Solid-State Polycondensation of Poly(ethylene terephthalate) Recycled from Postconsumer Soft-Drink Bottles. II

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SYNOPSIS

Poly(ethylene terephthalate) (PET) taken from postconsumer soft-drink bottles was subjected to solid-state polycondensation after cutting into small pieces or after dissolution in trifluoroacetic acid, trifluoroacetic acid/dichloromethane mixture (50/50%, v/v), or nitrobenzene, and coagulation in methanol. The effect of various reaction parameters such as time and temperature of reaction (180, 200, 220, and 230°C) on intrinsic viscosity $[\eta]$ and carboxyl and hydroxyl end-group content have been investigated. The highest number average molecular weight, $\bar{M}_n = 61,400$ was obtained from PET ($\bar{M}_n = 20,300$) dissolved in nitrobenzene and solid-state polycondensated by heating under vacuum at 230°C for 8 h. The thermal behavior of solid-stated samples was studied by differential scanning calorimetry (DSC); all samples showed a characteristic double endothermal melting peak and no glass-transition temperature. The PET samples taken from the bottles without dissolution were also studied by thermomechanical analysis. The heat distorsion temperatures obtained by this analysis were in very good agreement with the two endothermal melting peaks taken by DSC. This finding indicates that in these samples the crystallites form a coherent matrix and the amorphous phase is dispersed in the voids. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) with high molecular weight has a great demand and is usually produced by solid-state polycondensation of a prepolymer and not by continuation of the melt polymerization, because longer time in the melt state causes an excessive degradation of the final product. Recently many attempts are directed toward recycling of PET bottles, which are used in secondary end use applications. Demand for recycled PET continues to be strong in the United States, but is held back by lack of feedstock. It is said that there is a capacity of up to 319,000 tons for making fiber, sheet, strapping, and molding compounds from recycled PET. But in 1993 the industry collected only 205,000 tons.[1] From this amount 164,000 tons was derived from soft-drink bottles, while the total consumption in the same year was 462,000 tons, that is, 35% recycling.

In a previous work[2] we studied the solid-state polycondensation of PET recycled from postconsumer Coca-Cola bottles. These bottles, free from their polyethylene (PE) base and cups and polypropylene (PP) labels, were dissolved first in benzyl alcohol (BA), phenol/tetrachloroethane (60/40% w/w), or o-chlorophenol (OCP) and then the dissolved PET was coagulated by the addition of methanol and subjected to solid-state polycondensation. The aim of this dissolution was to provide samples with a high surface area, which facilitates the process of postpolycondensation.[3,4] It was found that the increase of the molecular weight of PET after solid-state polycondensation depends on the nature of the solvent used. In continuation of that work we studied the solid-state polycondensation of PET bottles after dissolution in three other solvents, such as trifluoroacetic acid (TFA), trifluoroacetic acid/dichloromethane (TFA/DCM) (50/50% v/v), or nitrobenzene (NB). From all the solvents used, the best results were obtained from OCP or NB, although
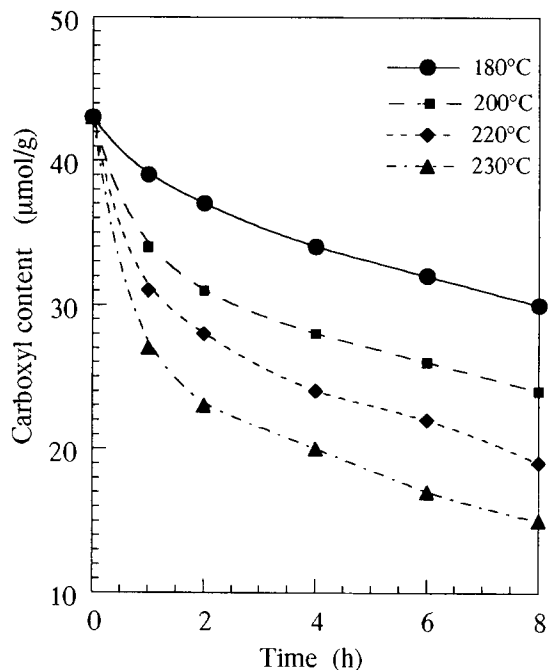

