Chain Extension of Recycled Poly(ethylene terephthalate) with 2,2'-Bis(2-oxazoline)

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SYNOPSIS

2,2'-Bis(2-oxazoline) was used as a chain extender during processing in a twin-screw extruder with the aim of counteracting degradation phenomena in recycled poly(ethylene terephthalate) (PET). The same experiments were performed on fiber-grade PET for comparison purposes. Rheological characterization showed that while the melt viscosity of fiber-grade PET at constant temperature and shear rate is quite constant with time, that of recycled PET decreases dramatically. By addition of oxazoline, an increase of melt viscosity occurs for fiber-grade PET, whereas for recycled PET, thermal and hydrolitic degradation effects are partially compensated. Characterization was performed by solution viscosity measurements, gel permeation chromatography, and COOH end-group titration on samples obtained at variable residence times at 280°C. Lower molecular weights accompanied by a higher amount of COOH were observed; the use of oxazoline resulted in higher molecular weights and lower COOH concentrations at equal residence times, while polydispersity did not vary. © 1993 John Wiley & Sons, Inc.
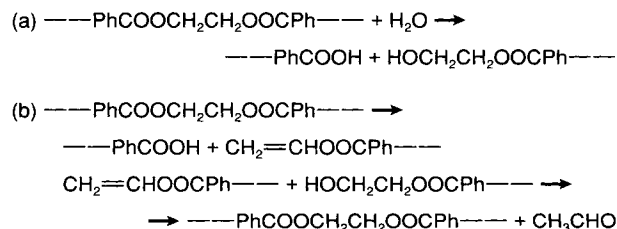
INTRODUCTION

Plastic recycling is currently in a growing stage of development. Poly(ethylene terephthalate) (PET) is a thermoplastic polyester widely used in the manufacture of textile fibers, soft drink bottles, magnetic tapes, and photographic supports; thus, due to the increase of environmental issues, the recycling of PET was the subject of several recent studies.[1-4]

Recycling of PET from soft drink bottles is based on the density separation from the high-density polyethylene (HDPE) cap and base-cup resin (when present) and washing for the elimination of labels and adhesives. In some European countries, where poly(vinyl chloride) (PVC) is also used as a raw material for bottle manufacturing, a further stage of separation from residues of such material is required.[5,6] A good separation is the key point of the whole process. Then, PET bottles are milled, producing scraps that can follow two main alternative routes: they can be depolymerized to low molecular weight compounds[7-22] or reextruded.[4,22]

Among the problems met in the reprocessing of PET soft drink bottle scraps, the degradation caused by the simultaneous presence of retained moisture and the contaminants is particularly relevant. Such contaminants, i.e., PVC and adhesives, generate acidic compounds[23] at the processing temperature (hydrochloric acid[24] and acetic or abietic acid, respectively), that catalyze hydrolysis[25-28] of ester bonds (Scheme I, reaction a):

(a) ——PhCOOCH$_2$CH$_2$OOCPh—— + H$_2$O →

      ——PhCOOH + HOCH$_2$CH$_2$OOCPh——

(b) ——PhCOOCH$_2$CH$_2$OOCPh—— →

  ——PhCOOH + CH$_2$=CHOOCPh——

 CH$_2$=CHOOCPh—— + HOCH$_2$CH$_2$OOCPh—— →

    → ——PhCOOCH$_2$CH$_2$OOCPh—— + CH$_3$CHO

Scheme 1

On the other side, since alkaline solutions are employed for scraps washing, ester bonds may be

broken by basic catalysis. No matter which type of catalysis prevails, hydrolitic degradation adds its effect to thermal degradation[27,29-31] (Scheme I reactions b), and, consequently, the content of carboxylic end groups increases while the molecular weight of polyester decreases, with the detriment of mechanical properties and thermal stability of the final material.[32] In two recent patents,[33,34] the extrusion of PET contaminated with chlorine-containing polymers is performed in the presence of acrylic copolymers carrying epoxy groups in the side chains. Epoxy groups neutralize the hydrochloric acid and prevent degradation; furthermore, they can react with carboxylic groups of PET.

In the case of virgin polyesters, the use of the so-called chain extenders has been proposed. Chain extenders cited in the literature[35-42] are polyfunctional compounds able to react with carboxylic end groups or alcoholic end groups or both, giving a molecular weight increase, and if the chain extender reacts with COOH, carboxylic group content decreases. Some examples of chain extenders are diepoxides, diisocyanates, dianhydrides, bis(oxazoline)s, bis(dihydrooxazine)s, carbodiimides, and bis(N-acyllactam)s.

