Thermal Properties of Poly(ethylene terephthalate) Recovered from Municipal Solid Waste by Steam Autoclaving

Kevin M. Holtman,[1] Alice Kodama,[1] Artur P. Klamczynski,[1] Allison Flynn,[2] David V. Bozzi,[1] Lennard Torres,[2] Diana Franqui-Villanueva,[1] Jingdong Mao,[3] Gregory M. Glenn,[1] William J. Orts[1]

[1]U.S. Department of Agriculture—Pacific West Area, Agricultural Research Service, Western Regional Research Center, Bioproducts Chemistry and Engineering, 800 Buchanan Street, Albany, California 94710
[2]E. Khashoggi Industries Limited Liability Corporation, 800 Miramonte Drive, Santa Barbara, California 93109
[3]Department of Chemistry and Biochemistry, Old Dominion University, 4541 Hampton Boulevard, Norfolk, Virginia 23529

ABSTRACT: The steam autoclaving of municipal solid waste followed by size separation was shown to be a way to recover virtually 100% of recyclable poly(ethylene terephthalate) (PET); this is a yield not attainable by a typical material recovery facility. The polymer properties of the recovered PET, which had undergone various degrees of thermal processing, were evaluated by thermogravimetric analysis, differential scanning calorimetry, gel permeation chromatography, viscometry, and solid-state NMR to assess the commercial viability of polymer reuse. The weight-average molecular weight (M_w) decreased as a result of autoclaving from 61,700 g/mol for postconsumer poly(ethylene terephthalate) (pcPET) to 59,700 g/mol for autoclaved postconsumer poly(ethylene terephthalate) [(apcPET)]. M_w for the reclaimed poly(ethylene terephthalate) (rPET) was slightly lower, at 57,400 g/mol. The melting temperature increased with two heat cycles from 236°C for the heat-crystallized virgin poly(ethylene terephthalate) (vPET) pellets to 248°C for apcPET and up to 253°C for rPET. Correspondingly, the cold crystallization temperature decreased with increased processing from 134°C for vPET to 120°C for apcPET. The intrinsic viscosity varied from 0.773 dL/g for the vPET to 0.709 dL/g for rPET. Extruded samples were created to assess the potential commercial applications of the recovered rPET samples. The M_w values of the extruded apcPET and rPET samples dropped to 37,000 and 34,000 g/mol, respectively, after extrusion (three heat cycles); this indicated that exposure to heat dictated that these materials would be better suited for downcycled products, such as fibers and injected-molded products. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

Key words: polyesters; recycling; separation techniques; thermal properties; waste

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a commodity plastic commonly used in a wide array of applications, most notably for injection stretch blow-molded drink bottles, because of its toughness, clarity, and low permeability to carbon dioxide.[1] PET bottles are typically single-use items, which, after use, are either recycled or thrown away, which in the United States, generally means that they are put in landfills. Roughly 2.7 million tons of PET drinking bottles are discarded in the United States per year; this represents a high volume of easily source-separated, recyclable material for reuse in bottle manufacturing or downcycled products, such as various injected-molded products or textile fibers (e.g., carpet fiberfill, covers).[2–4] Despite widespread municipal programs to encourage source separation from household waste, only about 23% of the available PET in the United States is recycled, even with extensive separation at material recovery facilities.[5] PET bottles represent roughly 1% of the 254 million tons of municipal solid waste (MSW) that is landfilled per year in the United States,[6] a figure that does not include sources such as carpet and textiles, which comprise an additional 2% of the yearly MSW totals.[7]

U.S. domestic demand for PET continues to outstrip supply, so significant quantities of PET are imported into the United States from Canada.[5] The demand for recycled PET has grown steadily in recent years, even though half of the reclaimed poly(ethylene terephthalate) (rPET) continues to be exported, largely because of U.S. Food and Drug Administration regulations concerning direct food

contact with these substances.[8] Wal-Mart's recent proclamation that they would give preferential treatment (and prime shelf space) to products with a positive life cycle profile suggests that demand for recycled PET should increase.[9]

MSW is a heterogeneous mixture composed of both residential and commercial refuse, much of which is enclosed in plastic bags, which are generally composed of polypropylene or polyethylene. MSW has had limited application as a feedstock for bioenergy generally because of this heterogeneity. The U.S. Department of Agriculture (USDA) and its partner, Comprehensive Resources, Recovery, & Reuse, Inc. (CR^3), have developed a system based on the steam autoclaving of MSW that results in uniform, predictable output streams that are consistent on a daily basis. This team, along with the Salinas Valley Solid Waste Authority, operates a pilot-scale autoclave in the city of Salinas, California, which was originally targeted toward the diversion of organics from MSW. This system is a 2-T batch pilot autoclave that steam-treats MSW; this process is followed by size separation via a rotary trommel screen to produce uniform and predictable output streams, most of which can be used for the production of ethanol, methane, or electrical power.[9] The autoclave exposes MSW to a saturated steam atmosphere, which serves to melt most plastic bags and steam-sterilize waste materials. The mechanical action provided by the rotation and shear forces within the autoclave further breaks down trash bags and reduces the paper components to a pulp. A simple, rotary-size separation after autoclaving separates about 90% of the fibrous fraction and enables nearly 100% recovery of high-melting plastics and metals.