Figure 1 Variation of carboxyl content with time at various SSP temperatures for sample recovered from nitrobenzene.
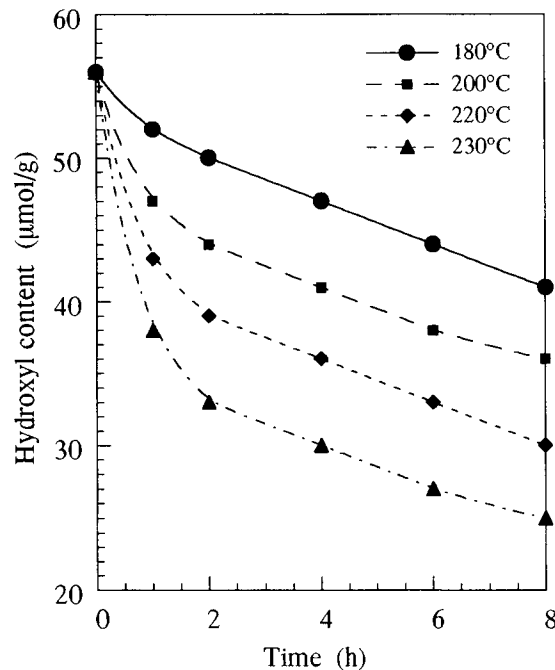

Figure 2 Variation of hydroxyl content with time at various SSP temperatures for sample recovered from nitrobenzene.

the best solvent of PET was found to be the mixture of TFA/DCM.

EXPERIMENTAL

Materials: Solid-State Polycondensation

Postconsumer PET bottles from Coca-Cola, free from PE bases and PP labels were treated as described in the previous article,[2] cut in small pieces (−0.80 to +0.40 mm), dried under vacuum at 110°C for 12 h, and dissolved in TFA, TFA/DCM (1 : 1), or NB. PET was recovered from these solutions by the addition of methanol as fibrous material in the case of TFA and TFA/DCM and as fine powder in the case of NB. Two g of PET sample were then introduced in each flask of an apparatus equipped with six flasks[2] and heated at a constant temperature (180, 200, 220, or 230°C) under vacuum (3–4 Pa). The reaction flasks were withdrawn successively from the bath after 1, 2, 4, 6, and 8 h.

Measurements

All PET samples were characterized by measurements of the intrinsic viscosity and the hydroxyl and carboxyl content. The viscosity measurements
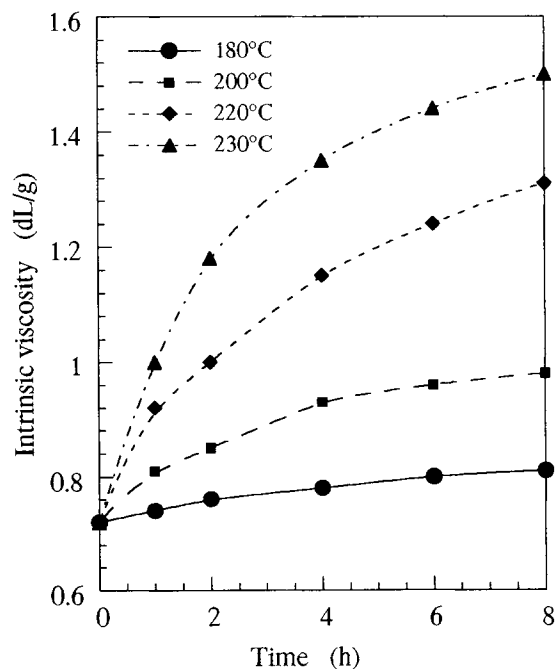

