrogen environment to prevent oxidative degradation. Crystallization and melting characteristics as well glass transition temperatures were evaluated. Prior to thermal analysis, samples were vacuum dried overnight at 120°C. Each sample was

heated to 300°C, held for 5 min to remove all of its inherent crystallinity, and then rapidly quenched to 40°C creating a completely amorphous sample. It was then reheated from the glassy state to record the glass transition temperature (T_g), crystallization and melting behavior. Crystallization behavior was also recorded while cooling from the melt.

The oxygen permeation rates of PET and the various scavenger blends were studied by means of a coulometric method, similar to the one described in ASTM Procedure D 3985.²⁴ Evaluations were performed at 1 atmosphere, 23°C, and 50% relative humidity using a MoCon OxTran 1050 permeability tester. Samples from sidewalls of stretch blow molded bottles were cut into 10.2 cm × 10.2 cm (4 inch × 4 inch) squares. Two samples of each material were analyzed and their average thickness values were calculated from thicknesses measured at nine evenly distributed points using a Magna-Mike® 8500. Samples were placed in chambers of the MoCon analyzer and conditioned for at least 12 h before being evaluated. During measurement, the permeation cell was flushed with oxygen gas on one side and nitrogen carrier gas on the other. The flow rates of the oxygen and nitrogen were both maintained at 25 cm³/min.

RESULTS AND DISCUSSION

Effectiveness of AA scavengers in reducing the detected amount of AA

Two gas chromatography techniques were used to study the relative efficiencies of the anthranilamide, alpha-cyclodextrin, and meta-xylenediamine (MXDA) scavengers in terms of reducing detectable AA concentrations in PET. An ATD 400 was used to establish apparent AA generation rates, while a TM 40 was used to quantify the residual AA concentrations after both extrusion and injection molding of samples. All AA scavenger/PET blend results have been compared to similarly prepared PET control samples.

Rates of detected AA generation were obtained under isothermal conditions of 280, 290, and 300°C, with heating times from 9 to 17 minutes at each temperature. As an example, Figure 1 shows AA generation rates determined for a 1200 ppm anthranilamide/PET blend sample. All data points represent at least three determinations at the indicated conditions, with standard deviations shown by error bars. Slopes of data collected at each temperature yield AA generation rates. The AA generation rate of this sample at 280°C is around 1.0 ppm/min. Increasing the temperature by 10°C raises the rate to about 1.9 ppm/min. At 300°C, the AA generation rate for this sample is 3.0 ppm/min. This trend indicates that increasing the melting or processing temperature of

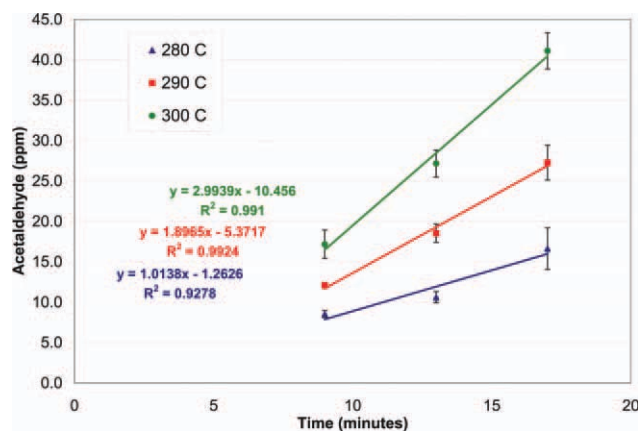


Figure 1 AA generation plots for the 1200 ppm anthranilamide/PET blend. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PET increases the rate of degradation within the polymer.

Plots similar to Figure 1 were prepared for virgin PET, the extruded PET control, and the various AA scavenger/PET blends. The general trend observed among these samples is that as the concentration of the AA scavenger is increased, there is a decrease in the apparent rate of detected AA at the various generation conditions. This behavior is illustrated by Figures 2–4, with the error bars representing standard errors calculated during linear regressions. These plots show the AA generation rates as functions of scavenger concentrations and temperatures for the respective anthranilamide, alpha-cyclodextrin, and MXDA blend samples. These three figures all indicate, that at some point, the AA generation rates become independent of scavenger concentration, and the slopes of the plots approach zero. In the case of MXDA, this appears to occur around 1,200 ppm, for anthranilamide between 1,200 ppm and 10,000 ppm, and for alpha-cyclodextrin the slope flattens in the region of 10,000 ppm. It is believed that the differences among these values are related to the molecular structures and interaction mechanisms of these scavenging agents.