The purpose of this study was to evaluate the quality of PET derived from the vacuum-assisted steam autoclaving of MSW. The specific goal of this research was to assess whether the PET recovered after the autoclaving of MSW could be considered a viable new source of recyclable PET and could compete with postconsumer recycled bottles. Ideally, reclaimed bottles would be used interchangeably with postconsumer poly(ethylene terephthalate) (pcPET) for high-value uses, but if not, any increase in the amount of PET bottles reclaimed would have a positive impact toward more efficient recycling programs.

EXPERIMENTAL

Materials

Figure 1 shows photos of the autoclaving process in Salinas, California; it depicts the incoming material [Fig. 1(a)], the pilot-scale autoclave in the upright loading position [Fig. 1(b)], the unscreened product after autoclaving [Fig. 1(e)], and rPET bottles [Fig. 1(d)]. In this study, curbside MSW was autoclaved at the Salinas facility, and PET bottles were reclaimed via size separation and hand sorting. These bottles, which would otherwise have been landfilled, were tested as a source of recycled PET. Comparisons were made between the autoclaved rPET, with several comparative controls, including virgin poly(ethylene terephthalate) (vPET) resin and unused pcPET. Four different PET materials were compared during this study: vPET, pcPET, autoclaved postconsumer poly(ethylene terephthalate) (apcPET), and rPET derived from autoclaved MSW. vPET resin pellets and postconsumer bottles that (the pcPET and apcPET fractions) were obtained from The Coca-Cola Co. The postconsumer bottles were divided into two fractions, in which pcPET was chipped into a powdered resin and used directly, and apcPET bottles were placed whole in a mesh laundry bag and inserted into the autoclave before a normal load of MSW was processed. This represented a control to evaluate the effect of autoclaving on rPET bottles commingled with MSW. The laundry bag was of sufficiently small mesh to exclude a majority of the large contaminants that would be in contact with the rPET but still allow heat treatment.

rPET bottles were isolated from the autoclaved residential MSW processed at the Crazy Horse Landfill near Salinas, California, on July 16, 2008. Vacuum-assisted steam autoclaving was discussed in more detail elsewhere.[9] The focus here is on the separation of PET bottles for enhanced recycling.

Autoclave processing

In brief, unsorted MSW [Fig. 1(a)] was used as received from residential curbside collection, with some removal of very large items, such as construction materials, refrigerators, and furniture. MSW was loaded into the CR^3 articulated 2-T batch autoclave [Fig. 1(b)], the system was hermetically sealed, the contents were heated via direct steam injection and indirect heating, and the heating process was held above 121°C for 30 min, a time that has been shown to ensure sterilization of the contents.[9] The vessel was slowly rotated about the longitudinal axis throughout. The rotation of the autoclave, combined with the patented helical design of the heating coils in the autoclave, provided mechanical action to open garbage bags, break apart the refuse, and reduce the paper components to a pulp material that allowed cellulose-rich streams to be easily separated from larger materials, especially PET bottles.

After vacuum evacuation of the autoclave, the hot autoclaved MSW was size-separated in a rotating trommel screen [Fig. 1(c)] in which PET bottles were hand-sorted from the rejects from the 1-in. screen [Fig. 1(d)]. rPET bottles tended to entrap some

Figure 1 Photographs of PET bottles reclaimed from MSW by vacuum-assisted steam autoclaving. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contaminants and were collapsed by the vacuum evacuation of the autoclave, yet caps, rings, and labels were also removed by this process. Simultaneously, a cellulose-rich organic stream was captured as the 3/8-in. minus fraction [Fig. 1(e)].

Polymer recycling

Figure 2 depicts the processing regime followed in the laboratory for each of the four PET samples. rPET bottles were washed and rinsed in a coarse mesh laundry bag in a commercial laundry machine on a warm cycle with Alconox detergent to remove contaminants, which included pulp materials and dissolved organic components. The bottles were cut into circular strips with a band saw, cut again with scissors into rectangular strips 1–2-in. in length, and were then chipped in a Waring Commercial CB-15 4-L blender (Torrington, CT) over a 5-min interval at high speed at 5 g in 100 g of water. The resulting flake material, with an average diameter of less than 0.25 in., was dried overnight at 70°C in a Thelco
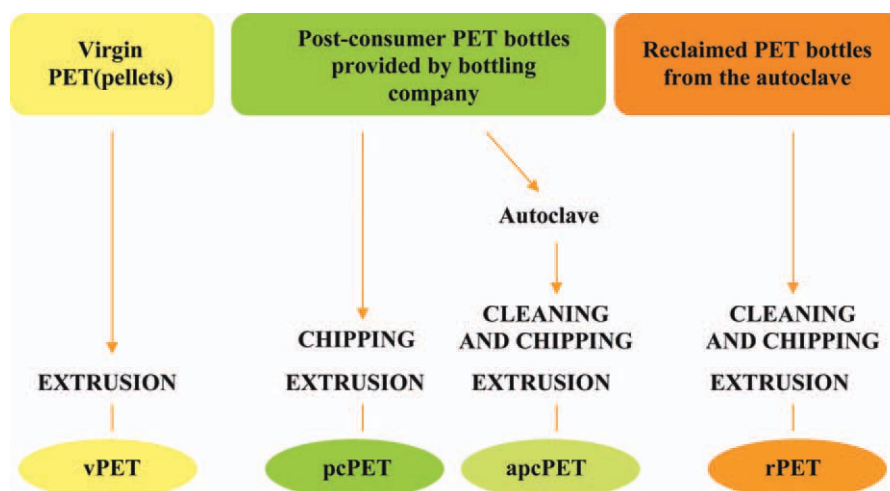
Figure 2 Schematic detailing of the processing steps required for each PET material: vPET, pcPET, apcPET, and rPET. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

laboratory oven and stored in a desiccator over Drierite. To further reduce the particle size, the flakes were milled with a Micron Powder Systems Mikro-Bantam impact mill at ambient temperature, dried again for 24 h at 70°C, and stored over a desiccant before further processing.

