

Decolorization of Colored Poly(ethylene terephthalate) Bottle Flakes Using Hydrogen Peroxide

Mohit Gupta,¹ Suneel A. Bandi,¹ Sanjay Mehta,² David A. Schiraldi¹

¹Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, Ohio 44106-7202

²INVISTA, Spartanburg, South Carolina 29307

Received 3 April 2006; accepted 3 November 2006

DOI 10.1002/app.27468

Published online 27 November 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A novel process for the oxidative decolorization of green and blue colored poly(ethylene terephthalate) (PET) bottle flakes, using an aqueous solution of hydrogen peroxide (H₂O₂) has been developed. A strong dependence of H₂O₂ concentration and temperature on decolorization rate has been found. The decolorized flakes were characterized for color and intrinsic viscosity (IV) values; decolorized flakes exhibit color values similar to those of colorless recycled PET. The IV of peroxide bleached PET flakes indicated a decrease in PET molecular weight, which correlated with the severity of decolorization conditions. Despite

decreases in PET IV values, the bleached flake still exhibited useful PET molecular weights. The consumption of H₂O₂ during the bleaching process was quantified titrating residual peroxide with a standardized potassium permanganate solution. H₂O₂ consumption rates of 0.3–0.9 g per gram of green PET flake were measured, depending on the specific bleaching conditions used. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 3212–3220, 2008

Key words: poly(ethylene terephthalate); hydrogen peroxide; oxidation; decolorization; recycling

INTRODUCTION

Poly(ethylene terephthalate) (PET) has become a dominant commercial polymer for use in food and beverage packaging over the past generation due to its high barrier properties and relatively low price. PET also possesses good thermal and mechanical properties, high chemical resistance, clarity, and processibility, which has resulted in its increasing use as an engineering plastic in automotive parts, industrial strapping, fiberfill, and as a fabric material. The recycling of PET has received considerable attention, as many applications lend themselves well to the use of postconsumer recycle as their partial or complete feedstock.^{1–7} Color represents a limitation to the use of recycled PET, often requiring expensive manual sorting of colorless bottles from the green, blue, and other colors associated with many brands of water and carbonated soft drinks, or leading to black products in which mixed colors are obscured by the addition of pigment. This limitation leads to an imbalance between the supply and demand for colored recycle bottle flakes, resulting in a difference in recycle flake pricing of at least 5–10 cts/lb at the

present time.⁸ This price difference represents a market opportunity, should a cost-effective process for the decolorization of green (and other) flakes be developed.

Colorants used in PET packaging include both organic dyes and inorganic pigments, with organic dyes most commonly belonging to the phthalocyanine and anthraquinone families.^{9,10} Previous work carried out in this field demonstrate the use of chemical processing steps, such as glycolysis or methanolysis, for the depolymerization of PET flakes, followed by repolymerization of the constituent monomers/oligomers^{6,7} as well as the use of highly toxic and expensive reagents, such as a 1,1,1,3,3,3-hexafluoroisopropanol solution containing silica gel as an absorbent, or extraction of colorants from the polymer in hot dichloromethane.^{11–13} Such processes tend to be expensive and generate significant quantities of hazardous waste, and to date have not been successful in the marketplace. Hydrogen peroxide (H₂O₂) could represent a more economical, lower toxicity reagent for the decolorization of colored PET flake; peroxide is used extensively as an oxidant for a wide range of organic and inorganic oxidations at the present time.¹⁴ Few references to the utilization of H₂O₂ for decolorization of PET resins exist, being primarily focused on bleaching of yellow catalysts residues generated from titanium catalysts.¹⁵ The current work details the potential use of H₂O₂ for oxidative decolorization of green- and blue-colored PET flakes.

Correspondence to: D. A. Schiraldi (david.schiraldi@case.edu).

Contract grant sponsor: INVISTA (Spartanburg, SC).

Journal of Applied Polymer Science, Vol. 107, 3212–3220 (2008)
© 2007 Wiley Periodicals, Inc.

EXPERIMENTAL

Safety Note: concentrated H₂O₂ can decompose rapidly, generating a potentially explosive pressurization. Such bleaching experiments as are described in this work should be carried out only after careful planning, which should include adequate provisions for pressure relief. Bleaching experiments should be carried out with proper operator safeguards in place.

Materials

The PET flake particles used were cut by hand from the bottle side walls of different brands (7UP[®], Sprite[®], Canada dry[®] gingerale, Sierra Mist[®], and Mountain Dew[®]) of green-colored PET soda bottles and from a poly(vinyl chloride) (PVC) mouthwash bottle (Act[™]) all purchased from a local grocery store. Flakes were washed thoroughly with running water and dried at 50°C under vacuum for 24 h before being used. Colorless postconsumer recycled PET flakes, purchased from the recycle market, were provided by INVISTA (Spartanburg SC, USA) and were used as received. A green colorant for PET (CT PET Green 521 dye) was provided by Milliken Chemicals (Spartanburg SC, USA) and was used as received. 30 wt % and 50 wt % aqueous solution of H₂O₂, 0.2N potassium permanganate (KMnO₄) solution and concentrated sulphuric acid were purchased from Fisher Chemicals and used as received. A Fisher–Porter bottle (a high pressure reaction vessel) having a capacity of 12 oz. and maximum operating pressure of 75 psi was purchased from Cole Parmer and was modified with a stainless steel pressure relief valve (operating pressure range of 20–225 psi) purchased from Swagelok; the pressure relief was manually set to 45 psi prior to use of the reactor for bleaching experiments.