Another common feature, among these figures, is the noticeable increase in the AA generation rate for lower concentrations of each scavenging agent at 280 and 290°C. This apparent anomaly can be observed in the case of anthranilamide concentrations between 0 and 500 ppm, alpha-cyclodextrin concentrations between 0 and 1200 ppm, and MXDA concentrations between 0 and 200 ppm. This behavior can be explained in terms of the following sample preparation process.

Step 1. A “master-batch” sample was prepared by twin-screw extrusion of a known amount of an AA scavenger with a known amount of virgin PET resin.

Step 2. Additional samples were generated by diluting the “master-batch” sample, made in Step 1, with additional virgin PET resin.

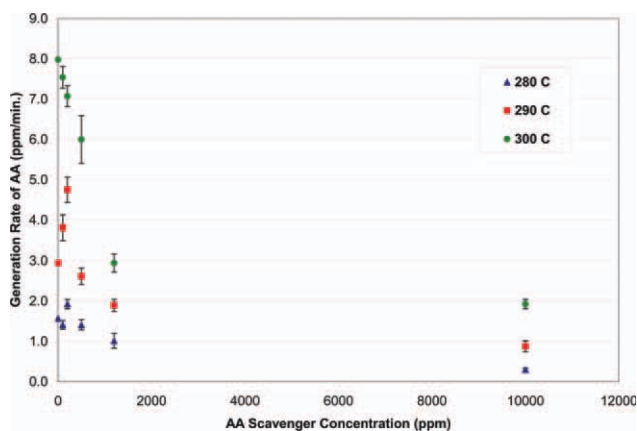


Figure 2 AA generation rates plotted as functions of anthranilamide concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Step 3. The very dilute AA scavenger/PET blend concentrations were produced by diluting a second “master-batch” sample (made in Step 2) with additional virgin PET resin.

The intent of this methodology was to help create more homogeneity within the least concentrated AA scavenger/PET blend samples. While this process may have minimized the variability and created more uniform AA scavenger dispersions, it also increased the thermal histories within these PET blends. As an example, examination of the 500 ppm alpha-cyclodextrin/PET blend sample reveals that it contains portions that have been processed up to three times:

- Extruded once: the virgin PET resin added to dilute the 1 weight % blend to the desired 500 ppm concentration.
- Extruded twice: the virgin resin melt-blended with the 5 wt % master-batch sample to yield

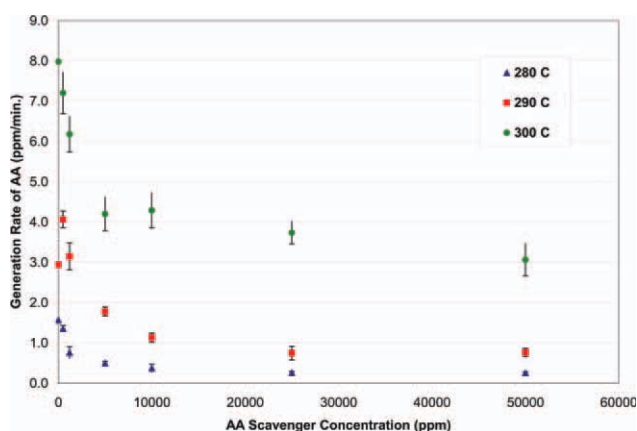


Figure 3 AA generation rates plotted as functions of alpha-cyclodextrin concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

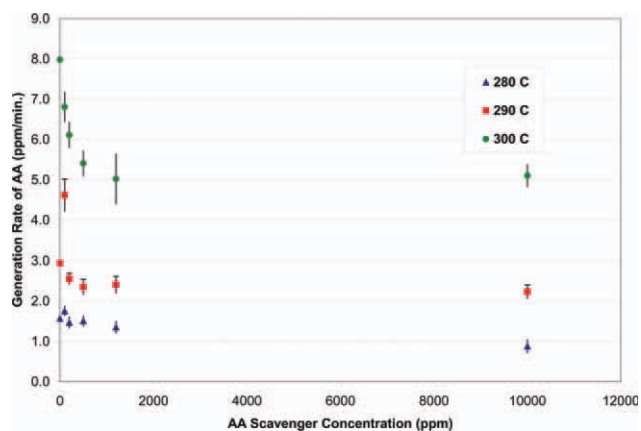


Figure 4 AA generation rates plotted as functions of MXDA concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

an overall alpha-cyclodextrin concentration of 1 wt %.

- Extruded three times: the 5 wt % master-batch sample that was extruded with virgin resin to dilute the blend’s alpha-cyclodextrin concentration to 1 wt % blend.

