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Modelling of PET Quality Parameters for a Closed-Loop Recycling System for Food Contact

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Summary: A rigorous process model has been developed which describes a closed-loop recycling system for PET beverage bottles. The reaction / mass transport model is aimed at the dominant quality parameters such as intrinsic viscosity, concentration of acetaldehyde, concentration of carboxylic end-groups, and concentration of vinyl end-groups, respectively. The model covers the main process steps being preform production (injection moulding), drying, solid-state polycondensation, and melt filtration. The simulation reveals that after a single recycling loop all the relevant quality parameters achieve the specification, if certain temperatures, residence times, and surface areas for degassing are provided during the recycling process. Another simulation showed the evolution of quality parameters in PET being subjected to an "infinite" number of recycling loops in a closed system. In this case, the concentration of acetaldehyde and vinyl end-groups decreases with the number of recycling loops, which is a desired effect. On the other hand, the concentration of carboxylic end-groups increases with every completed recycling loop. Higher concentrations of carboxylic end-groups make the polymer more susceptible to hydrolysis and increase the SSP process time needed to achieve the specified intrinsic viscosity for carbonated soft drink bottles. To overcome this problem, the recycled PET has to be blended with a certain amount of virgin PET in industrial processes.

Keywords: food contact; mass transfer; PET; poly(ethylene terephthalate); process model; reaction kinetics; recycling

Introduction

Poly(ethylene terephthalate) (PET) is a step-growth polymer which is formed by esterification and transesterification from ethylene glycol (EG) and terephthalic acid (TPA). PET is increasingly used to manufacture light and safe bottles for the packaging of soft drinks and mineral water.[1] Due to tightening packaging regulations, an increased quota of PET bottles is collected after usage and recycled.

Mechanical recycling comprising washing, sorting, and extrusion is a well established technology and market for the bottle to fibre recycling.[2] Nevertheless, "bottle-to-bottle" recycling is preferable due to its higher added value.[3] Recycled PET has to satisfy the requirements for bottle processing (melting temperature, melt viscosity, melt stiffness, glass transition temperature, rate of crystallization, thermal stability) as well as for food packaging (haze / transparency, colour, contamination levels below the EU and US FDA limits). Due to the required rigorous decontamination levels in recycled PET for food packaging applications,[4,5] bottle-to-bottle recycling should be a semi-chemical recycling process ("super-clean process") comprising decontamination and repolymerization to reinstall the specified molecular weight (or intrinsic viscosity, IV). By this procedure, contaminants will

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Table 1.
Typical quality parameters for recycled PET.

Intrinsic viscosity	IV	0.78 – 0.82 dL/g
Concentration of carboxylic end-groups	COOH	20 – 25 mmol/kg
Concentration of vinyl end-groups	tV	2 – 4 mmol/kg
Concentration of free acetaldehyde	AA	0.5 – 1 ppm
Colour, yellowness	b^*	$<1-3$
Melting temperature[a)]	T_m	235 – 248 °C
Content of PVC	PVC	<10 ppm
Coloured flake	CF	<50 ppm

[a)] depending on the kind and the amount of co-monomers.

be either degraded or evaporated, thus ensuring reliable decontamination of the recycled PET.

Two different technological approaches are available on the market, both meeting the requirements of decontamination and repolymerization. The first approach (flake process) is designed for decontamination and repolymerization in the solid-state. The shredded bottles ("flake") are treated solely in the solid-state. In the second approach (chip process), shredded bottles are extruded, granulated, and repolymerized by SSP. The decontamination is performed in the melt state in a vented extruder and in the solid-state, where chips of standard size and geometry (2.0 × 2.0 × 2.5 mm) are treated.

This paper considers the first type of semi-chemical recycling processes (flake process, mechanical recycling with upgrading). The development of PET quality parameters during flake drying, flake solid-state polycondensation (SSP), and melt extrusion is investigated. The recycling process is assessed for its capability to produce food grade PET with specified quality parameters being intrinsic viscosity (IV), concentration of carboxylic end-groups (tTPA), concentration of vinyl end-groups (tV), and concentration of free acetaldehyde (AA).[6] Table 1 summarizes

