ACETALDEHYDE GENERATION IN POLY(ETHYLENE TEREPHTHALATE) RESINS FOR WATER BOTTLES

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ABSTRACT

Acetaldehyde (AA) is a degradation byproduct formed when PET is melted. For the storage of beverages in PET bottles, minimization of the AA in the bottle wall is necessary as it can leach into the drink and alter its taste. Today's PET resins can easily meet the requirement for packaging strongly-flavored drinks such as colas (<8 ppm of AA in the preforms). However, the most stringent application is the packaging of potable water for which preforms with less than 3 ppm of AA are required. Major differences in the performance of commercial water-grade PET resins were observed. It is commonly believed that the key to reduced AA in preforms is a low I.V. resin (<0.75 dL/g), as it allows injection molding of preforms at low temperatures. However, this work shows that low I.V. is not a sufficient or even dominant factor for the AA obtained in preforms. It is possible to have a low I.V. resin that yields high AA in the preforms and conversely a high I.V. polymer that gives low AA. The intrinsic AA generation potential of the resin controls the AA in the preforms. This is not controlled by the resin I.V. but by the polymerization conditions.

Key Words: PET; Bottle resin; Acetaldehyde; Acetaldehyde regeneration; Injection molding; Stretch-blow molding

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INTRODUCTION

PET bottles are made by a two-step procedure. An amorphous preform is made first by injection molding, and is subsequently stretch-blow-molded to form a biaxially-oriented, semi-crystalline but transparent bottle. The first successful application of PET bottles was for colas and carbonated soft-drinks (CSD). After this, PET found another major market in bottles for potable water. PET has also started to replace glass in jars.

Currently, one can say that there are two major PET bottle-grade resins: one for CSD and the other for water bottles. The CSD grade is designed to meet the mechanical properties needed to withstand the high pressures in carbonated drinks. Generally, this requires very high molecular weight resins (I.V. > ~0.82 dL/g).

Acetaldehyde (CH_3CHO) is a major thermal degradation product that arises when PET is melted.[1,2] While acetaldehyde (AA) is of no concern in fiber and filament applications of PET, it is an important matter for bottles. This is because AA migration into the beverage from the bottle wall can create an off-taste in the drink.[3,4] Generally, there is residual AA left in the pellets as a result of the polymerization. The first generation of resins typically had residual AA levels of 2−3 ppm,[5] but today it is <1 ppm. However, the AA increases when the pellets are remelted and converted to performs.[6] The maximum AA that is acceptable in the preforms depends on the application. Colas and strongly flavored drinks can of course tolerate relatively high levels of AA. The maximum permissible AA in preforms for colas is 8 ppm. Today, most CSD resins can meet this.

For water bottles on the other hand, the mechanical properties need not be exceptional, and so high I.V. is not an absolute requirement. However, the AA requirement is very demanding, particularly in small bottles for table-top use (0.5 to 1.5 L sizes), where the surface-area-to-volume is high. This application requires that the AA in the preforms does not exceed 3 ppm, which means the average AA in the preforms must be 2.5 ppm or lower. The AA present in the bottled water after a period of storage of 180 days at room temperature is of the order of ~100 ppb (4). The organoleptic detection is reported to be in the range 4−65 ppb. It is also possible that the AA oxidizes and converts into other molecules that cause taste.[3]

Generally, for water bottles it is believed that low I.V. is helpful in reducing the AA in preforms. We found that commercial PET resins do not behave in the same way during injection molding, with some giving much higher AA in the preform than others, under identical processing conditions. Further, there appeared to be no correlation between the resin I.V. and the AA regeneration rate on remelting. The chemical composition and physical properties of the resins were analyzed in order to establish the causes for the differences in AA levels in preform obtained from them.

EXPERIMENTAL

Materials

Six resins, labeled A to G, were studied. A, B, C, D and E are commercial water-grade, PET resins from different countries. Resin F is a non-commercial product. Resin G is in fact a CSD grade and it will be used as the base for comparison−all water grades should have lower AA than polymer G.

Resin Testing

The resin characterization tests were conducted to measure the following: intrinsic viscosity (I.V.), residual AA in the resin, diethylene glycol (DEG) content, isophthalic acid (IPA) and cyclohexane dimethanol (CHDM) comonomer content, melting behavior, and catalyst and additive residues (Sb, Co and P). The results are shown in Table 1.

Intrinsic Viscosity (I.V.)

The molecular weights of the polymers were characterized by measuring the intrinsic viscosity (I.V., Table 1). All I.V.s were measured by solution viscometry using a single-point method. About ten pellets were dissolved at $110°C$ in the mixed solvent 60:40 phenol-1,4 dichlorobenzene. The viscometry was conducted at $25°C$. The Billmeyer equation[7] was used to convert the flow times from a measurement at a single polymer concentration into an I.V. The equation is valid for $c \sim 0.5 \, g/dL$.

$$[\eta] = 1/4 \, \eta_{sp}/c + 3/4(\ln \eta_{rel})/c$$

Table 1. Resin Analyses

Property	A	B	C	D	E	F	G
I.V. (dL/g)	0.768	0.741	0.819	0.694	0.776	0.73	0.835
AA (ppm)	0.3	0.8	0.7	0.4	0.8	0.5	0.64
DEG (wt/wt%)	1.12	1.27	0.82	1.5	0.92	1.33	1.33
IPA (wt/wt%)	1.7	1.47	0	0	1.4	2.06	1.55
CHDM	0	0	0	0.86	0	0	0
COOH (mVal/kg)	20.2	22.9	17.8	16.8	21.9	42.6	22.4
Sb (ppm)	200	200	130	200	230	230	250
P (ppm)	15	15	14	15	20	20	20
Co (ppm)	15	19	12	ND	9.5	15	15
L*	91	92.1	92.3	92.2	90.5	87.7	88.6
a*	−1.5	−0.62	−0.69	−0.53	−1.2	−1.0	−1.53
b*	−1.5	1.02	1.45	0.76	0.8	−1.5	−1.65

ND is not detected.

In the above equation, $[\eta]$ is the I.V., η_{rel} is the relative viscosity and η_{sp} is the specific viscosity given by $\eta_{sp} = \eta_{rel} - 1$. The relative viscosity, η_{rel}, is given by the ratio t/t_0 where t is the flow time of the polymer solution and t_0 that of the solvent.

Acetaldehyde in Resins and Preforms

The AA in the resin and the preforms was measured by headspace gas-chromatography (GC). The PET chips/preforms were ground after cooling in liquid nitrogen. The ground powder was placed in a GC vial, capped and then held at 150°C for 90 min; it is worth noting that the AA values depend on the temperature and time, so for absolute comparison between laboratories, it is necessary to have the same conditions for these two parameters. The AA was released into the vial headspace; this was withdrawn and injected into the GC column. Prior to this, the GC was calibrated with aqueous-AA solutions. After calibration, the AA peak-area of the unknown sample gives the AA content in ppm. The AA results for each injection temperature (Fig. 5) are the average of 6 tests, with preforms selected randomly.

The GC was a Hewlett Packard 6890 series model with Flame Ionization Detector. The GC parameters are given below:

Column:Poraplot Q, Chromopack (25 m × 0.32 mm × 10.0 μm); initial column-oven temperature: 100°C; initial hold-time: 2 min; Ramp rate: 10°C/min; final oven-temperature: 180°C; final hold-time: 6 min; carrier gas: Helium (flow rate 2.4 mL/min); injection:splitless; injector temperature: 200°C; detector temperature: 250°C.

The parameters for the headspace accessory are given below:

Head space sampler: HP 7694; vial-oven temperature: 150°C; loop temperature: 150°C; transfer-line temperature: 150°C; equilibration time: 90 min; sample pressurization-time: 0.5 min; loop fill time: 0.1 min; loop equilibration time: 0.01 min; injection time: 0.2 min; Data collection by HP Chem station.

DEG, CHDM, and IPA Comonomers

Diethylene glycol (DEG) is a diol that arises as a reaction byproduct and gets incorporated in the chain, so that even what is regarded as the homopolyester is a copolyester with an unavoidable amount of DEG. Further, either isophthalic acid (IPA) or cyclohexane dimethanol (CHDM) is added as a comonomer in most modern bottle-grade resins, to alter the crystallization behavior of the PET. The levels of these three comonomers vary between manufacturers, and these were quantified (see Table 1) as it helps in understanding the processing behavior.