Decolorization experiments

Initial open and closed vial decolorization experiments used 10 mL of 30 or 50 wt % H₂O₂ and one green soda bottle flake (ca. 1 × 1 cm²) added to each vial. The vials were then immersed in an oil bath over a range of (95–140°C) temperatures.

Initial Fisher–Porter bottle experiments made use of 25 g of PET flakes and 125 g of either 30 or 50 wt % H₂O₂. The reactor vessel was held in an oil bath at a fixed temperature for the indicated times. When sampling, the reactor was raised out of the oil bath, pressure vented, and then ca. 10–12 g of flakes were removed with a small aliquot of liquid. The flakes, after thorough washing with water and vacuum drying for 24 h, were shipped to INVISTA[®] for color and IV measurements. The aliquot of liquid was titrated against KMnO₄ to measure H₂O₂ concentration.

Other set of Fisher–Porter experiments for quantification of H₂O₂ used 30 g of H₂O₂ solution, with 3–9 g of PET flakes. This lower reactor loading, combined with a 45 psi pressure relief valve, was designed to enhance experimental safety.

A 500 ppm solution of the green dye from Milliken Chemicals was prepared by dissolving 11 mg of the dye in 22 g of 50 wt % H₂O₂ solution. This solution was then further used to prepare 25, 50, 100, 200, and 250 ppm solutions of the dye in 50 wt % H₂O₂. The solutions so prepared were left standing at room temperature until decolorized. Depending upon their concentration the solutions were decolorized in times ranging from 12 h to 4 days. The H₂O₂ consumed was determined by carrying titrations in the same manner as that performed for polymer flakes.

Melt blending

Commercial colorless recycled flakes and decolorized bottle flakes were melt blended in 80/20 wt/wt ratio. The melt blends were produced using a DACA twin screw mini extruder with a 4 g feed shot operating at a 270°C/4 min residence time. The flakes were dried at 100°C under vacuum for 24 h prior to extrusion.

Thermal properties

A Mettler Toledo DSC model 822e/700 differential scanning calorimeter (DSC) was used to measure the thermal properties of the blended samples. All the samples were first dried at 100°C under vacuum for 24 h prior to thermal analysis. DSC was performed under a nitrogen flow over the temperature range 20–280°C (5–6 mg sample sizes; 10°C min⁻¹ scan rate). The samples were heated to 280°C and held at 280°C for 1 min to remove any previous thermal history, cooled to 20°C, held there for 1 min (i.e. first cooling), then finally heated again to 280°C (i.e. second heating).

H₂O₂ concentration determination

H₂O₂ concentrations were determined by a titration procedure.¹⁶ An appropriate aliquot of H₂O₂ sample (~ 2 g) was transferred to a tared weighing bottle and the weight was noted. The sample was then washed carefully into a 250 mL volumetric flask with distilled water and diluted to the volume mark and mixed thoroughly. A 25 mL aliquot of this solution was then transferred using a graduated cylinder to a 500 mL beaker containing 250 mL of distilled water and 10 mL of concentrated sulfuric acid. Titration to first permanent pink color with a standard 0.2N KMnO₄ solution was carried out and volume

TABLE I
Open and Closed Vial Tests; 30 wt % H₂O₂/130°C

Temperature oil bath (°C)	7UP	Sierra mist	Canada dry	Sprite	Mountain dew
Open vial 130	50 min	50 min	80 min	100 min	100 min
Closed vial 130	No considerable decolorization (2 h)				

was recorded. Commercial 30 wt % and 50 wt % H₂O₂ samples routinely and reproducibly were measured to contain their advertised concentrations to within $\pm 1\%$ by this method. The wt % of H₂O₂ was determined using the following equation:

% H₂O₂ by weight = mL of KMnO₄ \times 0.2 \times 1.701 \times 10/g of H₂O₂ sample used; weight per milliequivalent of H₂O₂ \times 100; 10 = dilution factor. Blank titrations for baseline H₂O₂ consumption measurements were carried out by adding 30 g of 50 wt % H₂O₂ solution to a Fisher-Porter bottle (no flakes present). The H₂O₂ concentration was determined as is described above.

Intrinsic viscosity

Intrinsic viscosity (IV) was determined by dissolving 0.2 g of the polymer with 20 mL of dichloroacetic acid (DCA) at a temperature of 76.5°C for 40 min. The solutions were cooled and placed in an Ubbelohde viscometer in a constant temperature bath at 25°C for 30 min prior to the measurement of the drop time, which is compared to that of the pure DCA to determine the relative viscosity (RV). RV was converted to IV using the ISO certificated equation: $IV = [(RV - 1) \times 0.6907] + 0.0631$.¹⁷

Color measurement

Color of bottle flakes was measured with a Hunter Lab ColorQuest II instrument. D65 illuminant was used with a CIE 1964 10° standard observer and is reported using the CIELAB color scale, L^* is a measure of brightness, a^* is a measure of redness (+) or greenness (-), and b^* is a measure of yellowness (+) or blueness (-).¹⁸

PVC separation from PET

Experiments on PET/PVC separation work were carried out using either 10 or 20 mL of 50 wt % H₂O₂ solution with 5 flakes each of PVC and PET (7UP or Sprite) added to a vial. The vials were then immersed in an oil bath at 130°C for 1–6 h in the case of open vial experiments and 2–12 h in the case of closed vial experiments. The flakes were then removed, washed thoroughly with running water

and the transferred to an Erlenmeyer flask filled with water. The flask was shaken manually and the float/sink behavior of the flakes was noted. While those flakes which floated did so more or less immediately, samples were allowed to sit for 5 min prior to making observations. Thereafter, the flakes were dried under vacuum at 50°C for 12 h and their float/sink behavior was retested.