Table I gives detailed thermal history examples for the various alpha-cyclodextrin/PET blend samples. It shows how much of each sample was extruded one, two, and three times to achieve the desired AA scavenger concentrations. This table also shows thermal histories for the various anthranilamide/PET and MXDA/PET blend samples.

It is known that increasing a PET sample’s thermal history will also increase its amount of degradation, and consequently the AA concentration. To simulate this effect, a portion of once processed PET control sample was re-extruded to establish a twice processed control. A portion of this sample was then extruded again to produce a three times processed control. The AA generation rates of these three PET control samples are reported in Table II. It can be seen that as the thermal history of the PET sample increases, so does its AA generation rate. These results indicate that the initial increase in the AA generation rates of the lowest concentrated samples resulted from thermal history imparted by the sample preparation methodology.

Comparisons among these three scavengers reveal that in terms of weight/weight concentration, anthranilamide is the most efficient at reducing the apparent rate of AA generation. At the 1200 and 10,000 ppm addition levels, the anthranilamide/PET blend samples have lower AA generation rates than the alpha-cyclodextrin or MXDA samples. Anthranilamide (136.15 g/mol),²⁵ however, has about one-seventh the molecular weight of alpha-cyclodextrin (972.402 g/mol).²⁶ Since the concentration of these

TABLE I
The Thermal History for Each Scavenger/PET Blend

Scavenger type	Scavenger concentration in PET		Percentage of processed material		
	Weight %	ppm	1x	2x	3x
Anthranilamide	1.00	10,000	100.00	–	–
	0.12	1200	88.00	12.00	–
	0.05	500	95.00	5.00	–
	0.02	200	83.33	14.67	2.00
	0.01	100	91.67	7.33	1.00
Alpha-Cyclodextrin	5.0	50,000	100.00	–	–
	2.5	25,000	50.00	50.00	–
	1.0	10,000	80.00	20.00	–
	0.5	5000	90.00	10.00	–
	0.12	1200	88.00	9.60	2.40
	0.05	500	95.00	4.00	1.00
MXDA	1.00	10,000	100.00	–	–
	0.12	1200	88.00	12.00	–
	0.05	500	95.00	5.00	–
	0.02	200	83.33	14.67	2.00
	0.01	100	91.67	7.33	1.00

AA scavengers in PET is based upon weight, and not on the number of moles present, anthranilamide should be about seven times more effective as an AA scavenger than alpha-cyclodextrin. This was not observed.

When the molecular weights and the functionalities of the scavengers are taken into consideration, alpha-cyclodextrin is actually the most efficient at reducing the generation of AA. This is because at equivalent ppm concentrations, the numbers of moles of alpha-cyclodextrin are one-seventh those of anthranilamide or MXDA (136.2 g/mol).²⁷ Neither anthranilamide nor MXDA were shown to be seven times more efficient at scavenging AA than alpha-cyclodextrin. Since both MXDA and anthranilamide have approximately the same molecular weights, their chemical structures or functionalities determine the next most efficient scavenger. The two terminal amine groups make it theoretically possible for MXDA to react with two molecules of AA; making it di-functional. Anthranilamide, however, can only react with one molecule of AA. This implies that MXDA could be twice as effective as anthranilamide. This was not observed, indicating that anthranilamide is the second most efficient agent at sequestering AA, followed by MXDA as the least efficient of

the three additives. The reaction of an amine and carboxylic acid, to produce an amide with water as a by-product, has been documented.²⁸ It is thus possible for MXDA to react with carboxylic ends of the PET chains, during melting and processing. If this occurs, each reaction would consume an AA scavenger site, causing MXDA to be less effective than anthranilamide, as was observed.

Rates of AA generated at the different temperatures were used to calculate activation energies by means of Arrhenius plots. Table III gives these values for the PET and AA scavenger/PET blend

TABLE III
Activation Energies

Sample	Number of processing times	Scavenger concentration (ppm)	Activation energy (kJ/mol)
Virgin PET resin	0	–	277
Extruded PET (Control)	1	–	216
	2	–	196
	3	–	165
Anthranilamide blends	–	100	221
	–	200	172
	–	500	189
	–	1200	155
	–	10,000	244
Alpha-Cyclodextrin blends	–	500	220
	–	1200	267
	–	5000	281
	–	10,000	324
	–	25,000	347
	–	50,000	327
MXDA blends	–	100	179
	–	200	188
	–	500	166
	–	1200	173
	–	10,000	233