Unlike the residual acetaldehyde in the polymer, DEG, IPA or CHDM are bound in the chain and hence, are not volatiles that can be detected directly in the as-received polymer by headspace GC. The PET samples had

to be prepared to release the DEG, IPA or CHDM. For this, the polymers were trans-esterified with methanol in an autoclave at 220°C. During this procedure, the PET is depolymerized and converted to the dimethyl ester of terephthalic acid (i.e., dimethyl terephthalate, or DMT). DEG is liberated as the diol from the chain. If the PET is a copolyester containing IPA, the equivalent dimethyl ester (i.e., dimethyl isophthalate or DMI) will also be formed. If the PET is a copolyester containing the diol 1,6 cyclohexane dimethanol (CHDM), the CHDM would be also liberated as a liquid. The liquid formed after trans-esterification of the PET with methanol was tested by GC for DEG, IPA and CHDM content. An internal standard (triethylene glycol dimethyl ester, TEG-DME) was used. Figure 1 shows the GC peaks from three different polyesters and their assignments. It can be seen that all the chromotograms show peaks for methanol, ethylene glycol, TEG-DME, DMT and DEG. In Fig. 1a, resin C contains only these peaks. Figure 1b shows the typical trace for resins A, B, D, E, F and G; in these, there is an additional peak due to DMI. Figure 1c shows the trace for resin D; this shows no peak due to the DMI, but shows two additional peaks labeled CHDM 1 and CHDM 2. These are from the CHDM (two peaks arise because there are two isomeric forms). The relative amounts of these co-monomers were determined from the peak areas.
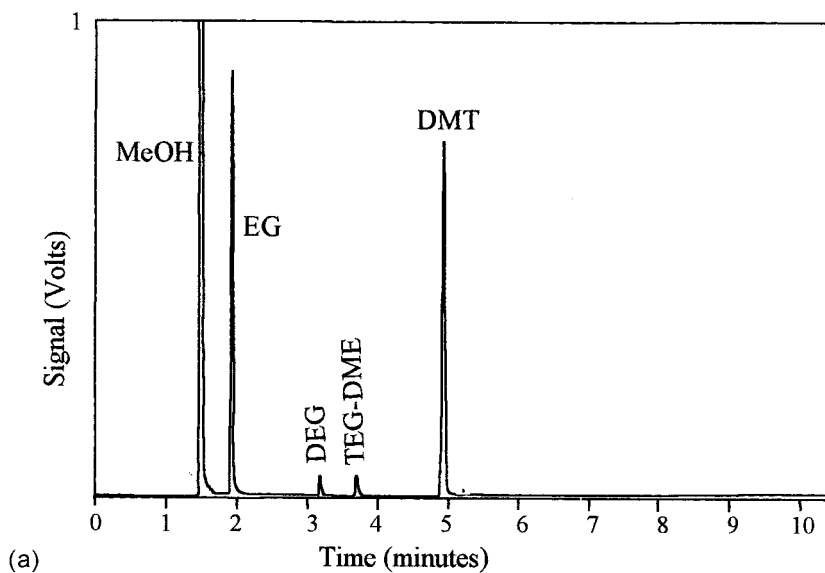
Figure 1.   (a) GC curve for homopolyester C show peaks for the standard TEG-DME, DEG, DMT, methanol, and ethylene glycol; (b) the GC curve for copolyester resins A, B, E, F, and G show an additional peak from the methyl ester of IPA; (c) the GC curve for copolyester resin D shows two additional peaks for CHDM (two isomers).

(*continued*)

(b)

(c)

Figure 1. Continued.
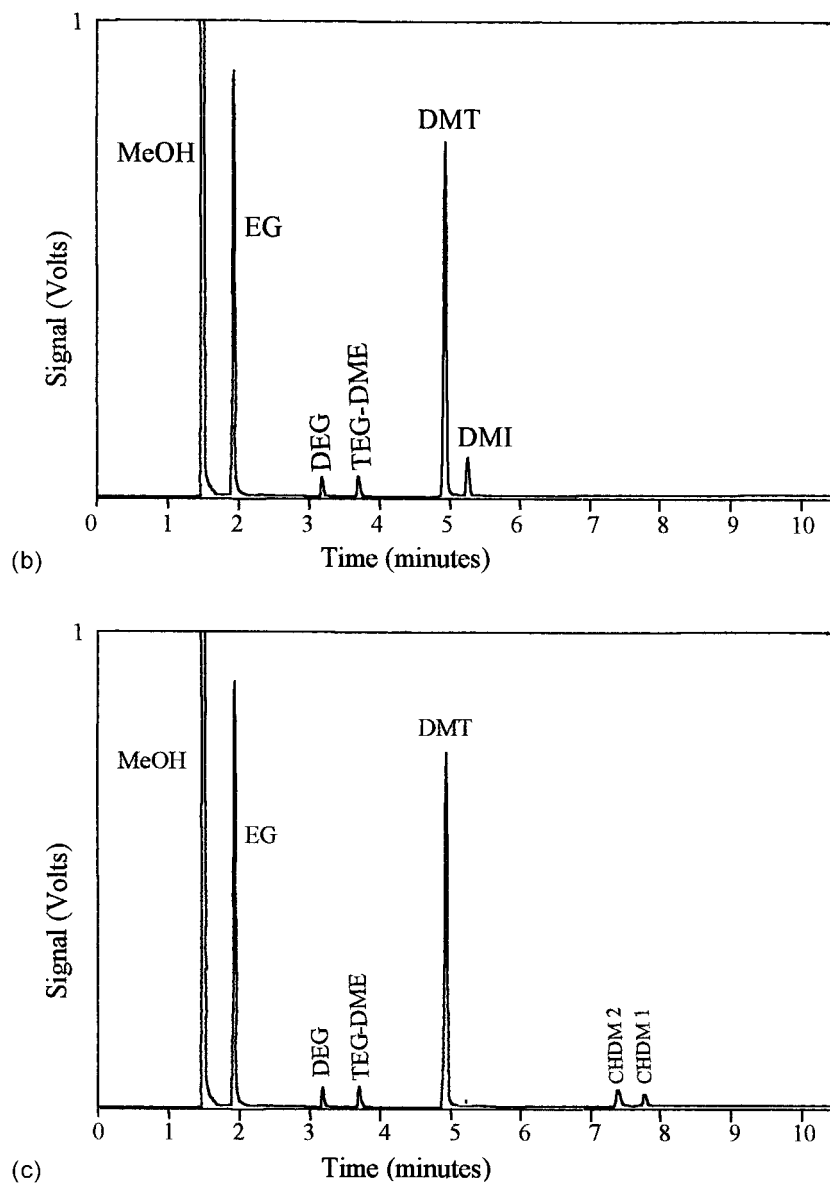
Melting Behavior by Differential Scanning Calorimeter (DSC)

The melting behavior of PET resins can show differences. For example, some PET resins have a double melting-peak, while others have a single peak. A sliced PET chip (5 mg) was heated in a TA Instruments DSC from 0–300°C at 10°C/min in a nitrogen atmosphere for the first heating-scan, to record the melting behavior of the as-received material (Fig. 2).

Figure 2. DSC first-heating curves for resins, at a heating rate of 10°C/min. (a) C shows a single peak; (b) D shows a small second peak as a shoulder and; (c) A, B, E, F, and G showed double melting-peaks.

(*continued*)

COOH Endgroup Concentration

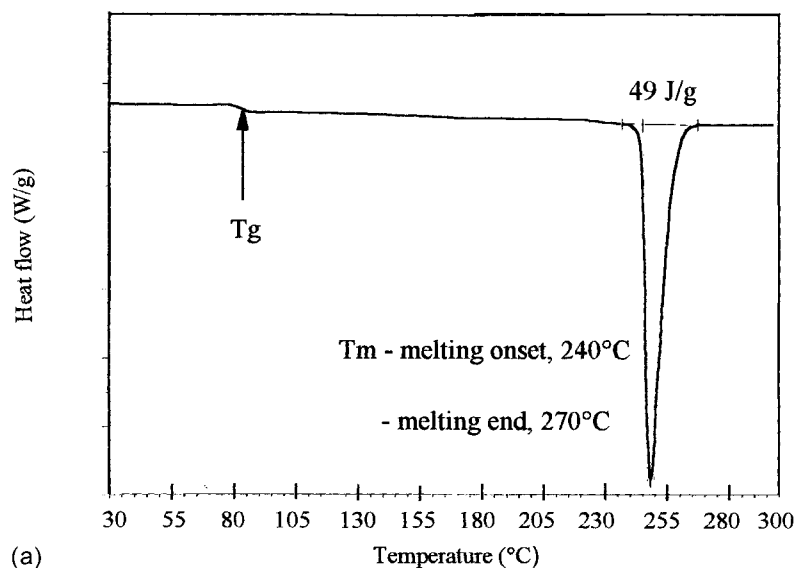The COOH endgroup content is a property usually specified for PET resins (Table 1), as it affects the degradation rate. It was measured by dissolving the PET in a 70:30 o-cresol:chloroform mixture at high temperature (boiling with reflux). After cooling, the solution was titrated with 0.05 N potassium hydroxide in an ethanol-water solution. The endpoint was determined potentiometrically using a Metrohm E 536/11 titrator.