Figure 3 Variation of intrinsic viscosity with time at various SSP temperatures for sample recovered from nitrobenzene.
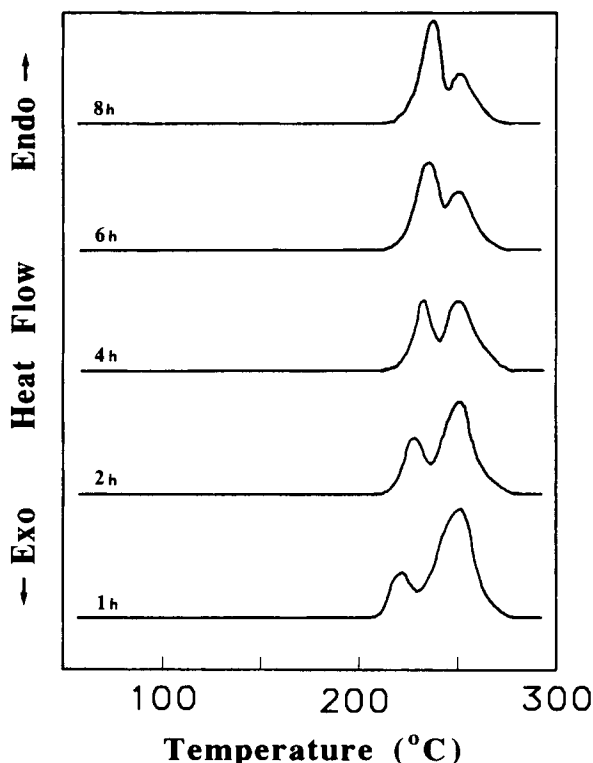
Figure 4 DSC melting behavior of SSP blank films at 200°C as a function of the reaction time.

were conducted at 25.0 ± 0.1°C in an Ubbelohde-type viscometer on solutions in 60/40% w/w, phenol/tetrachloroethane (P/TCE) at a polymer concentration of 0.25% w/v; The intrinsic viscosity was then calculated by using the Solomon–Ciuta[5] equation of a single point measurement.[6-8] The number average molecular weight ($\bar{M}_n$) of the samples was calculated from [η] values using the Berkowitz[9] equation and also from the end-group content of the samples. The carboxyl end-group content was determined according to Pohl's method,[10] and the hydroxyl end-group content according to the method proposed by Zimmermann and Kolbig[11] and reported also by Weisskopf.[12]

The thermal behavior of SSP samples (8 ± 0.1 mg) was studied using a differential scanning calorimeter, DSC-2 (Perkin–Elmer) at a heating rate of 20°C/min. The thermomechanical analyses (TMA) were performed on a Perkin–Elmer thermomechanical system, TMS-2, at a heating rate of 5°C/min, and load on the probe 50 g/mm².

RESULTS AND DISCUSSION

PET is generally insoluble in most common organic solvents at room temperature, and a slight solubility