TABLE II
AA Generation Rates of Control Samples

Sample	Number of processing times	AA generation rate (ppm/min)		
		280°C	290°C	300°C
Extruded PET	1	1.6	2.9	8.1
	2	1.8	3.5	8.2
	3	2.5	3.9	8.9

TABLE IV
Residual AA and I.V. Values for Pelletized Samples

Sample	Number of processing times	Scavenger concentration (ppm)	Residual AA (ppm)	AA reduction (%)	I.V. (dL/g)	I.V. reduction (%)
PET resin	0	–	0.8	–	0.80	–
Extruded PET (control)	1	–	8.9	–	0.78	2.5
	2	–	13.5	–	0.69	13.8
	3	–	14.5	–	0.65	18.8
Anthranilamide Blends	–	100	5.2	41.6	0.67	16.3
	–	200	3.5	60.7	0.68	15.0
	–	500	3.0	66.3	0.68	15.0
	–	1200	1.0	88.8	0.66	17.5
	–	10,000	–	–	0.51	36.3
Alpha-Cyclodextrin Blends	–	500	5.0	43.8	0.73	8.8
	–	1200	3.3	62.9	0.71	11.3
	–	5000	2.8	68.5	0.58	27.5
	–	10,000	2.6	70.8	0.54	32.5
	–	25,000	2.8	68.5	0.46	42.5
MXDA Blends	–	50,000	2.6	70.8	0.40	50.0
	–	100	4.1	53.9	0.68	15.0
	–	200	3.3	62.9	0.67	16.3
	–	500	3.6	59.6	0.70	12.5
	–	1200	3.4	61.8	0.68	15.0
–	10,000	2.8	68.5	0.34	57.5	

samples. According to these data, the anthranilamide and MXDA blends possess similar activation energies; with the exception of the 100 ppm samples. The similarity in values is attributed to the fact that both anthranilamide and MXDA scavenge AA by similar mechanisms. In comparison, Table III shows that similarly concentrated alpha-cyclodextrin samples generally have higher activation energies. Alpha-cyclodextrin sequesters AA by a mechanism that is completely different from those of anthranilamide and MXDA. This indicates that the activation energy (which corresponds to the generation of AA) is a function of the interaction method by which AA is scavenged. It is also shown that the activation energies generally increase with the higher scavenger concentrations, indicating that the greater the concentration of the scavenging agent the more likely generated AA will be prevented from diffusing out of the polymer.

In addition to characterizing effects of AA scavengers on acetaldehyde generation rates of PET blends, their effects on measured residual AA concentrations were also evaluated. Table IV shows residual AA concentrations obtained for the various pelletized AA scavenger/PET blends and control samples. The effectiveness of each blend sample, in terms of reducing levels of measured residual AA, has been quantified relative to the one-time processed PET control. It can be seen that residual AA results support trends observed for AA generation rates. As the concentration of AA scavenging agent increases, the percent reduction of AA also generally increases. These results also indicate that levels of

residual AA increase with increasing thermal history. The virgin PET resin has an initial residual AA concentration of less than 1 ppm. Processing this resin once increases its residual AA content to 8.9 ppm. Processing this resin second and then third times respectively increases AA concentrations to 13.5 and 14.5 ppm.

Six of the AA scavenger/PET blends and a control sample, were injection molded into preforms for evaluation in terms of their residual AA contents. Results given in Table V indicate that the respective scavenging agents reduced levels of detectable residual AA. This table also confirms that higher levels of scavenging agent give greater reductions in detectable residual AA. These blend samples have also been quantified relative to a PET control sample.

Effects of AA scavengers on intrinsic viscosity (I.V.)

Intrinsic viscosities (I.V.) were measured in terms of melt viscosity, for each of the previously described blend samples. These IV values, as well as % reduction comparisons to PET resin, with various processing histories, are given on Table IV. These data indicate that increasing scavenger concentrations result in decreasing I.V. values; however, scavenger concentrations are not the only causes for the observed reductions.