Metal Content

The contents of three elements antimony, cobalt and phosphorus, were measured (Table 1). PET resins generally contain the residue from the polymerization catalyst. The residual metals arising from the catalyst affects the thermal stability, AA regeneration and crystallization rates. Antimony trioxide or antimony triacetate is currently the most commonly used commercial PET catalyst. Phosphorus comes from an additive such as phosphoric acid that is added as a melt stabilizer during polymerization, in order to reduce thermal degradation. Cobalt acetate is often used as a bluing agent during the melt polymerization. The PET samples were digested in a mixture of nitric acid and perchloric acid. The metal content was then measured by atomic absorbtion.
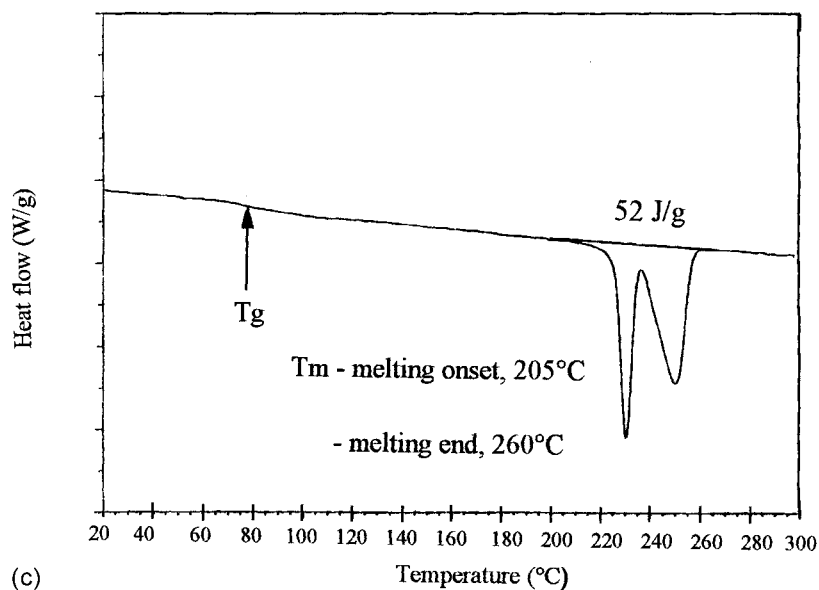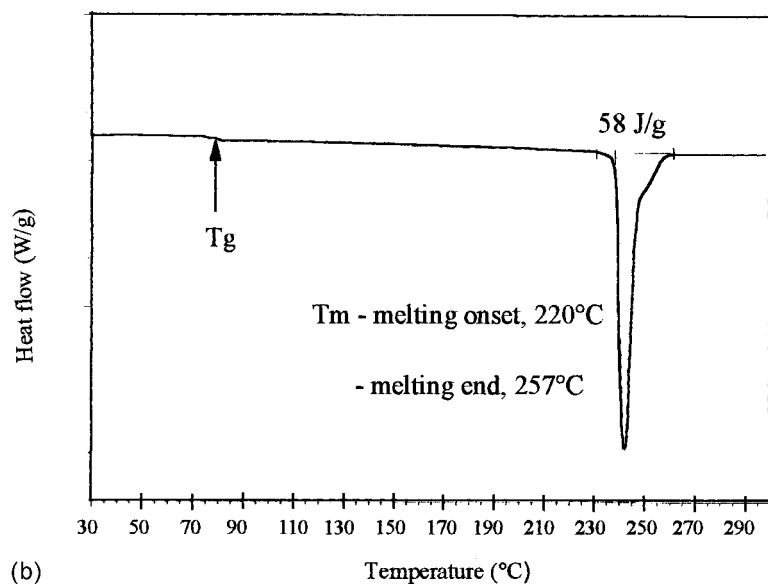
(b)

(c)

Figure 2. Continued.

Injection Molding of Preforms

The AA regeneration of different resins was compared by examining preforms molded under identical injection-molding conditions. We cannot consider AA in isolation, as we need to also check whether other preform properties are acceptable. Hence, among the important properties that will be

monitored (besides the AA) are the I.V. drop and the temperature for clearance-of-haze in the preforms.

The resins were dried in a Piovan dryer that was attached to a Husky LX160PT preform injection-molding machine. Injection was started only after 5 h of drying. The drying program had the following temperature ramp: 120°C for 1 h, 150°C for 2 h, 180°C for 2 h. The dew point of the dehumidified air was −43°C.

Preforms (32 g hyperstretch design, with a 28 mm Obrist 3 start neck finish from Husky) for 1.5 L water bottles were made from each resin. There were only two cavities in the mold, which meant that each shot produced two preforms.

The Husky injection unit used a special screw-and-plunger design (Fig. 3a). In the usual injection-molding machines, the reciprocating screw is used for both the plastification and injection functions. In Fig. 3a, the rotating screw is used only for plastification; the melt is transferred to

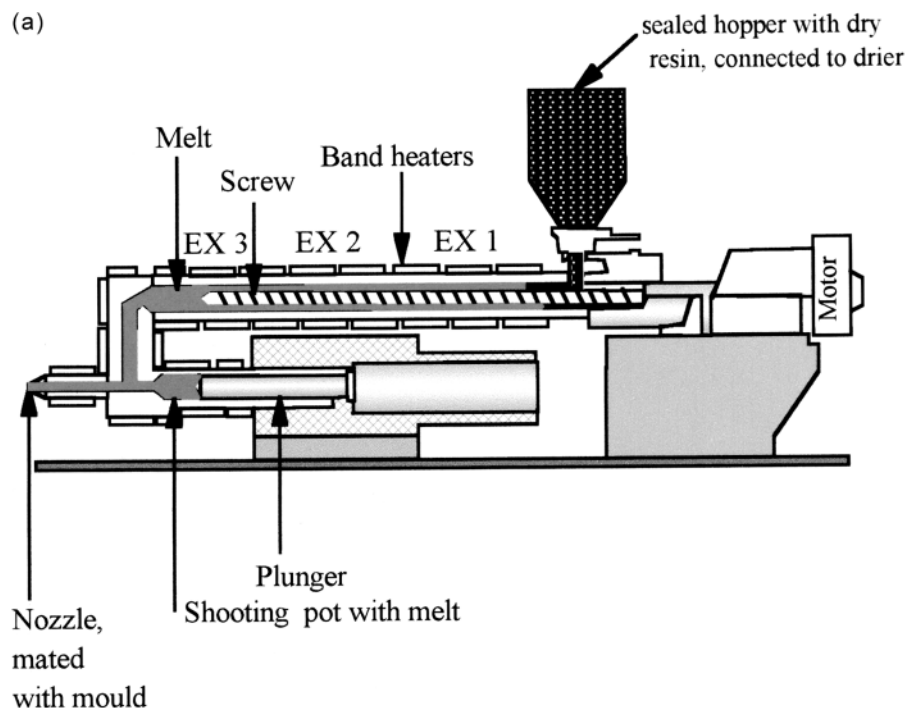*Figure 3.* (a) Injection molding machine with plasticating screw, shooting pot, and plunger, specially designed for producing PET preforms with low acetaldehyde; (b) extruder segments of the Husky laboratory machine: flat temperature-profile. EX 1−3 are the three extruder segments, SPH is shooting-pot head, BHE is barrel head extension, SP 1 and SP 2 are shooting-pot segments, DIS is distributor valve, and N/A is nozzle adapter.
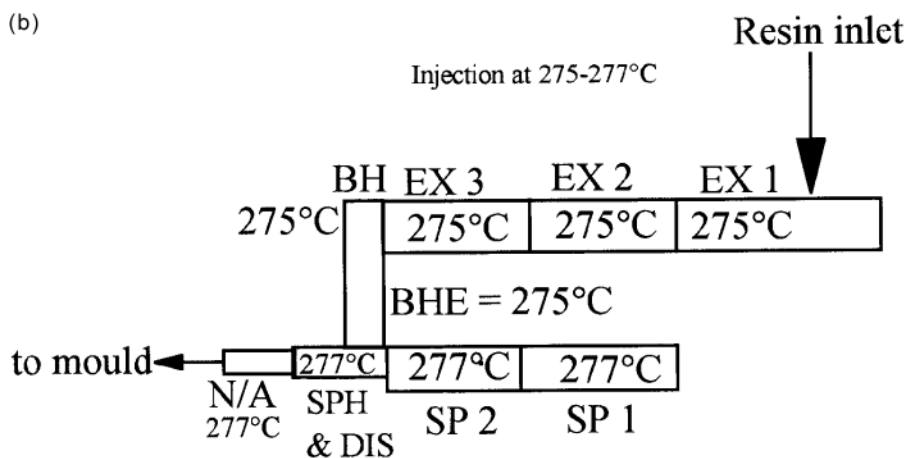
(b)