RESULTS AND DISCUSSION

Initial experiments: Open and closed vials

Qualitative (visual) decolorization time for open and closed vial experiments at 130°C using 30 wt % H₂O₂ are reported in Table I. For each of the different brands of soft drink bottles tested, it was found that flake decolorization proceeded more rapidly in open vial experiments than in closed vial. A difference in decolorization rates of approximately two was observed across the brands tested. Under these same conditions, little decolorization was observed when closed vials were employed for the experiments. The temperatures of H₂O₂ solutions within open vials were found to rise to ca. 120°C over the course of decolorization experiments, when heated in a 130°C oil bath. The boiling point of pure H₂O₂ is approximately 151°C¹⁹; these open vial experiments indicate that water is evaporated from the starting 30 wt % H₂O₂ solution, to produce considerably higher concentrations. Titration of the open vial H₂O₂ solutions with standardized KMnO₄ solution confirmed an increase in H₂O₂ concentrations, often reaching 70 wt % and in some cases as high as 90–95 wt % H₂O₂ after heating for several hours. To expand the time vs. oil bath temperature performance of the different commercial green bottle flakes, more decolorization experiments were carried out on a similar scale in open vials. The results are plotted in Figure 1, and show that time vs. temperature curves for different brands of bottles are parallel and show strong temperature dependencies. These data clearly shows that higher bath temperature lead to faster decolorization times. Higher bath temperature of course lead to accelerated rates of water evaporation (and ultimately higher H₂O₂ concentration), providing more driving force for the oxidation reactions. Conversely, closed vial experiments did not provide

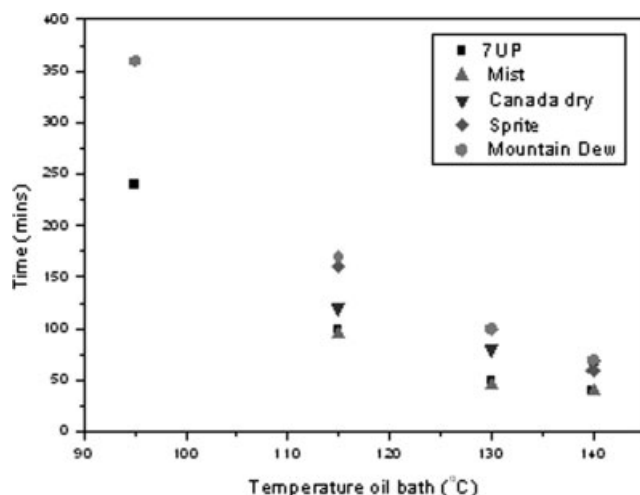


Figure 1 Decolorization time as a function of the oil bath temperature (open vial).

for increased H₂O₂ concentrations and thus longer decolorization times were required. From these initial experiments, a strong H₂O₂ concentration dependence for the PET decolorization rates was evident.

To further confirm the efficacy of highly concentrated H₂O₂ solution in decolorizing green bottle flakes, water was evaporated from a sample of 50 wt % H₂O₂ until it reached 85 wt % concentration. This highly concentrated solution was then used to decolorize samples of two green bottle sources (Sprite and 7UP). The decolorization was now found to occur rapidly and was independent of whether conducted in an open or closed vial. It should be noted that the two green bottle sources chosen for testing represented the two extremes in reactivity within the present study, which are reflected at each set of conditions tested (Table II). These results clearly show that the rate of decolorization of green PET flakes is dominated by the H₂O₂ concentration employed. As the concentration of H₂O₂ increases in bleaching experiments, so does the potential for safety problems (indeed, concentrated H₂O₂ is used as a propellant in rockets). Control of water evaporation becomes problematic in such a process, therefore it is reasonable to conclude that use of closed vessel system would be required for the large scale decolorization green color PET bottle flakes using H₂O₂ as the oxidizing agent.

TABLE II
Concentration H₂O₂ Solution ca. 85 wt %

Temperature oil bath (°C)	7UP (min)	Sprite (min)
130	10	30
105	30	75

TABLE III
Closed Vial Experiments (Qualitative Decolorization Times)

Temperature oil bath (°C)	Concentration H ₂ O ₂ (wt %)	7UP	Sprite
105	30	48 h (poor performance)	5 days (poor performance)
	50	12 h	24 h
130	30	4 h	72 h (poor performance)
	50	1.5 h	8 h

Two set of temperatures and H₂O₂ concentrations were compared in closed vial experiments before proceeding to scaled up closed vessel experiments using a Fisher–Porter bottle reactor system. The results, shown in Table III, indicate that under potentially reasonable process conditions (hours rather than days), both temperature and H₂O₂ concentration play important roles in determining decolorization rates. Under low temperature/low concentration conditions, decolorization did not proceed at “commercially viable” rates. Under the high temperature/high concentration conditions, decolorization times were short and of potential commercially utility. These same two flake sources were then carried on to experiments using Fisher–Porter bottle reactor.