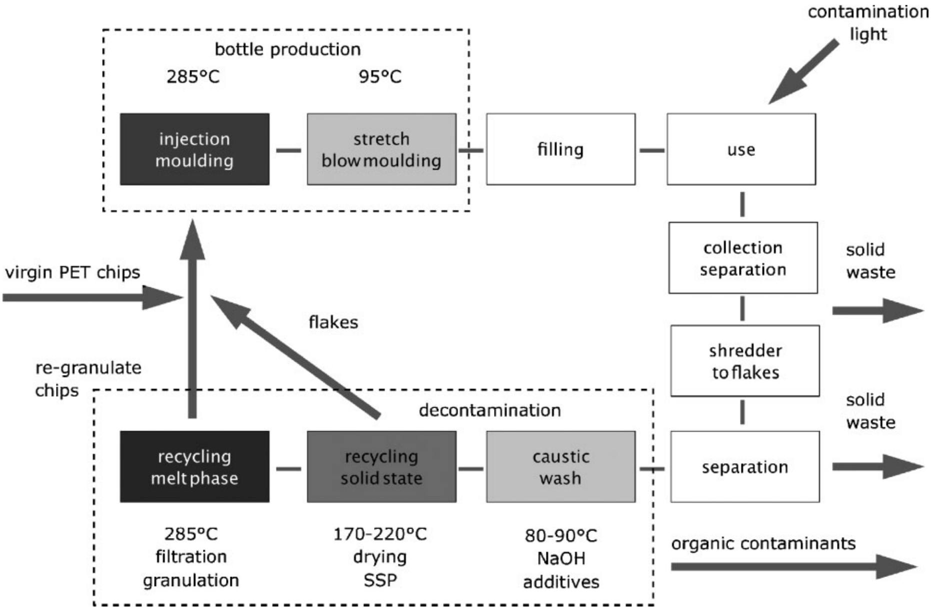

Figure 1.
PET recycling from bottle to bottle in a closed-loop recycling system.

typical values for quality parameters in recycled PET.

Figure 1 shows the simplified flow sheet of a bottle-to-bottle recycling loop, comprising the process steps 1) bottle production, 2) filling, use, and collection, 3) shredding, separation of labels, polyolefines, other foreign plastics, and metal, 4) caustic wash and 5) recycling in the solid-state (flake process) respectively recycling in the melt state and the solid state (chip process).

Process Model

A comprehensive reaction / mass transfer model has been developed to calculate the evolution of quality parameters during the recycling process. The model takes into account 1) kinetic data, 2) equilibrium data, and 3) mass transfer data for the volatile by-products ethylene glycol, acetaldehyde, and water.[7] The reactions are regarded as reactions between functional groups and are assumed to take place according to the Flory postulate.[8] The compounds and functional groups considered in the reaction model are listed in Table 2.

The process model comprises a set of 11 chemical reactions being:

- transesterification (polycondensation) and glycolysis:	reaction 1
- acetaldehyde formation:	reaction 2
- diethylene glycol formation:	reactions 3-5
- esterification and hydrolysis:	reactions 6-9
- vinyl end-group formation:	reaction 10
- transesterification of vinyl end-groups:	reaction 11

The reactions of compounds and functional groups are summarized in Table 3.

The kinetic parameters[9] used for the different reactions are summarized in Table 4.

The main reaction stages in PET recycling are:

- drying, crystallization, and polycondensation in the solid state and
- extrusion and filtration with and without vacuum degassing in the melt phase.

Table 2.
Compounds and functional groups considered in the PET reaction model.

Symbol	*Component or functional group*	*Molecular structure*
EG	ethylene glycol	$HOCH_2CH_2OH$
TPA	terephthalic acid	$HOOC-C_6H_4-COOH$
DEG	diethylene glycol	$HO(CH_2>2O(CH_2)2OH$
AA	acetaldehyde	CH_3CHO
W	water	H_2O
tEG	EG end group	R—OChfeChbOH
bEG	EG repeat unit	$R-OCH_2CH_2O-R'$
tTPA	TPA end group	R—OC—C5H4—COOH
bTPA	TPA repeat unit	$R-OC-C_6H_4-CO-R'$
tDEG	DEG end group	$R-O(CH_2)2O(CH_2)2OH$
bDEG	DEG repeat unit	$R-O\{CH2)2O(CH_2)2O-R'$
tV	vinyl end group	$R-OCH=CH_2$

The rate determining steps during these stages are mass transport by diffusion and mass transfer at the phase boundaries (solid / gas and liquid / gas). Therefore, diffusion and mass transfer models for the solid state and the melt phase were added to the reaction model.[9] The different processes put into account are:

1. Flake drying: 190 °C, 30 min, inert gas.
2. Flake SSP: 210 °C, t ≥ 45 min according to a final IV of 0.8 dL/g, p ≤ 2 mbar.
3. Extrusion and melt filtration: 285 °C, 90 s (shear effects were not considered).
4. Chip drying: 175 °C, 5 h, air.
5. Extrusion and injection moulding: 285 °C, 21 s (shear effects were not considered).

Table 3.
Reactions of compounds and functional groups. The reactions 1, 6, 7, 8, and 9 are equilibrium reactions, the reactions 2, 3, 4, and 5 have high equilibrium constants and the reactions 10 and 11 are irreversible.