Resin inlet

Injection at 275-277°C

Figure 3. Continued.

a shooting pot, and a separate plunger injects it into the cavities, via hot-runners. This type of two-stage injection unit is specially designed to reduce AA and is adopted in the best production machines for PET preforms. The melt is injected over water-cooled core pins. The preforms were withdrawn when sufficiently solid and transferred to a robot-driven, water-cooled take-off plate for further cooling. This reduces the cycle time and hence the preform acetaldehyde. The preforms were discharged onto a conveyor belt from the take-off plate. Attachments to the Husky (apart from the Piovan resin dryer) included a Fasti mold-dehumidification unit, to prevent condensation in the mold and over the water-cooled core pins.

The dominant AA-controlling variable is the injection temperature, and its effect was explored for each resin. For studying the relative performance of the resins, it was convenient to use a flat temperature-profile (see Fig. 3b which gives a diagram of the extruder heater-segments and the flat temperature-profile used in this work). When we refer for example to an injection temperature of $275-277°C$ in the text, the temperature profile of the extruder segments (Fig. 3b) is as follows:

Resin inlet temperature $= 154°C$, EX $1 = 275°C$, EX $2 = 275°C$, EX $3 = 275°C$, B/H $= 275°C$, BHE $= 275°C$, SP1 $= 277°C$, SP2 $= 277°C$, SPH $= 277°C$, DIS $= 277°C$ and N/A $= 277°C$, MN1 $= 275°C$, S/B $= 275°C$.

(Note: EX 1-3 = extruder segments, B/H = barrel head, BHE = barrel head extension, SP = shooting pot segment, SPH = shooting-pot head, DIS = distributor and N/A = nozzle adaptor, MN is mold manifold. For other injection temperatures X°C to (X + 2°C), replace 275°C by X°C for EX1, EX 2, EX 3, B/H and BHE, and put X + 2°C for SP1, SP2, SPH, DIS and N/A).

The injection temperature was raised in 2°C steps from the lowest extrusion-temperature ($\sim$258$-$260°C) till 298$-$300°C. Injection was allowed

to stabilize at each temperature for 20 min after which 30 preforms were collected for analysis, before the temperature was raised again. For blowing trials, 300 preforms were collected at a single injection temperature (275−277°C). For plotting the graph of AA vs. temperature (Fig. 5), the midpoint value of the temperature setting was used; for example, 275−277°C is taken as 276°C on the temperature axis.

The other injection-molding parameters that affect AA (screw back-pressure, screw speed, cycle time, screw and plunger melt-cushions) were optimized and kept constant. The settings were: screw back-pressure = 400 bars; mold-cooling water temperature = 7°C; and cycle time = 14.2 sec.

Stretch-Blow-Molding Parameters for Making 1.5 L Bottles

The blowing behavior of the 32 g preforms was tested by converting the preforms into 1.5 L bottles using a SIDEL SBO1 Labo laboratory stretch-blow molding machine. The 1.5 L bottles had a ribbed-wall design, typical of water bottles; the ribbing confers stiffness and resistance to squeezing. The machine ran at 1200 bottles/h. A rate of 1200 bottles per hour per mold is considered currently as the "super productivity" category in the two-stage process for making bottles. This is the same speed at which preforms are fed to the mold in commercial machines. Hence, our SIDEL SBO1 Labo machine can simulate the production machines. A preform unscrambler was attached to the machine to supply preforms in the right orientation. The machine had two modules of powerful infrared heaters. The first module was not regulated. The second heater module had 10 lamps that could be regulated individually (see Fig. 4a). In addition, there was a fan for distributing the heat evenly by forced convection. Without the fan, there would be hot spots on the surface of the preforms. An infrared camera placed at the exit of the oven could read the surface temperature of the preform (at a fixed spot), and this was used by the machine to regulate the temperature to the selected constant setting (Fig. 4b). The preforms were blown with the aid of a stretch rod, and compressed air. The bottles were blown with compressed air at a pressure of 35 bars. Usually, a compressor delivers the pressurized air in commercial production. Here, we used a bank of air cylinders. This is satisfactory for short running times (for blowing about 300 preforms).

The preforms from all the resins could be made into clear 1.5 L water bottles, under some attainable processing conditions. However, the width of the blowing window differed according to resin. The method to establish the process window was to seek first the conditions for optimum, clear bottles with good material distrbution. An example of the parameters needed in the SIDEL machine is shown in the Tables 2 and 3 for preform A. After this, trials were conducted, gradually lowering the preform setpoint-temperature on the SIDEL machine till we obtained pearlescence (stress whitening) at the
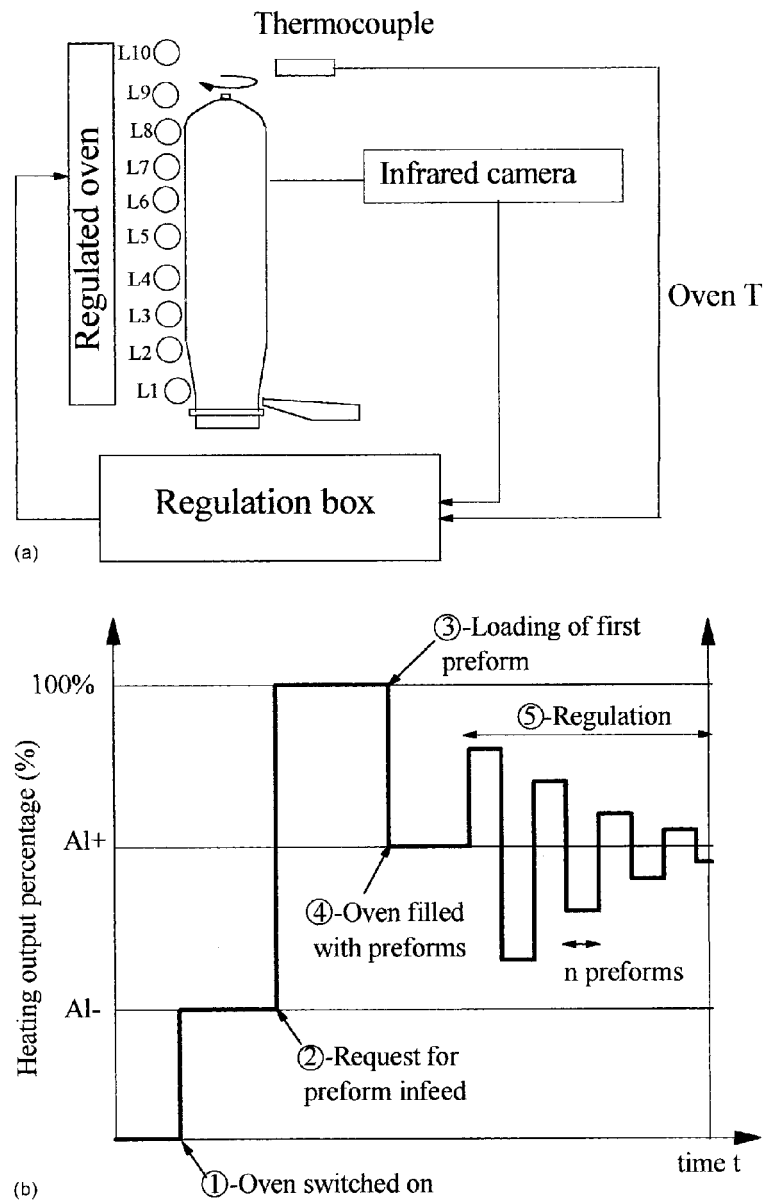
Figure 4. (a) Heating of preforms by infrared lamps L1 to L10 in the SIDEL machine, and principle of regulation; (b) the heater output of the SIDEL machine, showing the sequence as a function of time: (1) when the oven is switched on, the heating output percentage is Al−; (2) on request for preform infeed to the oven by the operator, the power turns up to 100%; (3) after loading of the first preform, the heater output % is lowered to Al + ; and (4) the power is cyclically adjusted every n preforms till the preform temperature measured by the infrared camera when the preform exits from the oven becomes equal to the set-point temperature. See Table 2 for example of values for Al +, Al−, n, and set-point temperature.