As previously described, the AA scavenger/PET blends are composed of portions that have been extruded up to three times. It can be seen on Table IV, that one pass through the twin-screw extruder

TABLE V
Residual AA and I.V. Values for Preform Samples

Sample	Preform scavenger concentration (ppm)	Preform residual AA (ppm)	Preform AA reduction (%)	Preform I.V. (dL/g)	Preform I.V. reduction (%)	Pellet I.V. (dL/g)
PET	–	8.3	–	0.76	–	0.78
Anthranilamide	100	4.5	45.8	0.78	–	0.67
Blends	200	3.7	55.4	0.78	–	0.68
Alpha-Cyclodextrin	500	4.8	42.2	0.73	3.9	0.73
Blends	1200	4.7	43.4	0.70	7.9	0.71
MXDA	100	5.3	36.1	0.77	–	0.68
Blends	200	4.6	44.6	0.76	–	0.67

degrades PET resin enough to reduce the I.V. by 2.5%. Second and third passes through the extruder further reduce the I.V. by 13.8% and 18.8%, respectively. Samples containing AA scavenger exhibit significantly more loss of IV than the PET controls. One of the lowest I.V. (0.34 dL/g) values belongs to the 1 wt % (or 10,000 ppm) MXDA/PET blend sample, with only one processing history. These results indicate that the loss in each sample's I.V. is due to a combination of both the addition of scavenging agents and the sample blending method.

Melt viscosity measurements were also performed on the PET control sample and AA scavenger/PET blends that had been injection molded into preforms. The purpose of this work was to isolate the effect of AA scavenger addition on I.V. by minimizing thermal history differences among the samples. The blending process used to prepare these preforms was designed to provide samples with equivalent thermal histories and involved AA scavenger/PET "master batch" blends with single previous processing histories and virgin PET resin. Table V, shows the results from these measurements. This table also includes values for pelletized samples with similar scavenger concentrations (but multiple thermal histories) presented in Table IV.

Data given in Table V reveal that additions of 100 and 200 ppm of anthranilamide or MXDA do not further reduce the I.V. values of these preforms, in comparison to the control PET sample. The alpha-cyclodextrin samples; however, exhibit small additional reductions in I.V., with the 500 ppm and 1200 ppm alpha-cyclodextrin samples respectively showing 4 and 8% reductions. One reason these samples have lower I.V. values than the others is that they contain additional levels of scavenger. Examples of these reductions are shown for the pellet samples in Table IV. In addition, when 500 ppm and 1200 ppm of anthranilamide or MXDA are melt-blended into PET, the viscosities of these AA scavenger/PET blend samples are lower than those of the 500 ppm and 1200 ppm alpha-cyclodextrin/PET blend samples. These results indicate that it may be possible to

add low levels of AA scavenging agents, without reducing the final I.V. of the product.

Comparisons of the previously described pellet I.V. data with those of the preforms (with reduced thermal exposures) illustrate the importance thermal history on I.V. loss as well as AA production. For the anthranilamide samples, the preform I.V. is 0.11 dL/g greater than that of the pellets. The same trend is true for the MXDA samples; this time, however, the difference in I.V. is 0.09 dL/g. There are two reasons for the disparities seen between pelletized and preform I.V. results. The first reason, as previously mentioned, is that the preform samples have less thermal history than the pelletized samples. The second reason is due to the mechanisms by which anthranilamide and MXDA each scavenge AA. For each of these reactions, between anthranilamide and AA and between MXDA and AA, water forms as a byproduct. It is well known that the presence of water decreases the I.V. of PET. Since the pelletized samples have more thermal history than the preform samples, there is greater chance for more reactions with AA and that residual water will be present in these samples. In the case of alpha-cyclodextrin, preform, and pellet I.V. values are more similar. These data indicate that additional levels of alpha-cyclodextrin melt-blended into PET play prominent roles in their I.V. values.

Color changes resulting from AA scavenger addition

Color changes resulting from processing and/or AA scavenger additive additions were quantified by determining the *L*, *a*, *b*, and yellow index (*YI*) values for the PET and AA scavenger/PET blends. These results are shown in Table VI. It can be seen that processing PET without AA scavenger greatly affects the *b* and the yellowness index values. As the number of passes through the twin-screw extruder increases, these two values also increase. The virgin PET resin, which had not been processed, has a *b* value of -2.3 and a *YI* of -7.2 ; while, the values for

TABLE VI
L, a, and b Values and Yellowness Index of Pelletized Samples

Sample	Number of Processing Times	Scavenger Concentration (ppm)	Averaged Values			Yellowness Index (YI)
			<i>L</i>	<i>a</i>	<i>b</i>	
PET resin	0	–	74.8	–1.8	–2.3	–7.2
Extruded PET	1	–	68.5	–0.4	0.7	1.4
	2	–	71.5	–0.4	4.0	9.5
	3	–	71.2	–0.4	5.6	13.7
Anthranilamide Blends	–	100	66.2	–10.0	2.4	–4.3
	–	200	69.9	–10.3	3.0	–2.9
	–	500	73.6	–7.2	7.4	11.0
	–	1200	72.6	–7.6	6.8	9.3
	–	10,000	68.5	–8.9	8.2	12.1
MXDA Blends	–	100	69.0	–11.4	3.3	–3.3
	–	200	69.0	–11.7	4.8	0.4
	–	500	73.5	–7.6	11.4	20.3
	–	1200	71.7	–9.4	14.6	27.0
	–	10,000	68.9	–10.8	11.6	18.8

the one-time processed sample are 0.7 and 1.4, respectively. A second and third pass through the extruder further increase these values. The results for all the PET samples containing alpha-cyclodextrin are not included because these samples all exhibited some brownness and the prominence of this color alters the *L*, *a*, *b*, and *YI* values.