No	*Reaction*	k_i +	k_i –
1	$tEG + tEG < bEG + EG$	k_1	k_1/K_9
2	$tEG + bTPA \rightarrow tTPA + AA$	k_2	–
3	$tEG + tEG \rightarrow bDEG + W$	k_3	–
4	$tEG + EG \rightarrow tDEG + W$	k_4	–
5	$EG + EG \rightarrow DEG + W$	k_5	–
6	$EG + TPA \leftrightarrow tEG + tTPA + W$	k_6	k_6/K_6
7	$EG + tTPA \leftrightarrow tEG + bTPA + W$	k_7	k_7/K_7
8	$tEG + TPA \leftrightarrow bEG + tTPA + W$	k_8	k_8/K_8
9	$tEG + tTPA \leftrightarrow bEG + bTPA + W$	k_9	k_9/K_9
10	$bTPA + bEG \rightarrow tV + tTPA$	k_{10}	–
11	$tV + tEG \rightarrow bEG + AA$	k_{11}	–

Table 4.
Kinetic parameters for the reactions in Table 3 $k_{i,o}$: pre-exponential factor, E_a: apparent activation energy, K_i: equilibrium constant.

Reaction	$k_{i,o}$	E_a / kJ/mol	K_i	Source
1	0.364 $(m^3/mol)^2\ min^{-1}$	74	0.5	[13]
2	8.32 $10^7\ min^{-1}$	125	–	[14]
3-5	2.17 $10^6\ (m^3/mol)\ min^{-1}$	125	–	[13]
6-7	4.68 $10^{-1}\ (m^3/mol)^2\ min^{-1}$	75	2.5	[13]
8-9	2.34 $10^{-1}\ (m^3/mol)^2\ min^{-1}$	75	1.25	[13]
10	7.2 $10^9\ min^{-1}$	158	–	[14]
11	1.36 $10^3\ (m^3/mol)\ min^{-1}$	77	–	[14]

The process parameters selected for this study are typical values taken from the patent literature [10] and own processing experience.

Bottle blowing by stretch blow moulding ($T < 100\,°C$) and the caustic wash ($T < 80\,°C$) were not considered in the process model because the main quality parameters are not affected during these process steps due to the low processing temperatures.

The process model has been validated for all process steps using experimental data. Experimental and calculated data for the development of the intrinsic viscosity (IV) with reaction time during SSP at 210 °C are compared for different particle sizes in Figure 2. The agreement between calculated and experimental data is quite satisfactory, even for long reaction times.

Experimental and calculated data for the concentration of carboxylic end-groups (COOH) after melt processing at 285 °C with an average residence time of 115 s versus the initial moisture content of the PET are shown in Figure 3. The initial moisture content of the PET was calculated from the residence time in the preceding drying process at 170 °C. The concentration of carboxylic end-groups after melt processing is clearly affected by the initial moisture content. If the PET is not dried, the concentration of carboxylic end-groups rises considerably during melt processing due to the massive degradation of the PET chain by hydrolysis. Modelling results calculated with a dynamic diffusion model

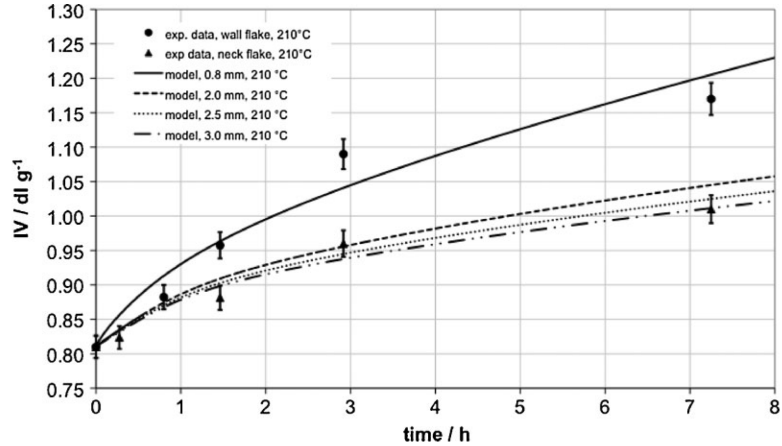

Figure 2.
Intrinsic viscosity (IV) versus reaction time during SSP for different particle sizes. The term "neck flake" refers to flake made from the thread of the PET bottle (particle thickness 2-3 mm), the term "wall flake" refers to flake made from the body of the PET bottle (particle thickness 0.8 mm).