Table 2. Example of Heating Parameter Settings for Obtaining Clear 1.5 L Bottles from 32 g Preforms of Resin A, Using the Sidel SBO 1 Labo Machine; Lamp L1 Is Near the Neck of the Preform; Lamp L8 Is at the Bottom of the Preform (see Fig. 4a); Lamps L9 and L10 Are Not Needed for the 32 g Preform; For a Preform Set-Point Temperature of 115°C, Al− = 40%, Is the Standby-Oven Percentage Power; Al+ = 65% Is the Production Start-Up Percentage Power; Frequency of Heating Correction n Was After Every 5 Preforms (See Fig. 4b)

Lamp	Heater Module 1 (Unregulated)	Heater Module 2 (Regulated), Lamp Heating Power = Al+ (%) * L%, See Fig. 4
L1	On	78%
L2	Off	78%
L3	Off	75%
L4	Off	70%
L5	Off	70%
L6	Off	58%
L7	Off	67%
L8	Off	85%
L9	Off	Off
L10	Off	Off

base of the bottle. Pearlescence occurs when the stretching temperature is too low. After pearlescence was obtained, the preform temperature and the power setting were increased till clear bottles were reobtained. The preform temperature where the pearlescence just cleared was regarded as the lowest operable temperature to obtain clear bottles. The preform temperature was increased further and this eventually led to collection of polymer at the bottle base. Going to still higher temperatures resulted in haze in the preforms when

Table 3. Other Blowing Parameters for 32 g Preforms in the SIDEL Machine

Parameter	Value
T_{ps}, preblowing time (sec)	0.45
T_s, blowing time (sec)	1.14
T_d, air exhaust time (sec)	0.49
$T_{Process}$ (sec) = Tps + Ts + Td (sec)	2.08
Stretch-rod speed (m/s)	1.2
Bottles/hour	1200
Preblow pressure (bars)	6.5
Full-blow pressure (bars)	35

Table 4. Correlation of Top-Load Strength with Preform I.V. and Blowing Temperature

Bottle	Blowing Temperature (°C)	Top-load Strength (N)	Preform I.V. (dL/g)	Comments
A	111	128.5	0.758, medium	clear
A	115	125.6	0.758, medium	clear
A	120	115.8	0.758, medium	clear
B	115	125.6	0.731, medium	clear
C	120	132.4	0.792, very high	clear
D	110	122.6	0.688, low	clear
D	120	103.9	0.688, low	slight haze
E	115	126.5	0.766, high	clear
E	120	119.7	0.766, high	clear
F	107	121.6	0.657, very low	clear
G	120	123.6	0.825, very high	clear

they exited the oven, and this led to haze in the bottles. The haze occurs due to cold crystallization. The onset of haze will be regarded as the upper limit for blowing. In this way, it was possible to measure a blowing window for clear bottles, the low end being the temperature where pearlescence occurred (due to cold stretching), and the high end being where haze appeared (due to cold crystallization).

Bottle Top-Load Strength

Unlike CSD bottles, for water bottles, high burst-strength, and high resistance to creep and stress-cracking are not necessary. However, the top-load strength should be sufficient to withstand the stacking of bottles on top of each other in a warehouse. The top-load strength was tested using a Mecmesin top-load tester for bottles, using a speed of 25 mm/min for the moving cross-head. The moving cross-head loads the bottle vertically by driving down on the bottle neck. The force at the crush, or buckling point of the bottle was determined and taken as the top-load strength. The top-load strengths for the bottles from the various resins and the relation to blowing conditions are indicated in Table 4. The values are the average of 5 readings.

RESULTS AND DISCUSSION

Resin Properties

Table 1 shows the characterization of the resins in this study. The I.V. is a major property of PET resins. Although the I.V. is predominantly determined by the polymer's molecular weight, there is a dependence on solvent and temperature as well.[8,9] With PET, there are several methods of

I.V. measurement (different solvents and temperatures) and hence cross-comparison of I.V.s based on manufacturers' data sheets is difficult and was avoided. The I.V.s for the same polymer measured in different solvents can differ by up to 0.15 dL/g. As all the I.V.s were measured for this work using the same method, the values in Table 1 can be compared. Most water-grade resins typically have an I.V. of 0.75 dL/g (Table 1) compared with CSD grades which have higher I.V.s (0.82 to 0.85 dL/g). In Table 1, we have specially included some water-resins with unusual I.V.s; for example, resin D has an I.V. as low as 0.69 dL/g while resin C has a high I.V. of 0.82 dL/g. The only non-water grade in Table 1 is the very high I.V. Resin G.

Modern PET bottle resins are usually copolyesters, with the most common comonomer being isophthalic acid (Fig. 1b). Resin D is a CHDM copolyester (Fig. 1c). Resin C is a homopolyester (Fig. 1a). The comonomer contents are shown in Table 1.

The melting behavior of the resins showed differences, and we thought this might also influence processing and hence the AA in the preforms. Some resins such as C had a single melting-peak on first heating (Fig. 2a); others such as D had a peak with a shoulder (Fig. 2b), while A, B, E, F and G had what appears like distinctly double melting-peaks (Fig. 2c). In the first case, melting occurred over a narrow range of ~30°C, instead of ~55°C (compare Figs. 2a and 2c); at a heating rate of 10°C/min, resin C (Fig. 2a) melted over a 30°C range between 240−270°C. Note the high melting temperature of resin C − one reason for this is the fact that it is a homopolyester. Resin D (Fig. 2b) melted over a 37°C range; melting started at a lower temperature of 220°C and was complete at a low temperature of 257°C. This is consistent with a low I.V. copolyester (Table 1). Resins E, B, F and G (Fig. 2c) melted over a 55°C interval with a double-melting endotherm; melting started as low as 205°C and was complete by 260°C. Note that these are first heating scans of the as-received resin before the polymer was placed in the drier.

All the resins examined used antimony-based catalysts. The maximum permissible level of antimony metal for bottle resin is 250 ppm. The resins in Table 1 show that the usual level is about ~200 ppm, but resin C had an exceptionally low level of 130 ppm.

The carboxyl-endgroup content reflects the degradation the resin has been subjected to during manufacture, as well as its degradative potential. The carboxyl content of bottle grade resins is generally low, below about 25 mVal/kg. Resin D is at the low end of the range. Resin E has an unusually high COOH content (43 mVal/kg, Table 1).

Preform Properties

Figure 5 shows the preform AA as a function of injection temperature. Before we examine the AA correlation between resin and preform, we need to

mention the contributing factors to AA from the injection-molding process itself. An early work by Leigner is very informative[6] about machine settings and their effect on AA. The processing factors that control preform AA are the following: injection temperature, the barrel temperature-profile (not mentioned by Leigner), screw back-pressure, screw and plunger cushions, screw rotation-speed and cycle time. Of the above factors, the injection temperature is by far the most dominant, in terms of AA.

Leigner's work was conducted with a conventional machine having just the screw for plastification and injection. We mentioned that the machine design also plays a role in the level of AA in the preform as AA is generated both by thermal and shear-induced degradation. If the experiments had been conducted with the conventional type of machine, the curves in Fig. 5 would be higher (even by a factor of 2 times) although the relative trend between resins would be maintained.

Since we are interested in examining primarily the AA regeneration from the resin point of view, we have concentrated on the effect of injection temperature while the other factors like back-pressure, screw speed, melt cushions and cycle time were optimised and kept constant. Any differences (AA, haze, I.V. drop) observed then in the preforms from various PETs directly reflects intrinsic differences in the resins.