appears in certain solvents, such as BA, P/TCE mixture, or OCP after heating at high temperatures.[2] In this work the solubility behavior of PET was studied in TFA, TFA/DCM, or NB; the results obtained are shown in Table I. Although TFA showed very good results (relatively high solubility of PET, 11% w/v, high recovery yield, 99%, and low relatively dissolution temperature, 70°C), it caused a degradation of the PET. The $\bar{M}_n$ of the recovered PET was decreased from 20,300 to 17,000 (Table I). This effect could be attributed to an acid hydrolysis reaction caused by the moisture of TFA (water content < 0.05%). However in such a case both hydroxyl and carboxyl content would be increased. On the contrary, the sample treated with TFA showed a higher hydroxyl content (72 μmol/g) than the untreated PET (58 μmol/g), and the carboxyl content remained about constant (45 and 43 μmol/g, correspondingly). The decrease of $\bar{M}_n$ could then be attributed to a transesterification reaction between the PET molecules and methanol, occurring during the precipitation of PET from its hot solution by the addition of methanol. According to this reaction only the hydroxyl content of PET is expected to be increased.
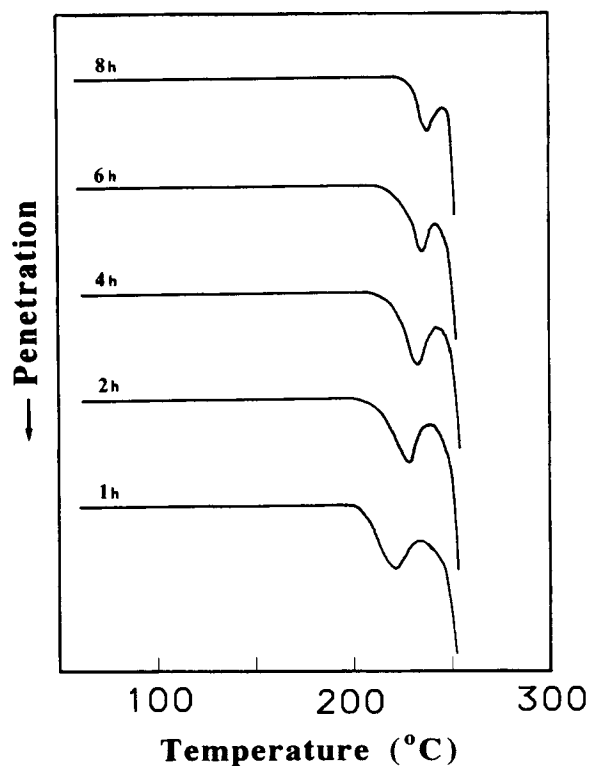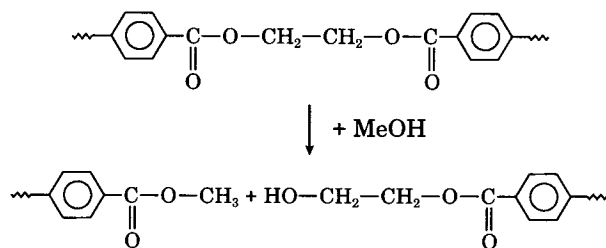

Figure 5 First derivative penetration traces of SSP blank films at 200°C, obtained at a heating rate of 10°C/min and load on the probe 50 g/mm².

When the TFA/DCM (50/50, v/v) mixture was used as solvent, the solubility was better (12.5% w/v), the recovery was quantitative (100%), and the dissolution temperature very low (35°C). The latter assures the nondecomposition of the PET sample. According to these data the TFA/DCM mixture is the best known solvent for PET until now. When NB was used low solubility (6.7%) and high dissolution temperature (180°C) was observed, but surprisingly the samples obtained from the NB-methanol system proved to be the most suitable for solid-state polycondensation.

The PET samples obtained after dissolution in TFA or the TFA/DCM mixture were fibrous but those from NB were fine powder. The DSC thermograms of all samples did not show the presence of a glass-transition temperature indicating that these are highly crystalline. If these samples were amorphous a more effective postpolycondensation reaction could take place. But, when amorphous PET is heated above its glass-transition temperature spontaneous crystallization occurs rapidly in the temperature range 140–220°C with 50% of the resulting crystallinity developing in "less than 30 seconds."[13] The PET sample recovered from a TFA/DCM solution was reported to be 40% crystalline.[3]

PET samples, after solid-state polycondensation, were characterized by determination of intrinsic viscosity and the carboxyl and hydroxyl group content. The results obtained for PET heated at 230°C are presented in Table II. The $\bar{M}_n$ calculated from the carboxy and hydroxy group content was not found to be in good agreement with those calculated from intrinsic viscosity for the samples recovered from TFA or TFA/DCM solutions. The former was always lower than the latter. An analogous deviation was also noted when BA was used as solvent.[2]