Fisher–Porter bottle experiments—Larger scale

Larger scale experiments were carried out using Fisher–Porter bottles as reactors (Fig. 2). Residual H₂O₂ concentrations were determined at times when PET flake samples were removed for analysis; these values are reported in Table IV. It can be seen from the data in Table IV that H₂O₂ concentrations fell as the bleaching experiments progressed. When lower concentration (30 wt %) H₂O₂ was charged to the system, the residual concentration fell to nearly zero during the experiment. Higher residual H₂O₂ concentrations persisted when an initial 50 wt % H₂O₂ was used. Samples were removed from the reactor

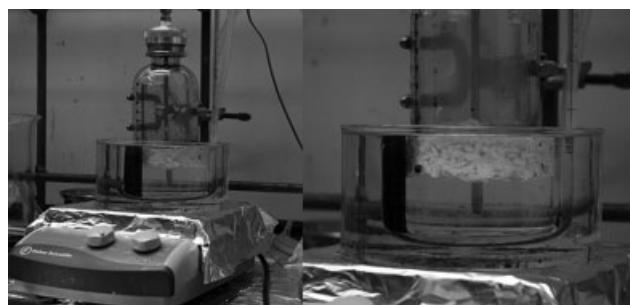


Figure 2 Fisher Porter experiments before (left) and after (right) decolorization.

TABLE IV
First Round Fisher-Porter Bottle Experiments 7UP Flakes

Temperature oil bath (°C)	Concentration H ₂ O ₂ (wt %)	Reading 1	Reading 2	Reading 3
105	30	30 h/H ₂ O ₂ conc. 5% ± 0.2%	60 h/H ₂ O ₂ conc. <1%	NA
	50	10 h/H ₂ O ₂ conc. 37% ± 1%	15 h/H ₂ O ₂ conc. 25% ± 0.8%	24 h/H ₂ O ₂ conc. 15% ± 0.5%
130	30	7 h/H ₂ O ₂ conc. 3% ± 0.1%	10 h/H ₂ O ₂ conc. <1%	NA
	50	2 h/H ₂ O ₂ conc. 45% ± 1.4%	4 h/H ₂ O ₂ conc. 38% ± 1%	NA

at indicated times and tested for color and IV (Table V). From these data it can be concluded that higher temperature and higher peroxide concentration generally accelerate bleaching of green flakes, as reflected by increased L^* (brightness), less negative a^* (reduced green color), and decreased b^* (decreased yellow color). It should also be noted that commercial green (and other) colorant packages typically include two or more dyes and/or pigments. These colorants would not be expected to have their chromophores oxidized at the same rate, so the overall path from starting bottle color to decolorized PET flake is observed to involve a change of perceived color, along with loss of color. Indeed, the green consumer bottles tested herein typically appeared to bleach first to yellow, then to white, suggesting that the blue component in the colorant package is more susceptible to oxidation than its yellow counterpart. Under severe bleaching conditions, yellow color was observed to be regenerated (increased b^*) which reflects polymer degradation.²⁰ Values of decolorized flake IV decreased with increased exposure time and temperature of the bleaching process but useful polyester molecular weights nonetheless persisted. Polyester products with IV values between 0.6–0.65 are widely used for applications in recording tape and fibers, for example.^{7,18} Should higher molecular weights be desired, solid-state polymerization of

PET could be carried out by heating the polymer to 200–220°C/12–24 h under vacuum or in a stream of nitrogen.^{7,21–23} Bleached PET IV values in the current study were found to closely correlate with color level reductions; changes in L^* and a^* each correlated well with IV drop; these findings are illustrated in Figures 3–7.

Thermal properties

The color and IV values of 80/20 wt/wt melt blend samples of commercial colorless recycled PET flakes and decolorized green color PET soda bottle flakes prepared using the DACA mini extruder are presented in Table VI. The 80/20 wt/wt blend ratio was chosen as a “worse case” commercial scenario, to exacerbate any issues that might arise from recycle of the bleached material. Color and IV values obtained for the blended samples were similar to that of colorless recycled PET showing substantial bleaching of the green color PET bottle flakes and showed rule of mixing-like behaviors. Typical DSC thermograms of the melt blended samples are shown in Figure 8, and show little difference in the polymer crystallinity or crystallization behaviors from non-bleached PET samples. Multiple melting peaks observed in during DSC thermal analysis are attributable to the distribution of crystals with different

TABLE V
Flake Color and IV Values for Decolorization at 105 and 130°C, Using Both 30 and 50 wt % H₂O₂ (7UP and Sprite flakes)