From Fig. 5, it can be seen that there is an exponential increase in AA with temperature, for all resins. The dissolved AA (or residual AA left in the chips from the polymerization before melting) was <1 ppm in *all* cases
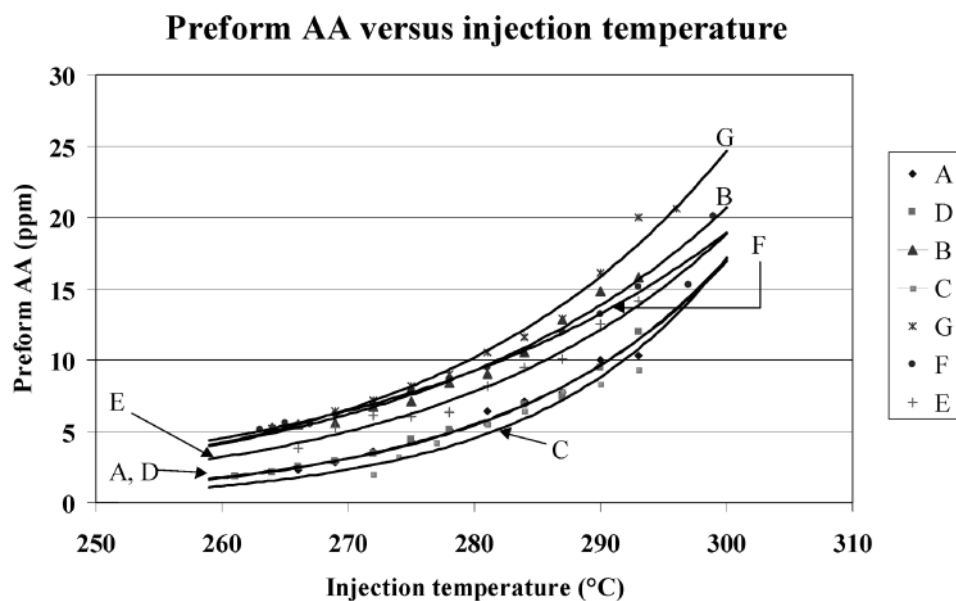

Figure 5. Preform AA vs. injection temperature for resins A to F.

(Table 1). However, the graph in Fig. 5 shows that there are significant differences in preform AA made from the different resins at the same temperature, keeping all other molding parameters the same. Some water resins generate nearly as high AA as found with CSD grades, and others show $\frac{1}{2}$ to $\frac{3}{4}$ of this. Clearly, the AA *regenerated on melting* varies between resins, a fact recognized by Kirshenbaum in an early work where the importance of low AA *and* low AA generation for colas was mentioned, although curves such as Fig. 5 were not shown.[1]

As expected, the preforms from the CSD grade (resin G) had the highest AA level, and of course it cannot be used for the water application. Even at the lowest injection temperature, the AA level was over 5 ppm for resin G. The I.V. drop (relative to the resin) was monitored by averaging the I.V. of 2 preforms collected at each injection temperature. For all resins, there was no significant increase in the I.V. drop with increasing injection temperature, but there were some differences between resins in this property (Fig. 6). In the preform G (Fig. 6), the I.V. drop was 0.01 dL/g and this was low. Although there are no published standards, a drop of $\sim$0.03 dL/g is considered the maximum acceptable − larger I.V. drops would lead to a deterioration of mechanical properties.

Now examining the water-grade polymers, starting with resin A, Fig. 5 shows the AA level at all temperatures is amongst the lowest. Resin A's curve overlaps with D, and only one resin, namely C, lies just below A (and D). It was mentioned that resin A had a double-melting behavior (Fig. 2c); resin D had a single peak with a shoulder (Fig. 2b) and resin C had a single, high melting-peak in the DSC (Fig. 2a). Initially, while examining many resins not described here, it was thought that there was a correlation between single-peak and double-peak melting, and AA in the preforms. However, as resins A, D and C have the lowest AA curves (Fig. 5), we can say that the differences in melting behavior shown in Fig. 2 do not in fact affect the preform AA. Fig. 6 shows that the I.V. drop in the A preforms was low (0.01 dL/g). Fig. 7 shows another important factor namely, the clearance temperature for haze in the preforms, when the injection temperature is progressively increased. Below a certain temperature, it is possible to inject preforms, but haze is present; above this temperature, clear preforms are obtained. Haze occurs due to spherulitic crystallization from the melt when the injection temperature is too low. As the melt is quench cooled in the mold, it might be asked why spherultic crystallization occurs and hazy preforms are obtained at low injection temperatures. During extrusion of PET, it is observed that below about 255°C, the screw stops turning as the melt solidifies. A few degrees above, it is possible to extrude but the melt is hazy because of incomplete melting. Injection in this regime leads to hazy preforms. Raising the temperature further leads to clearance of the haze in the melt, and hence clear preforms are obtained. Obviously, given the exponential dependence of AA on temperature (Fig. 5), the lower the clearance temperature for haze, the
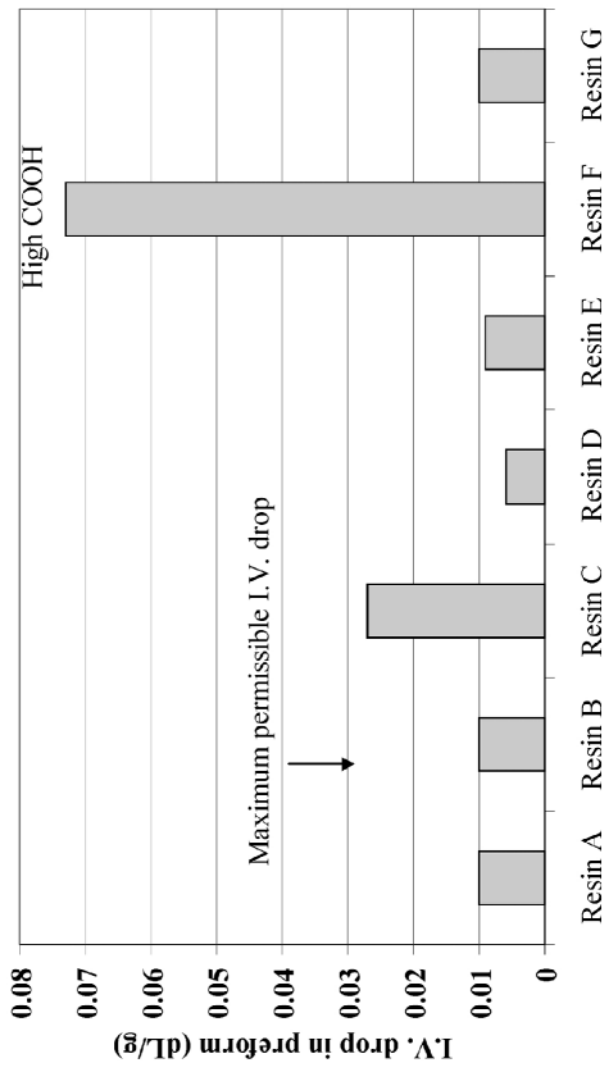
Figure 6. The I.V. drop in preforms after injection. The I.V. drop should be no more than ~0.03 dL/g. Only Resin F exceeds this and it is because of its high COOH content; all other resins are satisfactory.
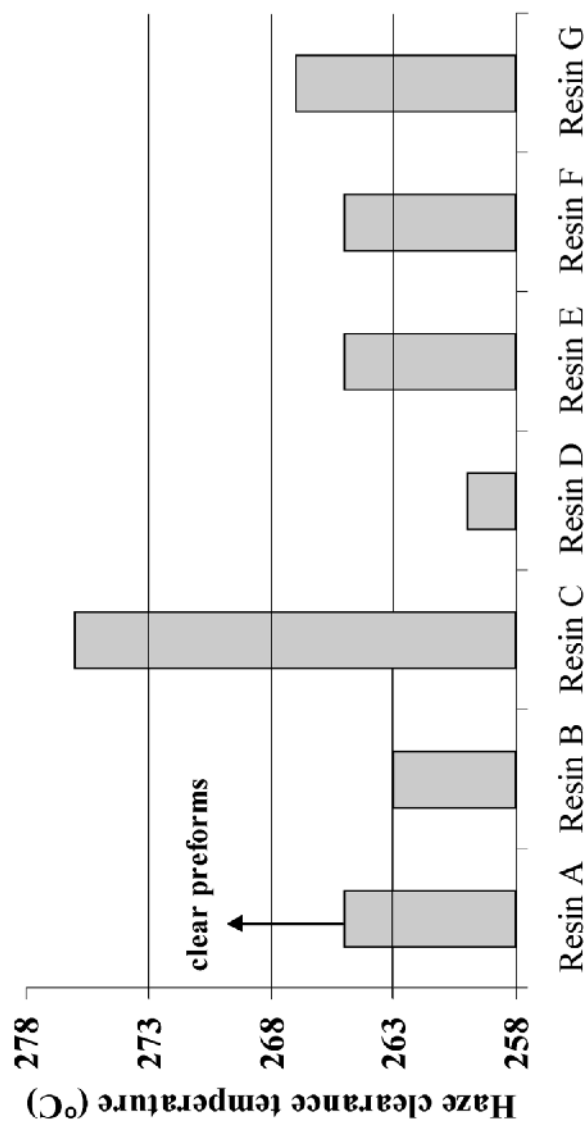
Figure 7. The temperature for clearance-of-haze in the preforms, as the extrusion temperature is increased. The melt can still be extruded in the regime shown by the bars, but the preforms show haze. Below 255°C, the melt soldifies and the screw is not able to turn. The lower the haze-clearance temperature, the better, as it reduces AA. Resin D is the best, and C is the worst as it requires high temperature injection to obtain clear preforms.

better, as low temperature injection is the best way from the processing side to reduce the acetaldehyde. The onset of haze in preform A was below 265°C (see Fig. 7). If we consider all three factors − low AA generation, low I.V. drop and low temperature operability − resin A is very good for water.