Examining the decrease of carboxyl and hydroxyl content of the blank sample with time at various temperatures of solid-state polycondensation, it is shown that $\Delta(COOH)_t$ is equal to $\Delta(OH)_t$ at 180, 200, and partly at 220°C; at 230°C the $\Delta(COOH)_t$ was less than $\Delta(OH)_t$. These results indicate that in this sample the main reaction up to 220°C is the esterification, but both esterification and transesterification take place at 230°C. Analogously it was observed that in the sample recovered from TFA the transesterification also takes place at 230°C but at a limited extent: in those recovered from TFA-DCM or NB, only the esterification occurs, even at 230°C. This can be seen in Figures 1 and 2, where the decrease of carboxyl and hydroxyl content of sample recovered from NB at various solid-state temperatures are shown. The $\Delta(COOH)_t$ is about the same with the $\Delta(OH)_t$.

The difference in the behavior of samples during the solid-state polycondensation must be due rather to their different content of Sb_2O_3, which is the main transesterification catalyst used generally for the production of PET. It is reported[3] that PET loses a considerable amount of Sb_2O_3 catalyst (80–94%) after dissolution in TCA/DCM and coagulation in acetone or methanol and that the amount of the extracted Sb_2O_3 depends on the nature of the coagulation solvent. Our results showed that the latter depends also on the nature of the dissolution solvent. Rather the transesterification reaction observed in the sample recovered from TFA is due to the high hydroxyl content of this sample (72 μmol/g).

In Figure 3 one can see the gradual increase of intrinsic viscosity of samples recovered from NB af-

Table I Solubility Data of PET in Various Solvents

Solvent	Dissolution				
	Solubility (% w/v)	Temperature (°C)	Yield (%)	$[\eta]$ (dL/g)	$\bar{M}_n$
Blank	—	—	—	0.73	20,300
TFA	11.0	70	99	0.65	17,000
TFA/DCM	12.5	35	100	0.71	19,400
NB	6.7	180	98	0.72	19,800

Solubility is after heating with stirring for 15 min. Yield is the yield of the recovered PET after precipitation with methanol.

Table II Solid-State Polycondensation of Bottle PET, at 230°C

Sample	Time (h)	$[\eta]$ (dL/g)	$\bar{M}_n{}^a$	[COOH] (μmol/g)	[OH] (μmol/g)	$\bar{M}_n{}^b$
As received	—	**0.73**	**20,300**	**43**	**58**	**19,800**
	1	0.87	26,500	34	44	25,600
	2	1.00	32,900	29	38	29,900
	4	1.15	40,800	27	31	34,500
	6	1.16	41,300	23	29	38,500
	8	1.22	44,700	22	28	40,000
From TFA	—	**0.65**	**17,000**	**45**	**72**	**17,000**
	1	0.78	22,400	29	55	23,800
	2	0.88	27,000	27	51	25,600
	4	1.05	35,500	24	47	28,200
	6	1.21	44,100	23	42	30,800
	8	1.32	50,500	18	38	35,700
From TFA/DCM	—	**0.71**	**19,400**	**43**	**57**	**20,000**
	1	0.95	30,400	34	47	24,700
	2	1.05	35,500	30	43	27,400
	4	1.18	42,500	27	40	29,900
	6	1.26	47,000	26	37	31,700
	8	1.32	50,500	24	36	33,300
From NB	—	**0.72**	**19,800**	**43**	**56**	**20,200**
	1	1.00	32,900	27	38	30,800
	2	1.18	42,500	23	33	35,700
	4	1.28	48,100	20	30	40,000
	6	1.36	52,800	17	27	45,500
	8	1.50	61,400	15	25	50,000

^{a} $\bar{M}_n$ was calculated from the $[\eta]$ value.
^{b} $\bar{M}_n$ was calculated from the end-group content.