	L^*	a^*	b^*	Yellowness	Brightness	IV
7UP control	49.38	-41.86	26.78	11.9	17.8	0.840
Sprite control	42.32	-40.68	24.75	13.3	14.9	0.848
7UP flakes, 105°C/30 wt % H ₂ O ₂ /30 h	67.90	-25.09	1.36	-25.6	37.3	0.645
7UP flakes, 105°C/30 wt % H ₂ O ₂ /60 h	71.33	-23.66	2.28	-21.4	42.0	0.613
7UP flakes, 130°C/30 wt % H ₂ O ₂ /7 h	74.15	-14.68	6.65	-0.9	45.4	0.628
7UP flakes, 130°C/30 wt % H ₂ O ₂ /10 h	76.01	-13.14	7.28	2.7	51.0	0.607
7UP flakes, 105°C/50 wt % H ₂ O ₂ /10 h	78.00	-12.09	8.58	5.0	51.7	0.615
7UP flakes, 105°C/50 wt % H ₂ O ₂ /15 h	83.73	-7.97	6.41	3.89	64.2	0.541
7UP flakes, 105°C/50 wt % H ₂ O ₂ /24 h	82.16	-8.64	6.99	4.69	60.4	0.531
7UP flakes, 130°C/50 wt % H ₂ O ₂ /2 h	75.66	-10.2	9.25	7.57	49.9	0.647
7UP flakes, 130°C/50 wt % H ₂ O ₂ /4 h	79.64	-6.75	7.70	7.82	56.7	0.578
Sprite flakes, 130°C/50 wt % H ₂ O ₂ /12 h	72.56	-16.12	-1.27	-21.62	44.6	0.649
Sprite flakes, 130°C/50 wt % H ₂ O ₂ /24 h	76.97	-12.41	17.60	21.85	52.8	0.585
7UP flakes, 130°C/70 wt % H ₂ O ₂ /75 min	88.35	6.30	9.71	11.40	72.9	0.537

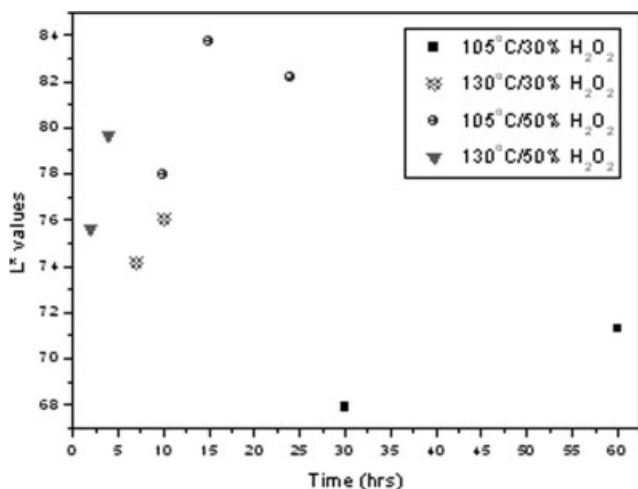


Figure 3 L* values for 7UP flakes versus time (h).

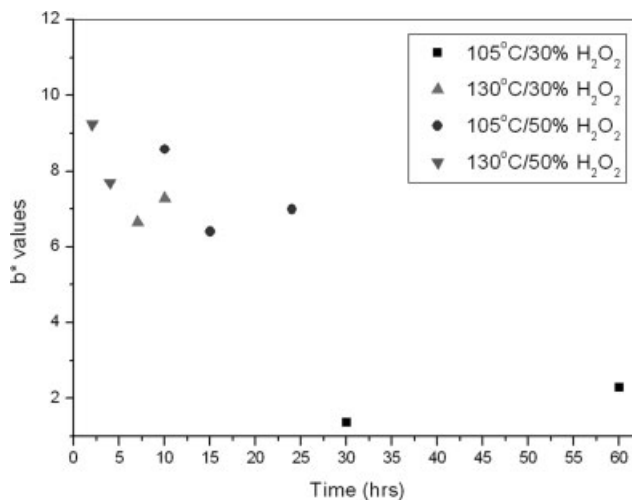


Figure 5 b* values for 7UP flakes versus time (h).

lamellar thickness, and to the melting of different crystal structure.^{5,7,23–25} Wang et al.²⁴ reported an extensive investigation into the nature of secondary crystallization in PET, and concluded that the primary and secondary crystals of PET have different melting enthalpies, which force double melting peaks. The first melting peak is attributed to the melting of secondary crystals while the second melting peak is attributed to the melting of the primary crystals. On the basis of these preliminary blend results, we see no property difference between bleached and unbleached bottle resin which would be expected to impact the commercial recycled PET stream.

Consumption of H₂O₂

Flakes

Results of peroxide consumption values are shown in Table VII. From these values it is evident that the

effect of temperature and solids to liquid ratio on H₂O₂ consumption is similar with both colorless recycled PET flakes and green color PET bottle flakes. The data show that under the similar conditions the H₂O₂ consumed per gram of colorless flakes is comparable with that of 7UP green soft drink bottles, indicating little H₂O₂ is consumed in decolorizing the green dye present in these bottles. Given that no thermal degradation of H₂O₂ in the absence of flakes was detected under similar test conditions, this suggests a second route for H₂O₂ consumption which involves the flakes exists (H₂O₂/PET system reactions). The most favorable decolorizing conditions required the highest temperatures and starting H₂O₂ concentrations employed within the study. The ratio of PET flakes to H₂O₂ within the bleaching solution had a small effect on the H₂O₂ consumption rate per unit weight of PET bleached.