Resin B gave a relatively high AA at all temperatures (see Fig. 5). Although the curve lies below the CSD resin G, B cannot be considered a good water-grade. The resin I.V. of B (0.741 dL/g) is in fact lower than that of A (0.767 dL/g). The I.V. retention of B was as good as A (I.V. drop 0.01 dL/g, see Fig. 6). The clearance temperature for haze was 263°C (Fig. 7), so the lower resin-I.V. of B compared with A allows a lowest injection-temperature that is 2°C less than for A. But in terms of AA generation, resin B behaves almost like a CSD grade. This suggests that just lowering the resin I.V. is not sufficient for low AA in the preforms; although it allows a lower injection temperature, this does not compensate sufficiently if the intrinsic AA regeneration rate is high. It can be seen from Fig. 5 that having low I.V. allows the data points to extend to lower temperatures, but generally the high AA curves like B do not drop below the low AA curves such as A at the low-temperature end.

Resin C is an interesting PET that has the I.V. of a CSD grade (0.819 dL/g). The average I.V. drop in preforms (0.027 dL/g) was within the acceptable limit (Fig. 6). Compared with all the other resins in this study, the striking feature of this polymer was that it crystallized much faster. The clearance temperature for haze was 276°C (see Fig. 7) and this was the highest of all the other polymers. Whereas with the other resins, clear preforms could be obtained as low as 264−266°C, with C, even at an injection temperature of 271−273°C, in fact completely opaque preforms were obtained (see Fig. 8). With all the other resins (which were copolyesters), although hazy preforms were obtained at low injection temperatures, completely opaque preforms could not be made. There are two factors about resin C that should slow crystallization relative to most of the polymers in Table 1 − its I.V. is on the high side and the metal content is unusually low. Yet, the crystallization rate for C was in fact the fastest. The reason for this can be seen from the resin analysis data in Table 1. Resin C has 0% IPA, 0% CHDM (Fig. 1a) and hence must be a homopolyester. Generally, the homopolyester has a faster crystallization speed than copolyesters (10).

However, the most surprising feature of C is that the AA in the preforms was low, despite the high I.V. and higher injection temperatures needed because of the high clearance temperature for haze. In Fig. 5, the AA curve of C is in fact the lowest, lying slightly below the best copolyesters A and D. With resin C, the AA level at an injection temperature of 271−273°C was 2.0 ppm, whereas with resin A, 2.0 ppm was not obtained even at an injection temperature of 265−267°C. It seems that the intrinsic AA generation in the melt is much lower for C, so much so that it can produce low AA

Figure 8. Resin C is a homopolyester that crystallises fast and its haze-clearance temperature is high; (a) transparent preform molded at 274−276°C; (b) lowering the injection temperature to 272−274°C makes the preform completely opaque.

preforms at higher temperatures. It also goes to prove that the final resin I.V. is not a controlling or even dominant factor for a good water-grade. If it was not for the speed of crystallization (Fig. 8), this resin would have been the best for water bottles, on the ground of low AA regeneration.

Resin D which was a CHDM containing copolyester (Fig. 1c) had the best *all-round* performance. As remarked, an exceptional feature of D is its extremely low I.V. It also had the lowest I.V. drop in the preforms (0.006 dL/g, see Fig. 6). Its low crystallization rate gave it the greatest processing width. Clear preforms could be obtained at temperatures as low as 263−265°C. Generally, very low I.V. increases crystallization rate, but Sakellarides has shown that CHDM is a more effective comonomer than IPA in slowing crystallization (10), even when added at lower levels (see Table 1). Due to the slow crystallization of D, haze appeared only at temperatures as low as 260−262°C. The acetaldehyde curve for preform D overlaps completely with resin A, the only difference being that the injection for D can extend to lower temperatures.

Coming to resin E, the starting I.V. was 0.776, which is intermediate (Table 1). The I.V. drop in the preforms was low (0.01, see Fig. 6) and the clearance of haze in the preforms was at 265−267°C (Fig. 7). Both these factors are satisfactory, but the AA curve for resin E (Fig. 4) lies in the

middle of the range − that is, while it is better than a CSD resin, it is still not a good water-grade.

Finally, we come to resin F. The AA values of the preforms from this resin lie just below the CSD resin G (Fig. 5). Again, the AA curve proves that the low I.V. of resin F (0.73 dL/g) does not help by itself to produce low AA in the preforms. Clearly, the advantage of having low I.V. cannot offset the disadvantage of an intrinsically high AA regeneration rate. At the low temperature end (Fig. 5), the high AA curves of low I.V. resins like F and B do not drop below the low AA generating resins like A, C and D. Another striking feature of resin F is that it showed the biggest I.V. drop of all the polymers (0.073 dL/g, see Fig. 6). Inspection of the resin properties (Table 1) reveals that it has an unusually high COOH endgroup content (42.6 mVal/eq). The typical values for COOH concentration lie between 15−25 mVal/eq (Table 1). Generally, high COOH content leads to poor I.V. retention after melting. This will have consequences for the mechanical properties of the bottles.

Factors Controlling AA Regeneration on Remelting

The resin properties in Table 1 do not show any obvious correlation with preform AA. Although we could not establish the exact reasons for the differences in AA generation in these commercial resins, it is worth examining possible causes. Thus, we searched the literature for the degradation chemistry that leads to AA generation in the PET melt. One of the latent sources of AA is the vinyl-ester endgroup …-OOC-Ar- COO-$CH=CH_2$.[2,6] These endgroups arise from thermal scission of the chain in the melt.[2,6] The vinyl-ester endgroup can react with a hydroxyethyl endgroup $HO-CH_2-CH_2-OOC-Ar-COO-$…, reforming the chain and eliminating AA.

PET bottle resin is made by a two-step (melt and solid phase) polymerization procedure. The melt and solid-state polymerization conditions (reaction temperature and reactor residence time) determine the vinyl-ester content. The melt-phase polymerization is conducted at temperatures between 275°C to 285°C, for residence times varying between 6−8 h. Melt polymerization yields an amorphous polymer precursor in the form of chips. The higher the melt-polymerization temperature, and longer the residence time, the greater is the vinyl-ester-endgroup content in the amorphous precursor. These chips have an intermediate I.V. of 0.60−0.65 dL/g and a high residual AA (∼50 ppm). This is then polymerized further in the solid-state at 200−220°C, thereby raising the I.V. to the final value (typically ∼0.75 dL/g for water grade) and reducing the residual AA to <1 ppm by diffusing it out of the chips. Some of the vinyl-ester chain-endgroups still remain in the final polymer chain (after solid-state polymerization) and these can react with

hydroxy ethyl chain-endgroups when remelted during injection molding, with AA elimination.[6]

Thus, we think that the key to lowering AA generation is to minimize the vinyl-ester content in the amorphous precursor and the final resin. As these were commercial resins, we do not have information on the properties of the amorphous precursor made by melt polymerization; these cannot be obtained from a post-analysis of the final resin (Table 1) obtained after solid-state polymerization. We are exploring the connection between AA regeneration and polymerization history by conducting laboratory scale melt and solid-state polymerization. Preliminary results confirm this link.