ter solid-state polycondensation at four different temperatures (180, 200, 220, and 230°C). The maximum value of intrinsic viscosity of 1.50 (8 h at 230°C) that corresponds to an $\bar{M}_n$ of 61,400 is a very satisfactory result indeed. This grade of PET could be used for industrial tire cords. The DSC measurements of solid-stated samples at temperatures between 180 and 220°C showed, except the original melting endotherm (T_{m_1}), an additional endotherm (T_{m_2}) at temperatures 20–30°C above annealing temperature (Fig. 4). When a higher temperature was used (230°C) this double peak appeared as a single one. According to the literature[14–16] the first endotherm must be attributed to the melting of the crystalline material formed during solid stating, and the second to the original crystalline material, reorganized into more perfect and larger crystals during DSC scan. According to Yagpharov,[17] there are two types of crystal formation and the presence of a premelting peak in the DSC curve is attributed to the melting of secondary crystals of the "fringed micelle" type. In order to obtain more information about this phenomenon, the thermomechanical be-

havior of some samples was studied (Fig. 5). It can be seen in that figure that the heat deflection temperatures HDT$_1$ and HDT$_2$ are in very good agreement with endotherms taken from the DSC traces T_{m_1} and T_{m_2} correspondingly (Table III), and no penetration was recorded around the glass-transition temperature $(T_g \approx 80°C)$. In contrast to other semicrystalline polymers, these heat deflection temperatures are clearly related to the melting process and not to the glass-transition temperature; that is, the penetration measurements showed that the crystallites form a coherent matrix and the amorphous phase is dispersed in the voids. This concept is opposite to that suggested for other semicrystalline polymers, where the crystallites are dispersed in the amorphous matrix and consequently the HDTs never rise above the glass-transition temperature.

CONCLUSIONS

In the frame of a PET recycling study, the solubility behavior of PET in six solvents or mixtures of sol-

Table III   Melting Points and HDTs of the Solid-State Polycondensated Blank Samples

SSP Temperature (°C)	SSP Time (h)	Melting Temperatures (°C)		Penetration Temperatures (°C)	
		T_{m_1}	T_{m_2}	$HDTs_1$	$HDTs_2$
180	1	201	252	200	252
	2	203	252	203	252
	4	204	252	204	252
	6	206	253	207	252
	8	209	254	208	254
200	1	222	251	223	251
	2	228	254	228	253
	4	233	254	233	252
	6	235	251	234	251
	8	237	251	239	253
220	1	246	246	250	250
	2	250	250	251	251

ᵃ T_m, melting temperatures determined from DSC measurements with a heating rate of 20°C/min. HDT, heat distortion temperatures determined from TMA measurements at a heating rate of 10°C/min.

vents (BA, P/TCE 60/40 w/w, OCP, TFA, TFA/DCM 50/50 v/v, or NB) was studied, aiming at the modification of PET film to a form more suitable for solid-state polycondensation. These solvents could be also used for a future separation process of PET from other plastics by selective dissolution. (e.g. PET from PE). From all the solvents used the mixture TFA/DCM was found to be the best.

Solvent dissolution, precipitation, and solid-state polycondensation was found to be an efficient process for preparing high molecular weight PET. So PET with an $\bar{M}_n$ of about 60,000 was obtained from bottle PET with $\bar{M}_n$ = 20,000 after dissolution in OCP or NB and heating at 230°C under vacuum for 8 h.

NOMENCLATURE

BA   Benzyl alcohol
DCM   Dichloromethane
DSC   Differential scanning calorimetry
HDT   Heat distortion temperature
NB   Nitrobenzene
OCP   o-Chlorophenol
P   Phenol
PET   Poly(ethylene terephthalate)
T_m Melting temperature
TCE   Tetrachloroethane
TFA   Trifluoroacetic acid
TMA   Thermomechanical analysis

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