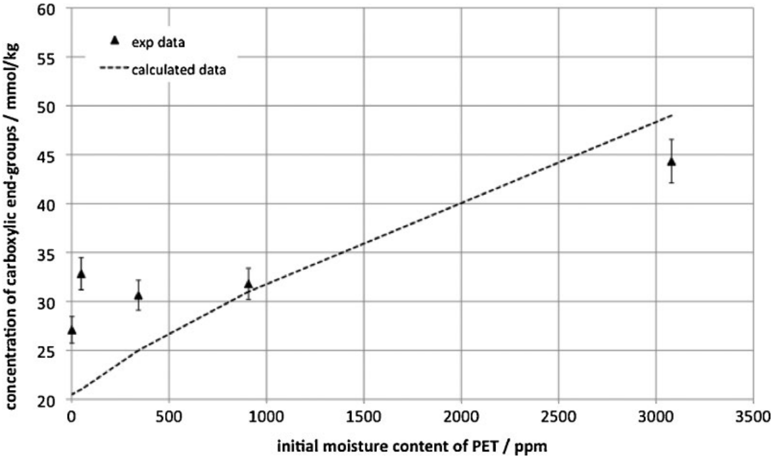

Figure 3.
Comparison of experimental data (▲) with calculated data (---) for the concentration of carboxylic end-groups after melt processing at 285 °C with an average residence time of 115 s depending on the initial moisture content of the PET (moisture content calculated from the drying time at 170 °C).

demonstrate that hydrolysis of the PET chain can effectively be avoided if the PET is thoroughly dried (8 h at 170 °C) before melt processing. The deviation between experimental and calculated results at low moisture contents in Figure 3 might be due to the difficulty to gain reliable experimental data of PET moisture at levels below 50 ppm because PET adsorbs moisture from the air very quickly.

In Figure 4, calculated and experimental data for the concentration of acetaldehyde after melt processing of dried PET at 285 °C with different residence times are compared. For low residence times, the AA values are over-predicted by the model, while for residence time longer than 300 s the model under-predicts the experimental AA data. The accuracy oft the prediction is still tolerable.

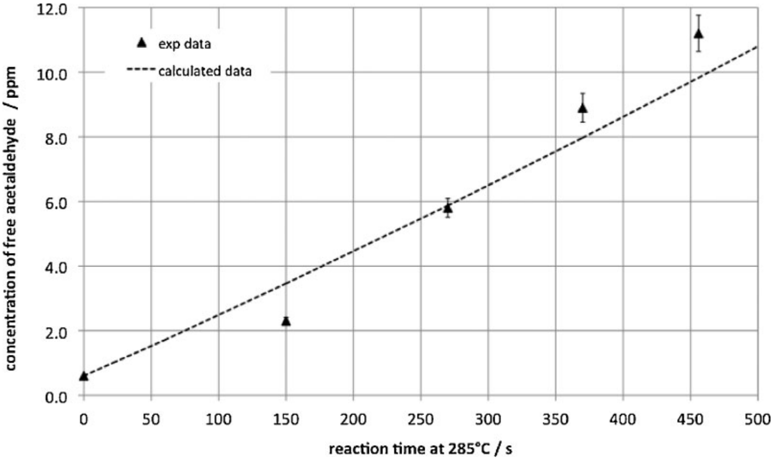

Figure 4.
Experimental and calculated data for the concentration of free acetaldehyde (AA) versus reaction time during melt processing of dried PET at 285 °C. The initial AA concentration was 0.6 ppm.

Table 5.
Modelling results for 5 subsequent recycling loops. Loop "0" refers to the quality parameters of virgin PET bottles (bottles after manufacture, filling and use).

Process Step	Recycl Cycle	IV	COOH	tv	AA
	No.	dl/g	mmol/kg	mmol/kg	ppm
	0	0.780	25.0	3.00	3.00
Dryer Flake 190 °C, 0.5 h	1.1	0.752	27.2	2.96H	0.54
SSP Flake, 210 °C	1.2	0.803	27.2	2.86	0.27
Extruder, 285 °C, 90 s	1.3	0.799	27.4	3.10	0.89
Dryer Chips, 175°, 5 h	1.4	0.798	28.5	2.97	1.38
Extruder Preform, 285 °C, 21 s	1.5	0.793	28.7	3.03	1.52
Dryer Flake 190 °C, 0.5 h	2.1	0.753	31.8	3.00	0.47
SSP Flake, 210 °C	2.2	0.797	31.8	2.90	0.25
Extruder, 285 °C, 90s	2.3	0.792	32.0	3.14	0.80
Dryer Chips, 175°, 5 h	2.4	0.786	33.2	3.02	1.31
Extruder Preform, 285 °C, 21s	2.5	0.780	33.4	3.08	1.44
Dryer Flake 190 °C, 0.5 h	3.1	0.732	37.0	3.04	0.46
SSP Flake, 210 °C	3.2	0.797	37.0	2.81	0.22
Extruder, 285 °C, 90s	3.3	0.792	37.2	3.05	0.68
Dryer Chips, 175°, 5 h	3.4	0.787	38.3	2.92	1.01
Extruder Preform, 285 °C, 21 s	3.5	0.782	38.4	2.98	1.12
Dryer Flake 190 °C, 0.5 h	4.1	0.723	42.5	2.95H	0.41
SSP Flake, 210 °C	4.2	0.798	42.4	2.62	0.18
Extruder, 285 °C, 90 s	4.3	0.793	42.6	2.86	0.55
Dryer Chips, 175°, 5 h	4.4	0.786	43.7	2.75	0.79
Extruder Preform, 285 °C, 21 s	4.5	0.781	43.8	2.81	0.88
Dryer Flake 190 °C, 0.5 h	5.1	0.712	48.4	2.79	0.35
SSP Flake, 210 °C	5.2	0.798	48.1	2.36	0.14
Extruder, 285 °C, 90 s	5.3	0.791	48.3	2.60	0.41
Dryer Chips, 175°, 5 h	5.4	0.778	49.5	2.51	0.59
Extruder Preform, 285 °C, 21 s	5.5	0.772	49.7	2.57	0.66