The apcPET was treated in a manner analogously to that of the rPET in that it was washed, cleaned, and chipped before it was milled into a fine powder. The pcPET was chipped directly before it was milled into a fine powder. The vPET was milled directly into a fine powder.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA)

A TA Instruments model 2910 modulated DSC instrument equipped with an autosampler was used for analysis of all of the samples throughout processing. Samples of 10.0 mg were weighed into aluminum DSC pans and heated at a rate of 10°C/min from room temperature to 300°C. The degree of crystallinity (X_c) was calculated by DSC from the heat flows of the cold crystallization enthalpy peak (H_c) and the heat of fusion (H_m) by the following equation[2,10]:

$$X_c = (H_m - H_c)/H_m^* \times 100$$

where H_m^* is the theoretical heat of fusion for 100% crystallinity (136 J/g).

TGAs were performed with a Hi-Res TGA 2950 manufactured by TA Instruments. All of the samples were heated at a rate of 10°C/min from room temperature to 800°C.

Extrusion of the isolated PET samples

All materials were extruded with a 0.5-in. single-screw microextruder (RC-0500) made by Randcastle

Extrusion Systems, Inc. (Cedar Grove, NJ). The extruder consisted of three heating zones, and the die heater and the temperature profiles are shown in Table I. The set temperature was increased progressively down the barrel from 166 to 254°C from zone 1 to zone 3, and the die zone was cooled to 222°C to facilitate collection of the product. The dried samples were pelletized with a Wayne Machine and Die Co. 2-in. micropelletizer and stored once again in a desiccator. The samples were labeled analogously to their unextruded analogs by the addition of the letter E.

Molecular weight determination

Gel permeation chromatography (GPC), percentage oligomer content measurement, and intrinsic viscosity (IV) measurement were kindly performed by The Coca-Cola Co. The system consisted of a Waters Alliance GPCV 2000 coupled with a Waters 2489 UV–vis detector system and a Precision Detectors PD2040 laser light-scattering detector. The column used for separation was a 7.5 mm (*i.d.*) × 300 mm polystyrene/divinylbenzene (PS/DVB) PLgel MIXED-B LS [10 μm particle size, weight-average molecular weight (M_w) range = 500–10,000,000 Da]. The mobile phase was 2% (v/v) 1,1,1,3,3,3-hexafluoroisopropanol in chloroform, with a flow rate of 1.0 mL/min. The injection volume was 100 μL.

TABLE I
Set and Actual Temperatures of the Microtruder Zones

	Zone 1	Zone 2	Zone 3	Die zone 1
Set temperature (°C)	165.6	241.1	254.4	221.7
Actual temperature (°C)	183.9	241.1	254.4	221.7

	GPC complete				GPC without oligomer			
	M_n (g/mol)	M_w (g/mol)	PD (M_w/M_n)	Oligomer (%)	M_n (g/mol)	M_w (g/mol)	PD (M_w/M_n)	IV (dL/g)
vPET	30,500	64,300	2.11	1.12	37,500	65,000	1.73	0.773
pcPET	26,500	61,700	2.33	0.92	33,200	62,300	1.87	0.749
apcPET	24,900	59,700	2.40	0.96	31,800	60,300	1.90	0.735
rPET	23,900	57,400	2.41	1.00	30,700	58,000	1.89	0.709
EvPET	26,000	61,400	2.35	1.11	33,100	62,100	1.87	0.743
EpcPET	20,500	49,600	2.42	1.04	26,100	50,100	1.92	0.636
EapcPET	15,100	37,000	2.45	1.07	18,900	37,300	1.97	0.513
ErPET	14,500	34,000	2.35	1.20	18,200	34,400	1.90	0.489

Solid-state NMR

NMR experiments were carried out with a Bruker Avance spectrometer at 75 MHz for ^{13}C, with 4-mm rotors in a double-resonance probe. [13]C cross-polarization/total sideband suppression (CP/TOSS) NMR experiments were acquired at a spinning speed of 5 kHz with a cross-polarization time of 1 ms, a [1]H 90° pulse length of 4 μs, and a recycle delay of 5 s. Four-pulse total suppression of sidebands (TOSS)[11] was employed before detection, and two-pulse phase-modulated decoupling was applied for optimum resolution.[12]

RESULTS AND DISCUSSION

Molecular weight variations with thermal processing

The M_w variations measured by GPC of the different PET samples with differing thermal histories (described in Fig. 2) are outlined in Table II. The unprocessed vPET pellets had a M_w of 64,000 g/mol, an IV of 0.773 dL/g, and a polydispersity (PD) index (M_w/M_n, where M_n is the number-average molecular weight) of 1.73. The stretch blow molding (of pcPET) caused some thermal degradation and reduced M_w to 61,700 g/mol and IV to 0.749 dL/g and increased PD to 1.87. Stretch blow molding represented at least one heat cycle, meaning that the processing temperature exceeded the glass-transition temperature (T_g) of the polymer.