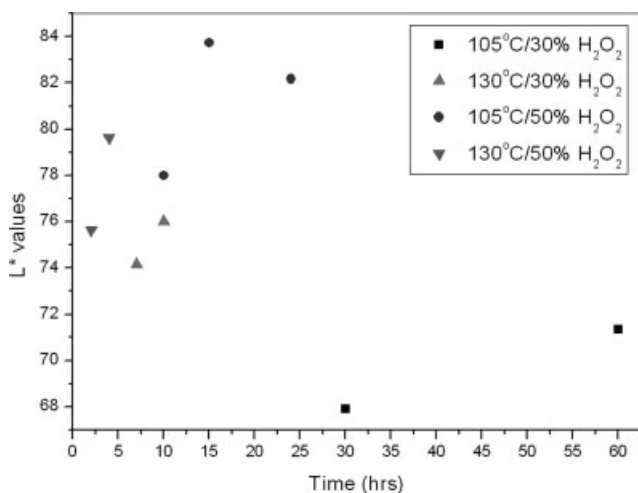


Figure 4 a* values for 7UP flakes versus time (h).

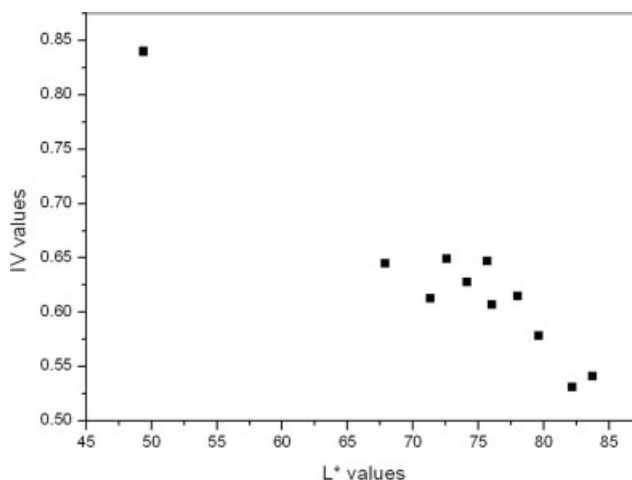


Figure 6 Plot of IV versus L* values for 7UP flakes after decolorization under different set of temperature and starting concentration of H₂O₂ solutions.

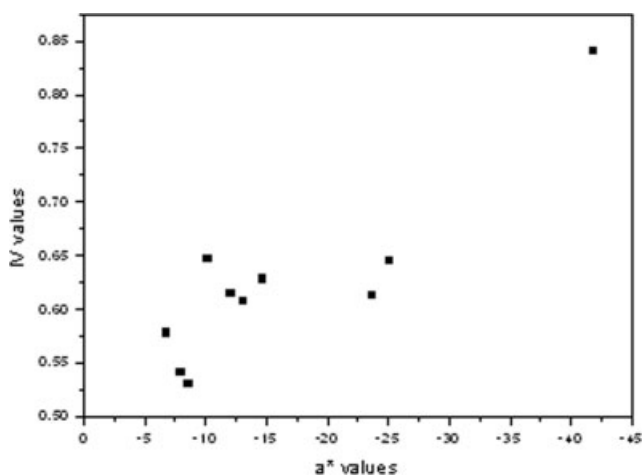


Figure 7 Plot of IV versus a^* values for 7UP flakes after decolorization under different set of temperature and starting concentration of H_2O_2 solutions.

The consumption of H_2O_2 at 10 : 1 liquid to solid ratio was found to be consistently lower than at 3.3 : 1 g peroxide/g flake.

Dyes

The results of H_2O_2 consumption for a typical green dye used in PET are shown in Figure 9. It can be seen that a considerable amount of H_2O_2 is consumed by the green dye. The H_2O_2 consumed per gram dye will of course depend upon the specific dye used with a bottle (as discussed above, different green-colored PET bottles required different bleaching times), as well as the concentration of dye employed in the polymer. Given the low overall contribution of dye to the total peroxide consumption during green flake bleaching, it can be safely concluded that extremely low dye levels are present in these commercial bottles.

Separation of PVC from PET using the H_2O_2 bleaching process

The removal of contaminants such as PVC, polyethylene and other plastics from PET is an important consideration in a commercial recycling process.

TABLE VI
Color and IV Values for the 80/20 wt/wt Melt Blends Prepared

	L^*	a^*	b^*	IV
Control-Colorless Recycled PET flakes	76.11	-0.99	2.64	0.647
80/20 Recycled/7-Up	73.89	-1.16	7.82	0.560
80/20 Recycled/Sprite	75.31	-2.71	6.01	0.595

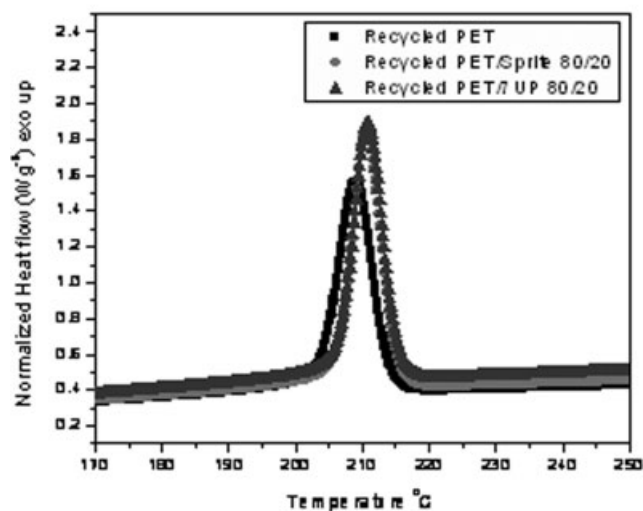
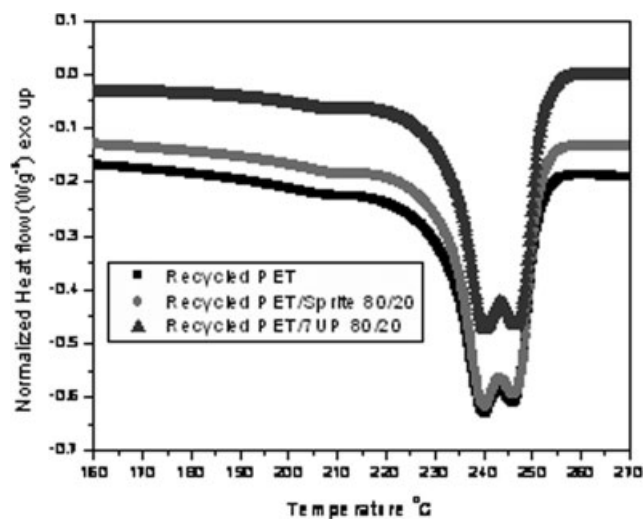