Results

In Table 4, the calculated evolution of the quality parameters intrinsic viscosity (IV), concentration of carboxylic end-groups (COOH), concentration of vinyl end-groups (tV), and concentration of free acetaldehyde (AA) during 5 subsequent recycling loops is summarized. Data were calculated for the exit streams of all the five process steps (x.1 – x.5) of the different recycling loops. Loop "0" refers to the quality parameters of virgin PET bottles (bottles after manufacture, filling and use). In the model, the moisture content of the flake at the inlet of the flake dryer was set to 3000 ppm for each recycling loop. In industrial applications, the moisture content typically ranges from 2000 to 5000 ppm [11], depending on the storage conditions of the flake. The moisture film on the flake surface is removed very quickly under industrial drying conditions and therefore was neglected in the process model.

Figure 5 shows the evolution of the intrinsic viscosity (IV) during 5 subsequent recycling loops. Due to the initial moisture content, the intrinsic viscosity is reduced in the flake dryer (step x.1) by hydrolysis. This IV drop is somewhat higher than expected from industrial experience, but is accounted for by the chosen drying process conditions with elevated temperature and heating rate. The IV drop increases with every completed recycling loop. This effect is caused by the increased concentration of COOH end-groups (Figure 6), which are involved in the proton-catalyzed chain degradation by hydrolysis.

During flake SSP (step x.2), the IV is restored to a value of 0.8 dL/g. This value was chosen for the modelling being a standard value for bottle-grade PET ensuring sufficient mechanical stability for the

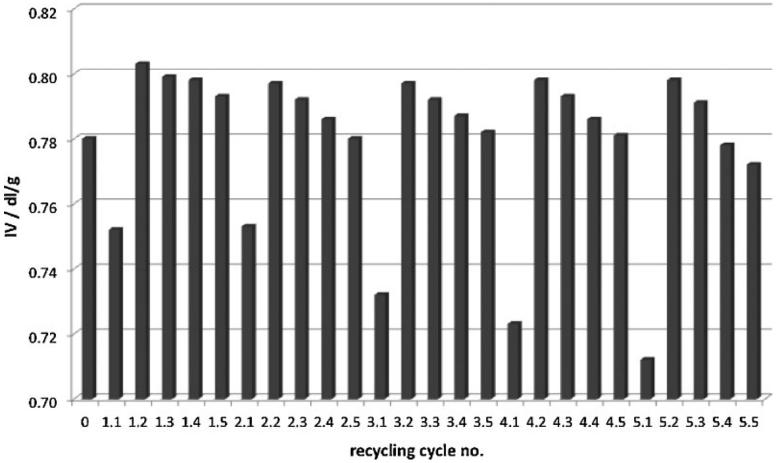

Figure 5.
Intrinsic viscosity after the different process steps for 5 subsequent recycling loops x from 1 to 5 (x.1 = flake dryer, x.2 = flake SSP, x.3 = extrusion and granulation, x.4 = chip dryer, x.5 = extrusion and injection moulding).

production of carbonated soft-drinks bottles. To restore this IV value, the SSP process time has to be increased with every recycling loop because 1) the IV drop is increased due to higher hydrolysis rates during flake drying and 2) the step growth reactions comprising esterification and transesterification (polycondensation) require an specific ratio of carboxylic end-groups to hydroxyl end-groups (tEG and tDEG).[12] This specific ratio is maintained in all industrial virgin PET processes but is shifted to unfavourable values in the recycling process due to the hydrolytic degradation during flake drying. The required SSP residence time increases over proportionally with respect to the IV drop from 45 min up to 6 h (Figure 7).