A comparison of pcPET and apcPET provided a direct measurement of the impact of autoclaving on the properties of the pcPET bottles; that is, apcPET was derived from postconsumer bottles that had been autoclaved in a mesh bag (for easy recovery). The M_w (61,700 g/mol) and IV (0.749 dL/g) for the pcPET bottles decreased to 59,700 g/mol (M_w) and 0.735 dL/g (IV) for apcPET. PD increased slightly to 1.90. Autoclaving resulted in a modest decrease in the molecular weight of the PET; this indicated that it was an applicable technique for reclaiming PET. A

comparison of the rPET and apcPET showed that the rPET was lower in M_w (59,700 vs 57,400 g/mol) and IV (0.735 vs 0.709 g/dL) and equivalent in PD. The differences could have been explained by debris or volatile acid incorporation for the rPET, whereas the apcPET was protected from such contamination by the fact that apcPET was a controlled sample, whereas the rPET was heterogeneous in nature. Compared with vPET, the autoclaved PET samples, apcPET and rPET, had each been through two additional heat cycles with modest decreases in molecular weight. Much of this study was designed to ascertain the effect of each of these processes on the PET properties.

Thermal characterization of the autoclaved PET bottles

Figure 3(a) shows DSC thermograms of the four PET samples, including the two samples of autoclaved PET bottles (apcPET and rPET). The vPET thermogram was typical of unprocessed PET, with a clear T_g from 70 to 80°C, an endothermic cold crystallization temperature (T_c), at 136°C and a melting endotherm [melting temperature (T_m)] at 237°C. Bottle formation by blow molding did not change T_m significantly (see Table III), but the DSC melting endotherm was less distinct, and the measured change in the heat of fusion (ΔH_m) was lower for pcPET (ΔH_m = 26.2 J/g) versus vPET (ΔH_m = 50.8 J/g). Accordingly, the calculated X_c dropped from 37.4% for vPET to 19.3% for pcPET upon heat cycling, and the pcPET showed some evidence (bimodal peaks) of thermal degradation that resulted from the processing and as depicted by TGA [Fig. 3(b)].

Thermal characterization of the autoclaved PET bottles (apcPET and rPET) revealed significant differences from the unautoclaved samples (vPET and pcPET). After autoclaving, the melting endotherm shifted to higher temperatures, with T_m = 248.3 and 253.3°C for apcPET and rPET, respectively, compared to T_m = 236.0°C for pcPET, the unautoclaved bottle.
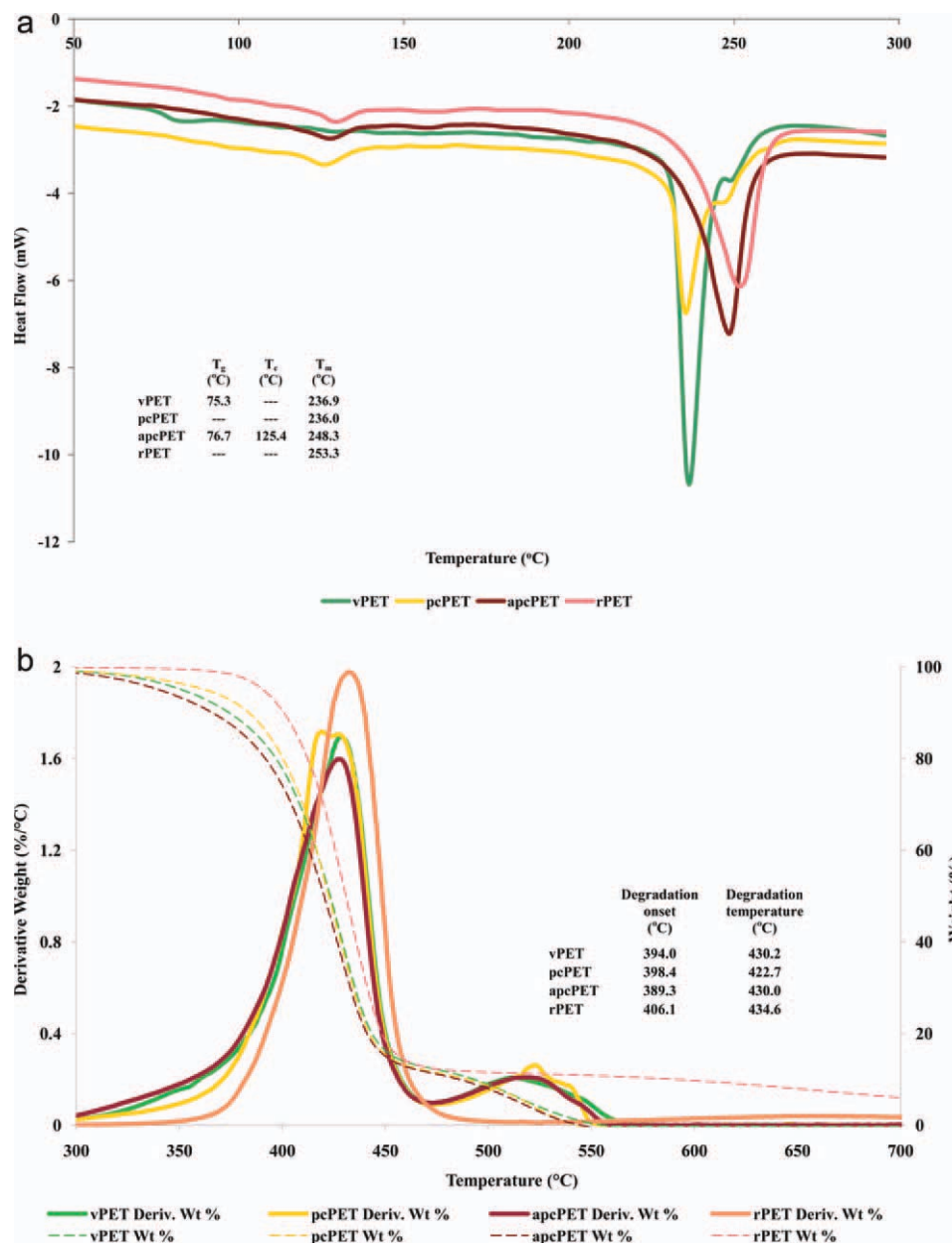
Figure 3 Thermal characterization of different PET samples as measured by (a) DSC and (b) TGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