Stretch-Blow Molding Behavior of Preforms from Different Resins

AA is not formed during the stretch-blow-molding operation; in fact, it decreases due to the increase in surface area, when the preform is converted to the bottle. However, other preform properties apart from AA content need to be satisfactory for the success of the stretch-blow-molding. We need to examine how the resin formulation affects the blowing behavior. The 32 g preforms from resins A−G were stretch-blow molded into 1.5 L bottles. The ease of processing (width of the blowing window) and comparison of the top-load strengths of the bottles will be made. In particular, we are interested in knowing how low in I.V. we can go before we start to compromise the mechanical properties too much.

The blowing windows for each resin are shown in Fig. 9. It was found that the preform from the CHDM copolyester D had the widest window of ∼10°C. Preform D had a low I.V. (0.688 dL/g) and so could be softened at a low temperature. The lowest temperature for blowing clear bottles was 110°C; below this pearlescence appeared (Fig. 9). At 120°C, the bottles showed a slight haze (due to haze appearing in the preforms after exiting from the oven).

Resin C had the narrowest processing window (118−121°C, Fig. 9). The same effect had been noticed during the injection molding of preforms with this resin. At 112°C, the bottle base and body were pearlescent and opaque. At 115°C, the bottle body became clear, but the base still showed pearlescence. Only between 118−120°C, the entire bottle was clear. At 121°C, haze started appearing in the bottle. The reason the processing window was so narrow for resin C is undoubtedly due to the fact that it was a homopolyester with high I.V. (0.82 dL/g). Spherulitic crystallization in PET can occur from two ends − from the melt and the glassy state. During injection molding, we are concerned about spherulitic crystallization from the melt initiated by unmelted crystalline nuclei; we said the crystallization rate from the melt was high for resin C because it is a homopolyester. In the blowing machine, we are concerned with cold crystallization above T_g from the amorphous state
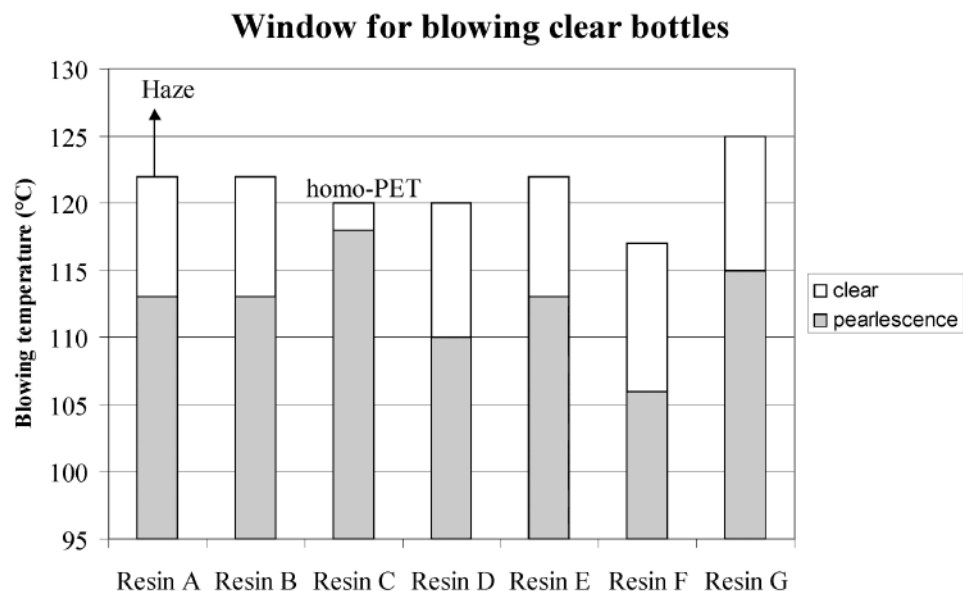
Window for blowing clear bottles

Figure 9. Temperatures for the appearance of pearlescence in the bottle (preform is too cold) and the appearance of haze in the bottle. In between, is a window for clear bottles. The co-polyesters all showed a comfortable window ($\sim$7$-$10°C wide) for obtaining clear bottles. However, the homopolyester C showed an excessively narrow window of just 2°C.

(the preform). Clearly, in this state also the homopolyester will crystallize faster than the copolyesters. Thus, an additional problem with resin C is that the stretch-blow molding window is very narrow, which could cause problems in production machines run continuously, where any small temperature-fluctuations could lead to pearlescent or hazy bottles, alternating with clear bottles.

The preforms from the IPA copolyesters A, B and E were intermediate between D and C with respect to the processing window (about 7$-$10°C, Fig. 9). At 111°C, pearlescence appeared in the base of the bottles. At 115°C, optimum bottles with good material distribution and clarity were obtained. At 120°C, the bottles were still clear but some excess material started col-lecting at the base of the bottle. Still higher temperatures (122°C) led to haze in the preforms, and thus in the bottles. Preform F also achieved a $\sim$7°C window, but this was at lower temperatures because of its very low I.V. (Fig. 9).

Finally, we must mention something about the mechanical properties of the bottles, in particular the top-load strength. The top-load strength de-pends on the bottle design, but relative comparisons for the same design can be made for different resins. As resin D had an exceptionally low resin and preform I.V., there was a concern about its mechanical stiffness and top-load

strength, although for AA it was excellent. This is because low I.V. generally leads to reduced mechanical properties. Table 2 shows some revealing correlations. It can be seen that the bottle top-load strength correlates with preform I.V. and the blowing temperature. These are in turn related to the crystallinity and orientation achieved in the bottle after blowing. Generally, high I.V. and low blowing temperature increase orientation and crystallinity. High I.V. resins like C, E and G will generally give acceptable strengths over a wider range of blowing temperatures, as the orientation relaxation rate is reduced compared to low I.V. polymer. Resin C gave the highest top-load strength (132.4 N) which again arises because it is a homopolyester; incorporation of comonomers always weakens the bottle (Table 2). The medium I.V. preforms from resins A, B (Table 2) are also satisfactory. The effect of increasing the blowing temperature at a constant I.V. is shown in Table 2 for resin A: the top-load strength decreases from 128.5 N to 115.8 N, when the blowing temperature is increased from 111 to 120°C. This is because at an elevated temperature, the orientation relaxation is greater. For very low I.V. resins such as D, it is particularly important to blow near the bottom temperature of the window, just above the pearl point (110°C, Fig. 9); blowing at the upper end of the window (120°C, Fig. 9) reduces the top-load strength substantially (from 122.6 to 103.9 N, Table 2). The low I.V. PET will have shorter relaxation times, hence, low-temperature stretching should be used to promote orientation retention. Thus, for very low I.V. preforms, if one wants to maintain good mechanical properties, the blowing window has to be narrowed from the one that is determined solely on the basis of optical clarity.

Although the I.V. of resin F was not the lowest (Table 1, 0.73 dL/g)), the I.V. of preform F was in fact the lowest (0.657 dL/g, Table 2), because of the large I.V. drop. However, even with this an exceptionally low I.V. preform, an acceptable top-load strength of 121.6 N was attainable by stretch-blow molding at a low temperature of 107°C (Fig. 9).

CONCLUSION

A good water-grade PET resin should give preforms with <3 ppm of AA. At the start of this work, we thought that a low resin I.V. is the key for obtaining low AA preforms because of lower melt-viscosity, which allows reduced injection temperatures. However, the results are more complex than anticipated. The conclusions of this work are:

The injection temperature is the strongest variable for AA level in the preforms, as reported by others. As there is an exponential increase of AA with temperature, it is sensible to have a low resin I.V. as it allows low-temperature injection, thereby reducing AA.

However, a low resin I.V. does not mean a low AA in the preform will be obtained always. This work shows that a low I.V. resin can give high AA; and conversely, a high I.V. resin can give low AA in the preforms.

The AA regeneration rate at a particular temperature is an intrinsic property of the resins and it does not correlate simply with the I.V. The disadvantage of an intrinsically high AA generation in the resin cannot be compensated by a low I.V. and low temperature injection.

Thus, the optimum resin for water should have low AA regeneration *and* low I.V.

The factors that control intrinsic AA regeneration are hidden in the polymerization conditions (temperature, residence time and catalyst).

The orientation and crystallinity achieved in very low I.V. preforms $(0.68-0.72 \, \text{dL/g})$ would be very sensitive to the blowing temperature. The lowest blowing temperature that still allows optical clarity should be used. In contrast, the higher I.V. preforms show a wider temperature tolerance in terms of orientation and crystallization.

There is no AA generation during preform blowing as the operation temperatures are low $(107-120°C)$. However, the resin formulation must be such that the stretch-blow molding window is not excessively narrow. This seems to be easily attainable at least with the copolyesters $(7-10°C)$, but is problematic with the homopolyester $(2°C)$.

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