The increase in the concentration of carboxylic end-groups over 5 complete recycling loops is depicted in Figure 9. Even with thoroughly dried material, a

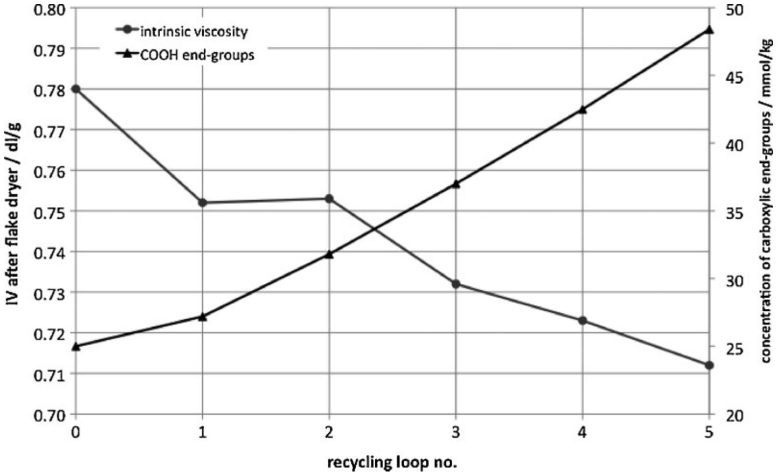

Figure 6.
Intrinsic viscosity after flake drying (190 °C, 30 min, 3000 ppm initial moisture content) together with the concentration of carboxylic end-groups (COOH) depending on the number of subsequent recycling loops.

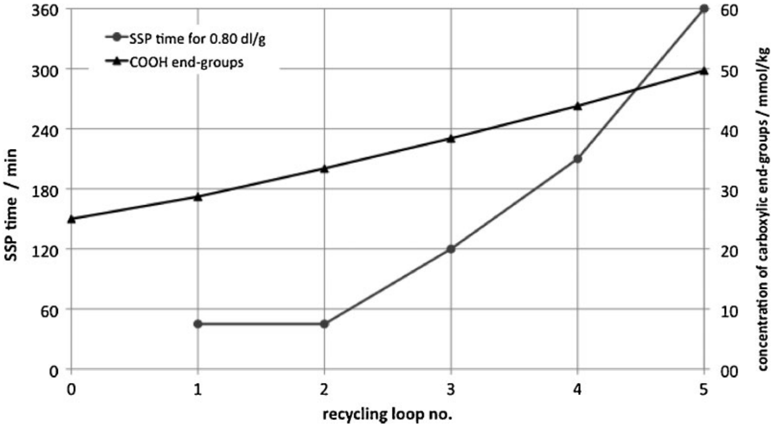

Figure 7.
Necessary process time for flake SSP at 210 °C and $p \leq 2$ mbar to restore IV = 0.80 dL/g together with the concentration of carboxylic end-groups (COOH or tTPA) depending on the number of subsequent recycling loops.

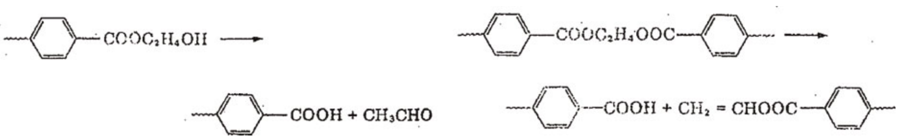

Figure 8.
Scission of terminal ester groups (tEG, left side) and diester groups (bEG, right side) forming carboxylic end-groups (COOH = tTPA).

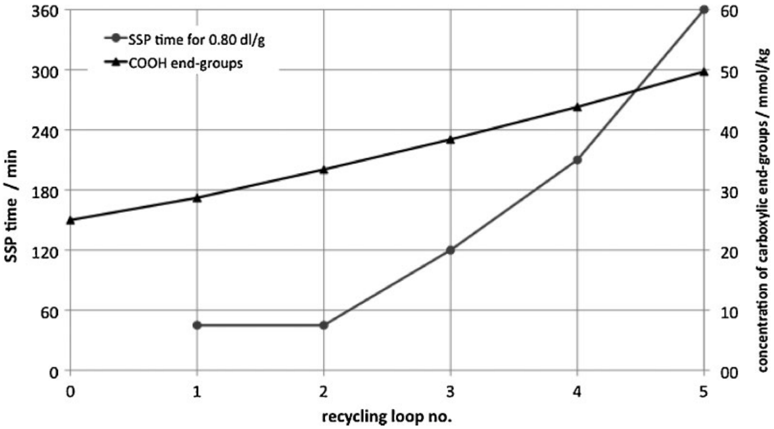

Figure 9.
Carboxylic end-group concentration (COOH) for 5 subsequent recycling loops x from 1 to 5 (x.1 = flake dryer, x.2 = flake SSP, x.3 = extrusion and granulation, x.4 = chip dryer, x.5 = extrusion and injection moulding). "0" refers to the initial value of virgin PET bottles.

small increase of carboxylic end-group concentration is unavoidable during the extrusion steps (x.3 and x.5) due to the scission of diester groups and terminal ester groups (Figure 8). These scission reactions depend only on time, temperature, and type and amount of polycondensation catalyst.