X_c increased with autoclaving (19% for pcPET compared to $\sim$ 27% for both apcPET and rPET). This indicated that the residence time in the autoclave was sufficient to allow for local polymer reorganization toward a more organized crystalline structure without a dramatic loss in molecular weight.

The interpretation of the TGA derivative weight curve in Figure 3(b) further outlined the differences due to autoclaving. The degradation onset for the apcPET (389°C) was lower than for pcPET (398°C), whereas the primary degradation temperature peak shifted to a higher temperature (422.7–430°C). The latter observation could be correlated to the disappearance of the bimodal nature of the primary deg-

radation peak, likely through hydrolytic mechanisms involving the amorphous, lower molecular weight material. The decrease in the degradation onset temperature may have indicated the presence of lower molecular weight degradation products produced by the degradation of polymer. The secondary degradation peak (centered at $\sim$ 520°C) remained mostly unaltered by the autoclave.

On the basis of the GPC, DSC, and TGA data presented previously, it is evident that steam autoclaving provided an environment that promoted the degradation of PET, which otherwise would be similar to an additional heat cycle. Degradation was due to its relatively high temperature and the presence

TABLE III
T_m, ΔH_m (Endothermic), and X_c Values as Determined by DSC

	Number of heat cycles	T_m (°C)	$|\Delta H_m|$ (J/g)	X_c (%)	$\Delta H_m/X_c$	Appearance
vPET	0	236.9	50.8	37.4	1.4	Opaque
pcPET	1	236.0	26.2	19.3	1.4	Clear
apcPET	2	248.3	36.6	26.9	1.4	Clear
rPET	2	253.3	36.8	27.0	1.4	Clear
EvPET	1	248.9	24.0	4.3	5.6	Clear
EpcPET	2	248.3	34.7	10.1	3.4	Clear
EapcPET	3	251.4	39.2	15.4	2.5	Partially opaque
ErPET	3	255.3	42.1	30.9	1.4	Partially opaque

of water and a multitude of potential contaminants, especially volatile fatty acids. Although the processing temperature was well below the T_m range of 245–265°C, it was far enough above the T_g of about 70–80°C to allow chain mobility. Chain mobility implied that small molecules could move readily within the amorphous domains, which enabled the PET to encapsulate small debris and contaminants, including fatty acids, from the MSW. Thus, potential oxidants, including water, could potentially migrate throughout the polymer amorphous substructure to promote hydrolysis and chain scission as the temperature and pressure were increased. The three primary mechanisms of PET degradation generally described in the literature—thermal, oxidative, and hydrolytic—were all possible within this autoclaving protocol.[10,13,14] The main consequences of degradation were chain scission with a subsequent loss in molecular weight and an increase in PD, both of which were seen in the GPC results. The ester bond is particularly susceptible to cleavage in a moist, acidic environment, especially at relatively high temperatures.

Not surprisingly, the blow molding of vPET, an additional heat-cycling step, resulted in a slight loss of molecular weight, whereby the M_w values of pcPET and vPET were 61,700 versus 64,300 g/mol, respectively, and IV was 0.749 versus 0.773 dL/g, respectively (Table II). The rPET and apcPET bottles resulted in similar materials, as determined by the GPC, DSC, and TGA results; this was not surprising given their similar thermal histories. The rPET exhibited slightly lower M_w (57,400 g/mol) and IV (0.709 dL/g) than the apcPET, but rPET was a heterogeneous source of PET products. Both materials exhibited a slight endotherm at T_c (~ 125°C) and strong T_m's at 248.3 and 253.3°C, respectively, for apcPET and rPET [Fig. 3(a)].

Solid-state NMR

[13]C CP/TOSS experiments were performed to assess whether autoclaving in the acidic environment induced chemical modification in the PET polymer.