For the anthranilamide/PET and MXDA/PET blends shown in Table VI, it can be seen that both the *b* and *YI* values increase with increased scavenger concentration. For both of these blends; however, changes in *YI* were minimal when the scavenger concentrations were below 500 ppm. At 100 and 200 ppm levels for these scavengers, their *b* values are higher, but their *YI* value are lower than that of the PET control sample that was extruded once.

These results were also confirmed by the physical appearance of 2-liter bottles that were stretch-blow-molded from the previously discussed PET preforms. Figure 5 shows a representative sample for each of the 500 and 1200 ppm alpha-cyclodextrin/PET blends, the 100 and 200 ppm MXDA/PET blends, the 100 and 200 ppm anthranilamide/PET blends, and pure PET resin. Similar to the results from color analysis of the pellets, the two MXDA/PET blends and the two anthranilamide/PET blends are indistinguishable in appearance from that of the pure PET bottle. The brownish tint of the alpha-cyclodextrin bottles; however, can be observed, relative to the other bottles.

Thermal properties of AA scavenger blends

The thermal properties of PET and its various scavenger blends were evaluated at heating and cooling rates of 10°C per minute in order to determine if any changes in behavior resulted from addition of the of AA scavengers. Table VII gives results obtained for these samples, heated from the glassy

state and cooled from the melt. It can be seen that no significant changes in glass transition (T_g) or melting behaviors occurred. Their rates of crystallization, however, increased in the presence of the AA scavengers. This can be observed as lower temperature crystallization peaks (T_{peak}) in the case of samples reheated from the glassy state. As the AA scavenger concentrations increase, peak crystallization temperatures decrease, indicating that the AA scavengers may act as nucleating agents. Their heats of crystallization (ΔH) and peak minus onset of peak ($T_{peak} - T_{onset}$) temperatures, that indicate how quickly a sample will crystallize, show changes similar to that of the extruded PET. In a few cases heats of crystallization are smaller than would be expected, probably because the samples crystallized to some extent while being quenched from the melt.

Crystallization behaviors, recorded for samples cooled from the melt, show trends similar to those described for the heated samples. As the AA scavenger concentration is increased, peak crystallization temperatures also increase, indicating faster rates of crystallization. Most of these samples also exhibit



Figure 5 Two-liter blow-molded PET bottles (from Left to Right: 1200 ppm alpha-cyclodextrin, 500 ppm alpha-cyclodextrin, 200 ppm MXDA, 100 ppm MXDA, 200 ppm anthranilamide, 100 ppm anthranilamide, pure PET). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VII
Thermal Properties of PET and Scavenger/PET Blends

Sample	Scavenger concentration (ppm)	Heating from the glassy state						Cooling from the melt	
		T_g (°C)	Crystallization			Melting		Crystallization	
			T_{peak} (°C)	ΔH (J/g)	$T_{peak} - T_{onset}$ (°C)	T_{peak} (°C)	ΔH (J/g)	T_{peak} (°C)	ΔH (J/g)
PET Resin	–	78	168	–18	27	223	17	166	–5
Extruded PET	–	79	160	–33	15	229	31	162	–15
Anthranilamide Blends	100	78	155	–34	13	231	32	162	–25
	200	77	152	–32	13	227	34	167	–25
	500	78	149	–31	11	226	32	161	–15
	1200	77	147	–32	11	228	36	166	–28
	10,000	78	150	–33	11	231	35	170	–20
Alpha-Cyclodextrin Blends	500	79	158	–33	12	229	31	156	–15
	1200	79	153	–33	12	230	32	167	–24
	5000	78	149	–34	10	232	35	172	–29
	10,000	76	144	–36	10	232	39	176	–33
	25,000	77	141	–44	10	234	45	185	–44
	50,000	76	137	–22	14	234	46	191	–45
MXDA Blends	100	78	156	–32	12	229	28	161	–17
	200	79	153	–33	13	230	31	167	–25
	500	79	155	–34	12	230	32	161	–13
	1200	79	151	–33	11	229	33	162	–17
	10,000	78	151	–37	14	228	34	188	–26

higher ΔH values than either the virgin or extruded PET. The observed faster rates of crystallization indicate that the AA scavengers may act as nucleating agents in PET.