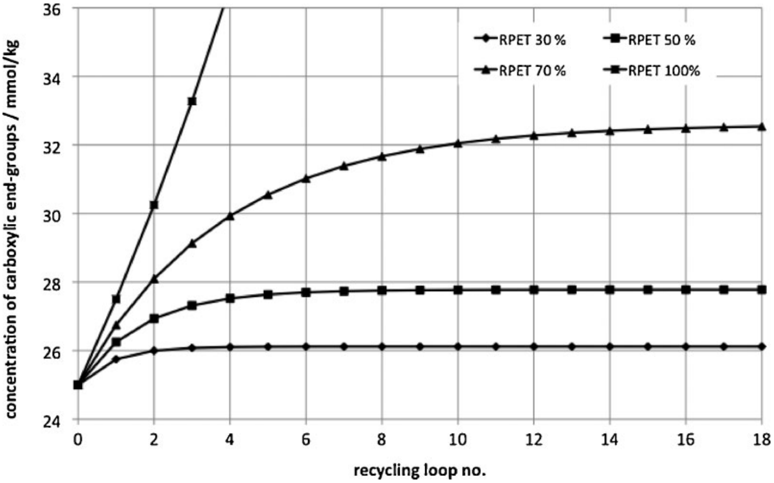

Figure 10.
Concentration of carboxylic end-groups (COOH) depending on the number of recycling loops for different contents of recycled polymer (RPET) of 30%, 50%, 70%, and 100% in the bottles. For this calculation, an increase in the concentration of COOH end-groups of 10% with every completed recycling loop was assumed (initial value $COOH_0$: 25 mmol/kg).

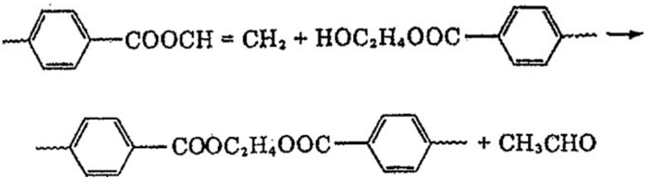

Figure 11.
Transesterification of a vinyl end-group with a terminal ester group forming free acetaldehyde.

An increase of the concentration of carboxylic end-groups during the solid-state process steps (flake drying x.1 and flake SSP x.2) can be avoided if the flake drying prior to SSP is performed sequentially in two steps with increasing temperature of the purge gas or if an apparatus with subsequent zones with increasing temperature is used.

Figure 9 refers to a scenario with bottles made from 100% recycled polymer. In reality, the content of recycled polymer in the bottles will be limited to values between 30% and 70%. Thus, the concentration of carboxylic end-groups will show an asymptotic behaviour with increasing numbers of recycling loops at much lower concentrations. In Figure 10, this situation is shown for different contents of recycled polymer in the bottles. The maximum value for the concentration of carboxylic end-groups at an infinite number of recycling loops increases disproportionate to the content of recycled polymer in the bottles.

Figures 12 and 13 show the concentrations of free acetaldehyde (AA) and vinyl end-groups (tV) for 5 subsequent recycling loops. The vinyl end-groups act as ''potential'' acetaldehyde as they can react with terminal ester groups in a transesterification reaction forming free acetaldehyde (Figure 11). This reaction has relatively high activation energy and is therefore favoured at higher temperature that is under melt processing conditions.

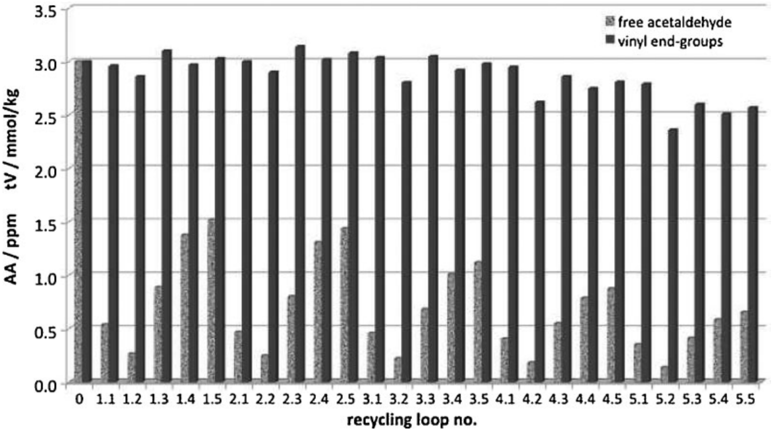

Figure 12.
Concentration of free acetaldehyde (AA) and concentration of vinyl end-groups (tV) for 5 subsequent recycling loops x from 1 to 5 (x.1 = flake dryer, x.2 = flake SSP, x.3 = extrusion and granulation, x.4 = chip dryer, x.5 = extrusion and injection moulding. "0" refers to the initial value of virgin PET bottles. For the initial concentrations of AA and tV the typical values of 3 ppm respectively 3 mmol/kg have been used in the modelling.