The structure of PET was represented by the carbonyl (170–160 ppm), ethylene (70–60 ppm), and nonprotonated and protonated aromatic carbons at 134 and 131 ppm, respectively (Fig. 4). Subtle changes in the character of the carbonyl and ethylene functionalities did indicate a broadening in the chemical environments found in the polymer structure. Both tailed slightly downfield; this was indicative of a transition toward an amorphous structure
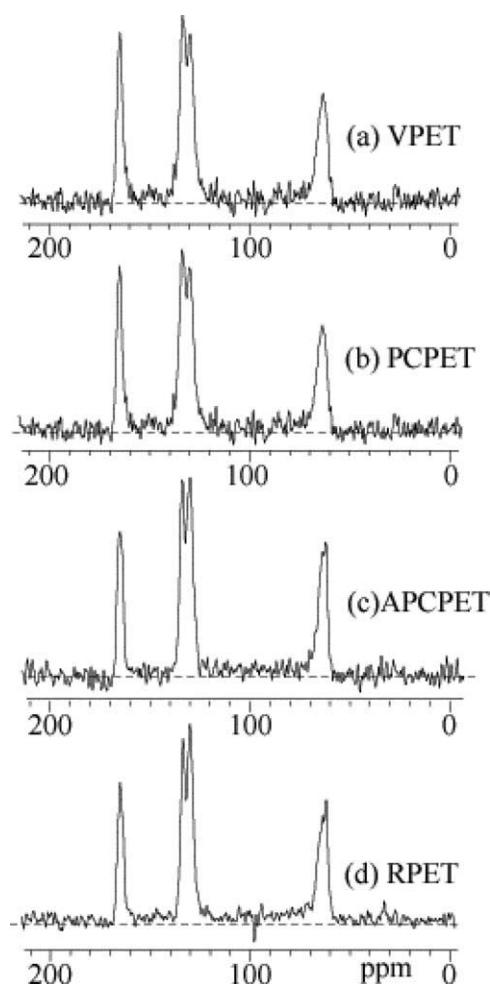

Figure 4 Solid-state NMR spectra of the processed PET samples.
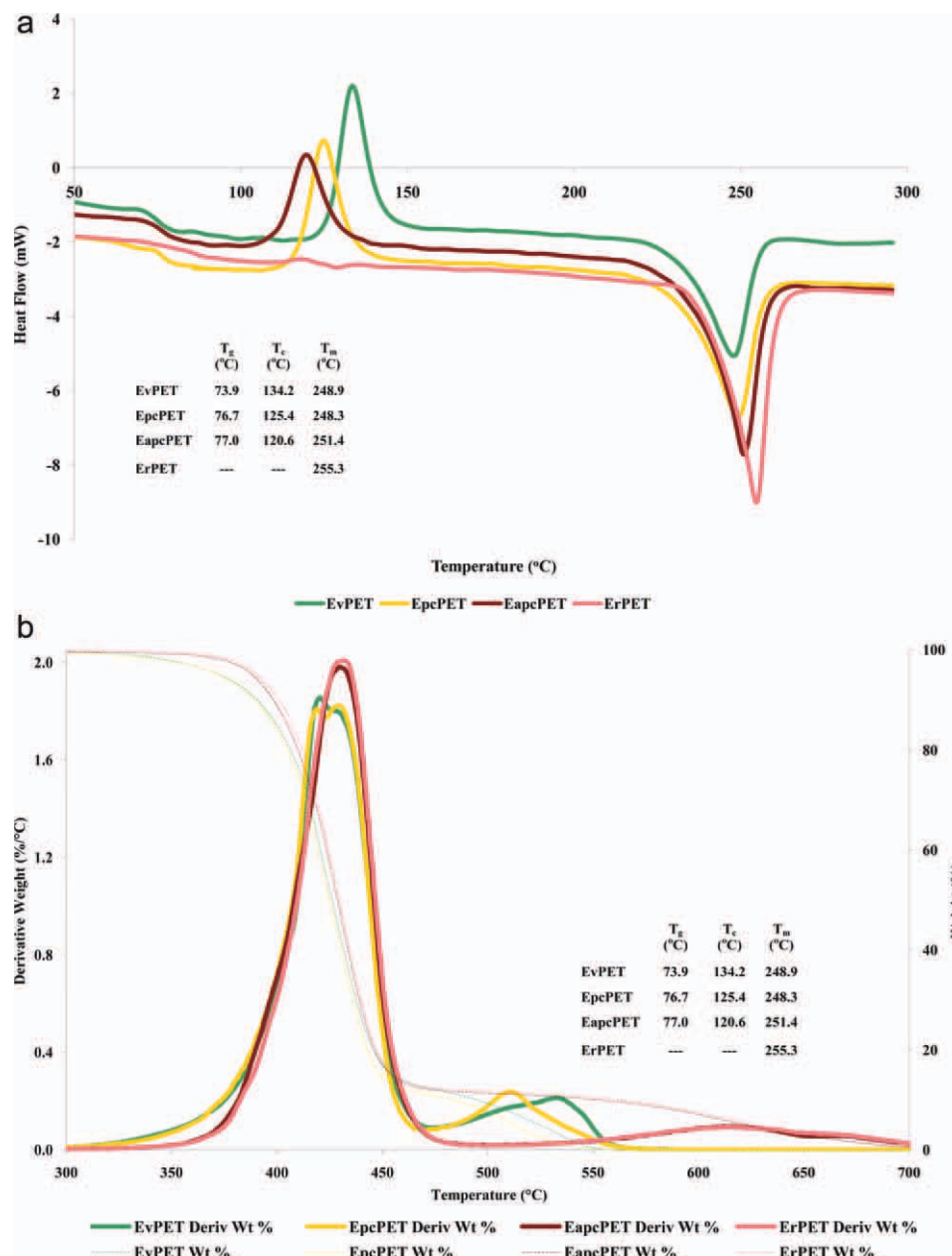
Figure 5 Effects of extrusion on the polymer properties of vPET as depicted by (a) TGA and (b) DSC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with increasing heat cycling. A study highlighting a deconvolution spectrum for PET illustrated this transition well.[15] There was no evidence that side products were present in sufficient quantity to be detected by NMR; this indicated that chemical modifications did not occur and that chain scission was the likely mechanism for the changes in the molecular weight and thermal properties.