Oxygen permeation properties of AA scavengers in PET films

In order to determine if the presence of AA scavenging agents in PET would affect its oxygen barrier properties, sidewall samples of selected bottles were evaluated. Samples were cut from sidewalls of 2-L bottles of the 500 and 1200 ppm alpha-cyclodextrin/PET blends, the 100 and 200 ppm MXDA/PET blends, the 100 and 200 ppm anthranilamide/PET blends, and pure PET resin. The data in Table VIII show that these three AA scavenging agents are not detrimental to the oxygen barrier properties of PET.

CONCLUSIONS

The overall effects of melt-blending three acetaldehyde (AA) scavengers into poly(ethylene terephthalate) have been comprehensively studied. The ability of anthranilamide, MXDA, and alpha-cyclodextrin to reduce measured AA in PET were evaluated by two techniques; one to quantify the apparent rate of AA generation and the other to determine the concentration of AA that remains residually trapped in the polymer's matrix. The results from both of these techniques indicate that in general as the concentration of the AA scavenger increases, the amount of detectable AA decreases. Beyond just reducing measurable AA in PET, the addition of anthranilamide, MXDA, and alpha-cyclodextrin were also assessed to determine their effects upon the physical properties and appearance of PET. These properties included: intrinsic viscosity (I.V.), color, thermal

TABLE VIII
Oxygen Film Permeability

Scavenger/sample	Concentration (ppm)	Oxygen permeability $\left(\frac{cc \times STP \times mil}{100in^2 \times day \times atmospheres} \right)$
PET	–	5.3
Anthranilamide	100	5.3
	200	5.2
Alpha-Cyclodextrin	500	5.3
	1200	5.1
MXDA	100	5.6
	200	5.4

properties, and oxygen permeation. Determining any changes in these properties was critical to understanding the overall benefit of adding these AA scavenging agents to PET. The following are specific conclusions resulting from this work.

1. The pelletized (twin-screw extruded) AA scavenger/PET blend and PET control samples, were melt-blended to obtain good dispersions within the PET. This process, however, created samples with various thermal histories. Multiple passes through the twin-screw extruder were shown to increase AA generation rates, residual AA concentrations, and color; while decreasing sample I.V.
2. As concentrations of each AA scavenger were increased, it was observed that generation rates of detectable AA became independent of scavenger concentrations. For anthranilamide and MXDA, this occurs around 1200 ppm. In the case of alpha-cyclodextrin the slope flattens in the region of 10,000 ppm. These differences appear to result from their molecular structures and interaction mechanisms.
3. Increased AA scavenger concentrations result in corresponding reductions in levels of detectable AA for both the pelletized samples and injection molded preforms. As little as 100 ppm of anthranilamide and MXDA were shown to respectively reduce detected residual AA concentrations in PET preforms by 46% and 36%, while 500 ppm of alpha-cyclodextrin reduced residual AA by 42%.
4. When molecular weights and functionalities are considered, alpha-cyclodextrin is the most efficient scavenger for reducing detectable levels of AA in PET. This is because for an equivalent ppm (weight) concentration, the number of moles of alpha-cyclodextrin (972.402 g/mol) is about one-seventh those of anthranilamide (136.15 g/mol) or MXDA (136.2 g/mol). Anthranilamide is the second most efficient scavenger at sequestering AA. The MXDA had the potential to be twice as efficient as anthranilamide, because of its di-functionality with two primary, terminal amines; however, this was not observed.
5. The alpha-cyclodextrin, anthranilamide, and MXDA scavengers added to PET appeared to act as nucleating agents, causing increased rates of crystallization, while heating from the glassy state and cooling from the melt.
6. Oxygen barrier properties were not affected by the addition of alpha-cyclodextrin, anthranilamide, or MXDA AA scavengers to PET.
7. Processes for melt-blending alpha-cyclodextrin, anthranilamide, and MXDA scavengers into

PET were found to reduce intrinsic viscosity values. In the case of pelletized samples, the I.V. loss appeared to be influenced by thermal history. The preforms were injection molded with equivalent and minimized thermal histories. Addition of 500 ppm and 1200 ppm alpha-cyclodextrin resulted in respective 4% and 8% reductions in preform I.V., while the addition of 100 ppm and 200 ppm of anthranilamide or MXDA did not alter preform I.V.