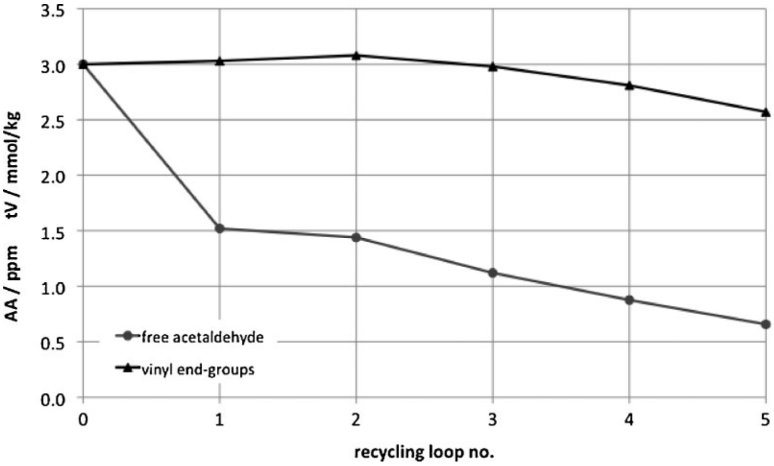

Figure 13.
Concentration of free acetaldehyde (AA) and concentration of vinyl end-groups (tV) in recycled PET depending on the number of recycling loops.

During flake processing (process steps x.1 and x.2), the concentrations of free acetaldehyde and vinyl end-groups decrease systematically. The reduction of free acetaldehyde is huge during flake drying (x.1) and still significant during flake SSP (x.2). The subsequent recycling steps (x.3 – x.5) each increase the concentration of free acetaldehyde by transesterification of vinyl end-groups but the concentration of free acetaldehyde remains well below the value of the feed material to the respective recycling loop. The reduction of vinyl end-groups is comparatively small during flake processing and is more pronounced during flake SSP (x.2). The concentration of vinyl end-groups also decreases during chip drying (x.4) but increases during extrusion (x.3 und x.5) due to the scission of ester groups. Overall, the concentration of vinyl end-groups varies only slightly with a tendency to lower values at a higher number of recycling loops.

With increasing numbers of recycling loops, the concentration of free acetaldehyde decreases continuously. The decrease of free acetaldehyde is most pronounced after the first recycling loop when the concentration of free acetaldehyde is reduced to the half of its original value. The concentration of vinyl end-groups remains more or less unaffected after the first three recycling loops. With further recycling loops, the concentration of vinyl end-groups decreases in the same manner as the concentration of free acetaldehyde.

Conclusion

A process model comprising chemical kinetics and mass transport can monitor the main quality parameters of PET during all kind of process steps with good accuracy. In this study, the process model has been used to investigate the behaviour of PET quality parameters such as intrinsic viscosity, concentration of acetaldehyde, concentration of carboxylic end-groups, and concentration of vinyl end-groups during a closed-loop bottle to bottle recycling process. The simulation revealed that after a single recycling loop all the relevant quality parameters achieve the specification, if certain temperatures, residence times, and surface areas for degassing are provided during the recycling process.

Another simulation showed the evolution of quality parameters in PET being subjected to an ''infinite'' number of recycling loops in a closed system. The main reactions of PET chemistry are equilibrium reactions. Therefore, most of the damage to the polymer chain during its ''eternal'' life in a closed-loop recycling system can be healed. This accounts for the molecular weight together with the formation of vinyl end-groups and free acetaldehyde. The latter can be removed easily by diffusion during solid-state processing. The concentration of acetaldehyde and vinyl end-groups decreases continuously with the number of recycling loops, which is a desired effect. On the other hand, the concentration of carboxylic end-groups increases with every completed recycling loop. The increase in the concentration of carboxylic end-groups results mainly from hydrolysis reactions due to the moisture content of the polymer feed. This increase is proportional to the initial moisture content of the polymer and cannot be compensated by solid-state processing. Higher concentrations of carboxylic end-groups 1) make the PET susceptible to hydrolysis by residual moisture even at low process temperatures and 2) give rise to lower reactivity during solid state polycondensation (SSP) and significantly longer process time needed to achieve the specified intrinsic viscosity for carbonated soft drink bottles, respectively. To overcome this problem, the recycled PET has to be blended with a certain amount of virgin PET in industrial processes. The amount of virgin PET needed becomes lower with increasing severity of the flake drying process.

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