Extrusion of the PET and recovered PET after autoclaving

To explore whether the rPET derived from autoclaved MSW could be extruded into useful recycled

products, a preliminary extrusion study was performed on the four PET samples studied here. It is well established that the extrusion of PET changes its thermal properties, as confirmed by a comparison of the DSC thermograms [Fig. 5(a)]. The extrusion of vPET [i.e., vPET vs extruded virgin poly(ethylene terephthalate) (EvPET)] resulted in (1) a more distinct T_g, measured at 73.9°C; (2) a exothermic T_c at 134°C; and (3) a shift of the melting endotherm to a higher temperature. The crystallinity of vPET was calculated to be 37% before extrusion, whereas that of EvPET was 4% (Table III). The extrusion of vPET, which represented only the first heat cycle, resulted in a slight loss of M_w (from 64,300 to 61,400 g/mol)
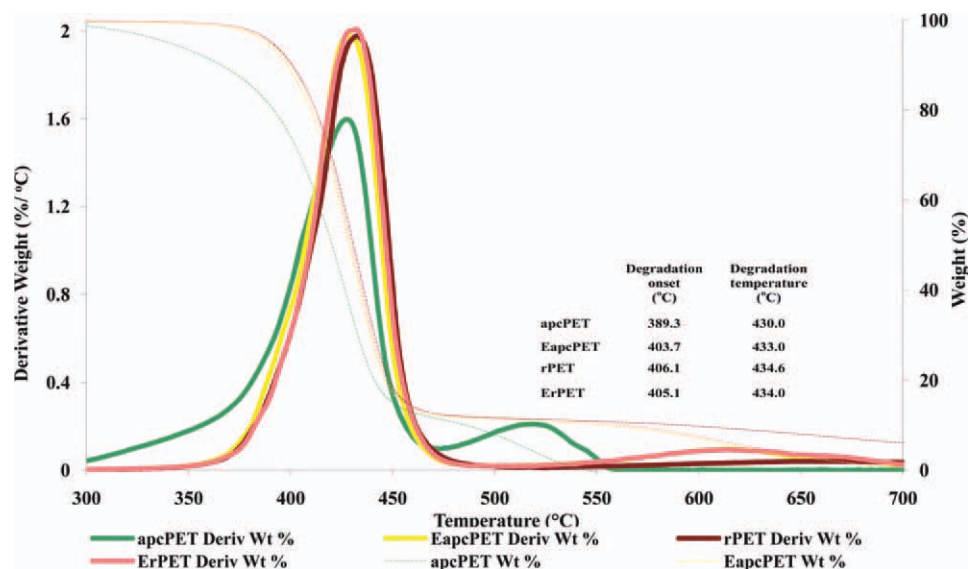
Figure 6 Thermal characterization of different extruded PET samples as measured by (a) DSC and (b) TGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and a decrease in IV to 0.743 from 0.773 dL/g (Table II); this was similar to the attrition observed in the blow-molded products (pcPET). The TGA thermograms of EvPET exhibited more of a bimodal nature than those of vPET, as shown in Figure 5(b), and was also reminiscent of the pcPET. The H_m/X_c ratio of the extruded postconsumer poly(ethylene terephthalate) (EpcPET) was 3.4 versus 5.6 for the EvPET; this indicated that the H_m required to melt the crystalline regions was substantially less.

EpcPET experienced more substantial changes as a result of extrusion, with M_w = 49,600 g/mol and IV = 0.636 dL/g. M_w for the extruded autoclaved postconsumer poly(ethylene terephthalate) (EapcPET) was 36,900, and IV was 0.513 dL/g; this was likely due to the fact that extrusion represented a third heating cycle (blow molding, autoclaving, and extrusion) for EapcPET versus a second heating cycle for EpcPET. T_c of the EapcPET further decreased to 120.6°C (cf. 125°C for EpcPET), and T_m increased from 248.3 to 251.4°C [Fig. 5(a)]. The ratio of H_m to X_c was lower for the EapcPET sample (2.5) compared to the EpcPET sample (3.4); this reflected the decreases in the molecular weight and IV and implied that the resulting crystallites were smaller and less organized. The extruded analogs showed an increasingly higher X_c, 10.1 and 15.4% for EpcPET and EapcPET, respectively, and a higher heat flow requirement to achieve fusion of the crystalline structure (34.7 vs 39.2 J/g, respectively). The increased crystallinity upon extrusion under identical conditions indicated a continual decrease in the molecular weight from processing. A loss in chain length facilitated crystallization and resulted in some opaque product upon extrusion.