Figure 8 DSC plots for the recycled colorless/bleached PET blends.

PVC, which has a density nearly identical to that of PET, has been the one polymer present in the recycle stream that poses difficulties with current technologies. The presence of PVC within recycled PET can lead to degradation, discoloration, and equipment corrosion due to thermal generation of hydrogen chloride. Various methods for the separation of PVC and PET have been proposed²⁶⁻³⁰ which include manual separation or automatic separation such as those based on the detection of chlorine atoms²⁹ or micronyl process, which is a multistage grinding process proposed by Famechon³⁰ compete with each other on a cost basis. The fact that neither of these processes is 100% efficient and at the same time is quite expensive indicates that new separation techniques that would be more feasible to use in the industry are required. Some key results of the current PET/PVC separation work are shown in Table

TABLE VII
Summary of Hydrogen Peroxide Consumption Values

Temperature oil bath (°C)	Concentration H ₂ O ₂ (wt %)	Time (h)	Solution:Flake	H ₂ O ₂ consumption g/g		
				7UP	Colorless	Sprite
105	50	15	10 : 1	0.86	0.98	NA
105	50	15	5 : 1	0.90	0.87	NA
130	50	4	10 : 1	0.32	0.22	0.52
130	50	4	5 : 1	0.36	0.42	0.53
130	50	4	3.3 : 1	0.44	0.47	0.63

VIII. When kept for usual durations for decolorization, the PET bottle flakes did not swell sufficiently to float in water—both PET and PVC flakes sunk together. However, when kept for an extended period, PET flakes swelled/de-densified and easily floated while the PVC flakes still sunk. Broadly, it can be said that when thoroughly bleached, green PET flakes de-densify such that they float upon water while under these same conditions, clear uncolored PVC does not swell or float. Most PVC used in consumer packaging is clear/uncolored, so it is likely that a H₂O₂ bleaching step would allow operators to use float/sink separation as a means of removing any PVC contamination. When colorless PET flakes (such as from a cola bottle) was used instead of green flakes, little/no de-densification of the PET was observed, and no obvious means of separating this PET stream from PVC recommends itself. Also observed was that while wet separation of bleached PET/PVC can be accomplished by density, should these flakes be subjected to standard PET drying conditions, PVC undergoes some conversion that leads to its floating as well, and separation from PVC ceases to be possible. The

exact nature of PET “foaming” during H₂O₂ colorization is not sufficiently understood to allow for a quantitative analysis of the phenomenon. Similarly, the interactions of PVC with H₂O₂ are also ill understood.

CONCLUSIONS

A process for the oxidative decolorization of green and blue color PET bottle flakes has been developed which involves contacting those flakes with aqueous H₂O₂ (30–50 wt %, preferably 50 wt %) at temperatures in the range of 100–130°C (130°C preferred). The process requires from 2 to 15 h depending on the severity of the bleaching conditions and the specifics of the green chromophore used in the bottles. All green bottles tested were shown to bleach, with a spread of approximately twofold in rates across those commercial products. Once bleached, the PET flakes can be melt mixed with normal colorless recycled PET flakes without any major detrimental effects. PET IV does fall with degree of decolorization, but useful polyester molecular weights still persisted after bleaching. Temperatures in excess of 100°C are needed to drive the bleaching reactions at commercially viable rates. H₂O₂ consumption rates of 0.3–0.9 g H₂O₂ per gram green flake were measured running within a 355 mL closed reaction vessel. Conditions which expedite decolorization such as high initial peroxide concentration and high temperature also correspond to the lowest peroxide consumption rates observed as well. A range of liquid:solids between 3.3 : 1 and 10 : 1 in the reactor were tested, with lower solids conditions giving slightly lower peroxide consumption rates. It was also found under conditions leading to significant decolorization, bleaching process leads to a foaming or de-densification of the PET flakes. The flakes become less dense than water and can be separated from PVC contaminants by a float/sink process. Colorless PET flakes, lacking the necessary colorant with which to react H₂O₂, do not de-densify upon heating with H₂O₂, and therefore cannot be separated from PVC using this technology.