8. Preform and bottle samples containing 500 and 1200 ppm alpha-cyclodextrin/PET blends exhibited slightly brownish appearances. At levels of 100 and 200 ppm both anthranilamide and MXDA were used to produce 2-L bottles that were indistinguishable in appearance from equivalent PET bottles.

The authors gratefully acknowledge the members of the PET Industrial Research Consortium who have supported this research at the Polymer Institute of the University of Toledo.

References

1. Jabarin, S. A. In Salamone, J. C., Ed.; *Polymeric Materials Encyclopedia*, CRC Press: Boca Raton, FL, 1996, p 6078.
2. Rieckmann, T.; Volker, S. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; Scheirs, J.; Long, T. E., Eds.; Wiley: West Sussex, England, 2003; p 31.
3. Al-AbudulRazzak, S.; Lofgren, E. A.; Jabarin, S. A. *Polym Int* 2002, 51, 174.
4. Kim, T. Y.; Jabarin, S. A. *J Appl Polym Sci* 2003, 89, 228.
5. Shukla, S. R.; Lofgren, E. A.; Jabarin, S. A. *Polym Int* 2005, 54, 946.
6. Massy, S.; Cloutier, P.; Sanche, L.; Roy, D. *Radiat Phys Chem* 2008, 77, 889.
7. Urbanova, M.; Subrt, J.; Galikova, A.; Pola, J. *Polym Degrad Stab* 2006, 91, 2318.
8. Dollimore, D.; Gamlen, G. A.; Jeffries, M.; Shah, T. H. *Thermochim Acta* 1983, 6, 97.
9. Khemani, K. C. *Polym Degrad Stab* 2000, 67, 91.
10. Montaudo, G.; Puglisi, C. *Dev Polym Degrad* 1987, 7, 48.
11. Marshal, I.; Todd, A. *Trans Faraday Soc* 1953, 49, 67.
12. Riche, P. D.; Roy, C. *Soc Chem Ind (London)* 1961, 13, 107.
13. Buxbaum, L. H. *Angewandte Chemie, Int Ed English* 1968, 7, 182.
14. *Material Safety Data Sheet - Acetaldehyde, 99.5%*, Fisher Scientific 2005.
15. Van Aardt, M.; Duncan, S. E.; Bourne, D. Marcy, J. E.; Long, T. E.; Hackney, C. R.; Heisey, C. *J Agricultural Food Chem* 2001, 49, 1377.
16. *Controlling AA in Mineral Water Bottles*, in PETplanet, publisher GmbH, Landhausstr, 4, 69115 Heidelberg, Germany 2003, issue 1.
17. Suloff, E. C. *Sorption Behavior of an Aliphatic Series of Aldehydes in the Presence of Poly(ethylene terephthalate) Blends Containing Aldehyde Scavenging Agents* 2002, Thesis, Virginia Polytechnic Institute and State University, Blacksburg.
18. Go, S. W.; Burzynski, D. J. *Polyester Stabilization and Composition* 1982, Owens-Illinois, Inc., U.S. Patent 4,357,461.
19. Rule, M. *Process for Reduction of Acetaldehyde and Oxygen in Beverages Contained in Polyester-Based Packaging* 2001, The Coca-Cola Company, WO 2001/030900 A1 (Patent application).

20. Rule, M. Process for Reduction of Acetaldehyde and Oxygen in Beverages Contained in Polyester-Based Packaging 2002, The Coca-Cola Company, U.S. Patent 6,569,479.
21. Rule, M.; Shi, Y. Polyester Composition and Articles with Reduced Acetaldehyde Content and Method Using Hydrogenation Catalyst 2006, The Coca-Cola Company, U.S. Patent 7,041,350.
22. Tharnapuram S. R.; Jabarin, S. A. *Adv Polym Technol* 2003, 22, 137.
23. ASTM, Method D 1925 - Test Method for Yellowness Index of Plastics, 1988.
24. ASTM Method D 3985 - Standard Test Method for Oxygen Gas Transmission Rate Through Film and Sheeting Using a Coulometric Sensor, 1981.
25. Material Safety Data Sheet - Anthranilamide, 99+%. Fisher Scientific, 2005.
26. Material Safety Data Sheet - Alpha-Cyclodextrin, Fisher Scientific, 2005.
27. Material Safety Data Sheet- MXDA. Mitsubishi Gas Chemical Company, Inc., 2005.
28. Fox, M. A.; Whitesell, J. K. *Organic Chemistry*, 2nd ed.; Jones and Bartlett Publishers: Sudbury, MA, 1997.