X_c of the extruded reclaimed poly(ethylene terephthalate) (ErPET; 31%) was slightly higher than that of rPET, an observation that appeared to run counter to the other trends observed thus far. Likewise, the H_m/X_c ratio was equivalent to all of the nonextruded materials; this indicated that anisotropy no longer had an impact on the polymer properties and was lower than that of EapcPET (2.5). This indicated that debris may have allowed for nucleation sites in ErPET. ErPET exhibited no T_c, and its T_m, at 255°C, was the highest of all of the samples assayed in this study. The TGA results were almost identical to that of EapcPET and rPET (Fig. 6).

The TGA results (Fig. 6) also show that successive heat cycling resulted in a material of higher degradation onset and peak temperatures. The TGA curves for EapcPET, rPET, and ErPET were all Gaussian-shaped and showed no hysteresis. This likely indicated that all of the easily degradable regions of the polymer were decomposed and left behind a relatively stable recyclable polymer.

Effects of heat cycling on the polymer properties

One way to think of autoclaving is as an additional heat cycle. In simple terms, the first heat cycle, the blow molding of the PET into bottles, did not have a significant impact on M_w or IV (the values for vPET vs pcPET are shown in Table II). However, each processing step adding a heat cycle and subsequent heat cycles, especially when melting was involved, caused dramatic losses in the molecular weight. In part, these processes were under less controlled conditions. It was hypothesized that a loss in the molecular weight and shorter polymer chains allowed for

easier crystallite formation, and hence, the crystals formed at a lower temperature. T_c progressively decreased from 134°C for EvPET to 125°C after the extrusion of the blow-molded product (EpcPET) and 120°C after the extrusion of the autoclaved postconsumer material (EapcPET). ErPET exhibited no T_c because of its proclivity to crystallize during extrusion. Progressive heat-cycling resulted in an increasingly higher T_m from 236°C for vPET to 255°C for ErPET.

The extruded materials possessed a higher X_c with progressive heat cycles ranging from 4% for EvPET to 31% for ErPET. Correspondingly, the H_m/X_c ratio decreased with heat cycling to the point that anisotropy was no longer observed, and the ratio was equivalent to the unextruded analogs, which never experienced the proper conditions necessary to cause polymer chain realignment.

Prospects for reuse

The IV of pcPET is nearly equivalent to that of the vPET and hence it can be reused as a substrate for bottle manufacture. The IV of apcPET and rPET are lower, implying that the material is more likely to be downcycled to products such as films or fibers. The autoclaved bottles absorbed color from the MSW and integrated fine debris. It was unclear whether debris was incorporated into the plastic or was a byproduct of insufficient cleaning. In any case, a 0.6 wt % incorporation was detrimental to the mechanical properties of the strand, as evidenced by processing. Because the rPET samples lost their clarity, they were unlikely to be reused in bottle manufacturing. The origins of rPET also made it such that it was unlikely to be reused for food-contact applications in any case. rPET may be a good candidate for a chemical recycling study.

The IVs of rPET and apcPET, however, were plenty sufficient for reuse as starting materials for films, fibers, or non-food-contact molded products. A caveat to films or fiber products is that proper cleanliness must be achieved to ensure that adequate mechanical and optical properties for processing and performance are attainable. The results presented here include concerns about fine contaminants arising from the MSW. It is unclear whether this is a cleanliness issue or whether the contaminants actually become embedded in the plastic bottles above the T_g. In the latter case, the most likely reuse would be for injection-molded products.

CONCLUSIONS

The goal of this study was to evaluate the effects of steam autoclaving on the properties of PET, data which could ultimately be applied to determine the most likely end use of this potentially huge waste stream. Through the course of the study, we determined that stretch blow molding in bottle manufacturing has little impact on M_w or IV but causes some change in morphology, as indicated by the decrease in T_c from 134 to 125°C. A substantial X_c persisted through the blow-molding process. Autoclaving resulted in a decrease in T_c and an increase in T_m. Apparently, this processing temperature, which exceeded the T_g of PET was high enough to allow for some local reorganization of the polymer. Incorporated debris may have acted as a nucleating agent, inducing crystallinity at a lower T_c (120°C) and increasing T_m to a higher temperature (253°C) as a result of more stable crystallites.

The steam autoclaving process used in this study represented an additional heat cycle, which affected both the molecular weight and IV, as well as the polymer morphology. Specifically, M_w decreased from 61,700 g/mol for pcPET to 59,700 g/mol for apcPET and 57,400 g/mol for rPET. IV also decreased from 0.749 dL/g for pcPET to 0.735 and 0.709 dL/g for apcPET and rPET, respectively. Because this process maintained the PET in a moist, acidic environment, these modest losses in M_w were not surprising. These changes implied that it was more than likely that rPET will be used for downcycling uses. Color and contamination will likely dictate that non-food-contact blow-molding applications be the primary end use of these products.

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