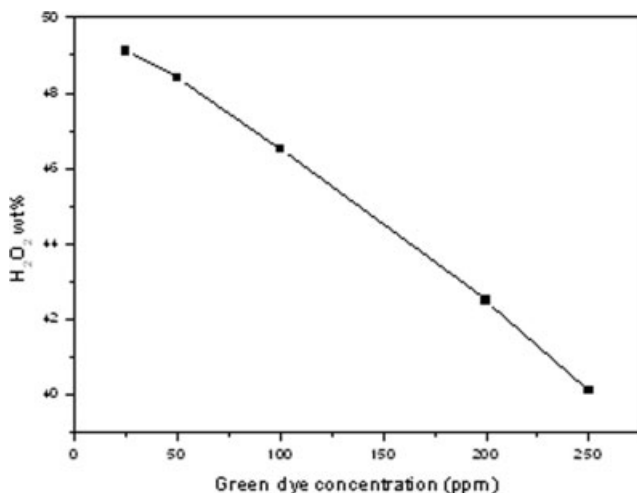


Figure 9 Final peroxide concentration versus green dye concentration.

TABLE VIII
PVC/PET Separation Results

Volume of H ₂ O ₂ solution used (mL)	Time (h)	PVC	Sprite	7UP	PVC after drying	
Open vial experiments						
10	1	Sink	NA	Sink	Sink	
	2	Sink	Sink	Float	Float	
	3	Sink	Float	Float	Float	
20	2	Sink	Sink	Float	Sink	
	3	Sink	Sink	NA	Some flakes float	
	4	Sink	Some float	NA	Float	
6	6	Sink	Float	NA	Float	
	Closed vial experiments					
	10	2	Sink	NA	Some float	Sink
4		Sink	NA	Some float	Sink	
6		Sink	NA	Float	Some float	
8		Sink	Sink	NA	Some float	
10		Sink	Some float	NA	Float	
12		Sink	Some float	NA	Float	

Sprite[®] is the registered trademark of the CocaCola Company. Canada Dry[®] gingerale and 7UP[®] are the registered trademarks of Cadbury Schweppes. Sierra Mist[®] and Mountain Dew[®] are registered trademarks of the Pepsi Company.

References

1. Sekelik, D. J.; Stepanov, E. V.; Nazarenko, S.; Schiraldi, D. A.; Hiltner, A.; Baer, E. *J Polym Sci Part B: Polym Phys* 1999, 37, 847.
2. Natu, A. A.; Lofgren, E. A.; Jabarin, S. A. *Polym Eng Sci* 2005, 45, 400.
3. Olabisi, O. *Handbook of Thermoplastics*; Marcel Dekker: New York, 1997; p 417.
4. Kulkarni, N. G.; Avadhani, C. V.; Sivaram, S. *J App Poly Sci* 2004, 91, 3720.
5. Oromiehie, A.; Mamizadeh, A. *Polym Int* 2004, 53, 728.
6. Paszun, D.; Szychaj, T. *Ind Eng Chem Res* 1997, 36, 1373.
7. Awaja, F.; Pavel, D. *Eur Polym J* 2004, 41, 1453.
8. <http://www.plasticsnews.com/subscriber/resin/price5.html>
9. Callander, D. D.; Massey, F. L. U.S. 4,365,031 (1982).
10. Tanton, R. EP 455,370 (1991).
11. Hirayama, K.; Kamaeoka, H.; Kokumara, H. *Ehime-ken Kogyokei Shiken Kenkyu Kikan Kenkyu Hokoku* 2000, 38, 19.
12. Ishii, K.; Hibino, N.; Naruo, K. JP 51,084,873 (1976). Jpn Kokai Tokkyo Koho.
13. Naruo, K.; Ishii, K. JP 51,096,871 (1976). Jpn Kokai Tokkyo Koho.
14. Lewis, S. N. *Oxidation* 1969, 213.
15. Sakamoto, J.; Yoshihiro, H.; Masatoshi, A. JP 269,602A to Toray Industries, 2004.
16. <http://www.h2o2.com/intro/highrange.html>
17. Brandup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989; Chapter VII/23.
18. Hunter, R. H.; Harold, R. W. *The Measurement of Appearance*, 2nd ed.; Wiley: New York, 1987.
19. Maass, O.; Hiebert, P. G. *J Am Chem Soc* 1924, 46, 2693.
20. Bandi, S.; Mehta, S.; Schiraldi, D. A. *Polym Degrad Stab* 2005, 88, 341.
21. Karayannidis, G. P.; Kokkalas, D. E.; Bikiaris, D. N. *J Appl Polym Sci* 1993, 50, 2135.
22. Al-Ghatta, H.; Cobror, S.; Severini, T. *Polym Adv Tech* 1997, 8, 161.
23. Karayannidis, G. P.; Kokkalas, D. E.; Bikiaris, D. N. *J Appl Polym Sci* 1995, 56, 405.
24. Wang, Z. G.; Hsiao, B. S.; Sauer, B. B.; Kampert, W. G. *Polymer* 1999, 40, 4615.
25. Tan, S.; Su, A.; Li, W.; Zhou, E. *J Polym Sci Part B: Polym Phys* 2000, 38, 53.
26. Serad, G. A.; Thornburg, T. S. U.S. 5,462,973 (1995).
27. Sisson, E. A. EP 512,464 (1992).
28. Drelich, J.; Kim, J. H.; Payne, T.; Miller, J. D.; Kobler, R. W. *Sep Purif Tech* 1999, 15, 9.
29. Gottesman, R. T. *Makromol Chem Macromol Symp* 1992, 57, 133.
30. Famechon, R. *Makromol Chem Macromol Symp* 1992, 57, 95.