Oxazolines are of particular interest. They can be easily synthesized[43] and react with carboxylic compounds,[44] forming an esteramide moiety (Scheme II):
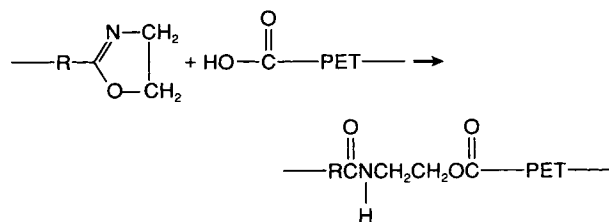
Scheme 2

In this work, the use of 2,2'-bis(2-oxazoline) (BO; Scheme III) with recycled PET is reported:

BO
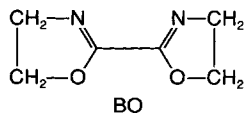
Scheme 3

Because of an uncontrolled increase of carboxylic end groups of recycled PET during processing does not allow an accurate dosage of the chain extender, the efficiency of bis(oxazoline) cannot be obvious. Moreover, due to the sensitivity of the oxazolinic

ring to acidic compounds, it can undergo undesired side reactions.[45,46]

EXPERIMENTAL

Materials

Pellets of fiber-grade PET (PETF) were supplied by Montefibre (Milano, Italy): intrinsic viscosity (IV) = 0.64 dL/g, COOH = 33 meq/kg. Scraps of postconsumer recycled PET (PETR; nominal content of PVC = 2000 ppm) were purchased from Tecoplast (Ferrara, Italy): IV = 0.77 dL/g, COOH = 27 meq/kg. 2,2'-Bis(2-oxazoline) (BO) was supplied by Enichem ANIC (Porto Torres, Italy):[47] mp = 209–212°C.

Apparatus

A twin-screw extruder Rheomex TW-100 Haake System 90 with conical screws (diameter 20–31 mm and length 330 mm), equipped with a gravimetric feeder in nitrogen atmosphere and a vertical head (D = 3 mm, L/D = 8) was used for the extrusion tests.

Procedure

PET scraps or pellets (dried at 120°C for 16 h) were fed to the extruder using amounts of polyester of 750–1000 g and amounts of BO corresponding to once, twice, and thrice the equivalents of COOH in PET. Runs are labeled with "F" or "R" followed by the quantity of BO used (Table I); PETF and PETR represent the starting materials. The temperature profile in the plasticating cylinder ranged from 240 to 260°C; the feeding rate was set at 2 kg/h and the screw speed was 70 rpm.

Table I Chain-extension Reaction of PETF with 2,2'-Bis(2-oxazoline): Stoichiometric Ratio of Reagents, Intrinsic Viscosities (IV), and Carboxylic End-group Concentration (COOH)

Run	eq BO / eq COOH (Starting)	COOH (meq/kg)	IV (dL/g)
PETF (starting)	—	33	0.64
F	0	37	0.56
F+BO	1	25	0.62
F+2BO	2	16	0.63
F+3BO	3	22	0.62

Analytical

Intrinsic viscosities (IV) were measured in phenol/trichlorobenzene (50 : 50 v/v) at 30°C with an automatic Schott-Geräte viscosimeter equipped with Ubbelhode capillaries.

GPC analysis was performed in phenol/trichlorobenzene (50 : 50 v/v) at 85°C with a Waters 150-C ALC/GPC instrument equipped with μ-Styragel columns and a refractive index detector. GPC calibration was performed using six PET standards of different molecular weights; the calculated Mark–Houwink constants were a = 0.81 and k = 1.48 $\times 10^{-4}$.

Carboxylic end-group concentrations were determined by dissolving the samples in hot benzyl alcohol, diluting with chloroform, and titrating with benzylalcoholic sodium hydroxide.[48] Rheological measurements were performed by a Göttfert Rheograph 2002 capillary rheometer. Moisture content was measured by the manometric method.[49]

RESULTS

Virgin PET was preliminarily reacted with variable amounts of BO to assess the effect of stoichiometric ratios on chain extension. Extrusion of PETF with or without oxazoline was carried out as reported in Table I. Amounts of oxazoline corresponding to once, twice, and thrice the equivalents of COOH in

PET were used. A blank run was also performed with PETF alone. An increase of carboxylic end groups is caused by processing (see Table I). Their amount is decreased in the presence of BO, suggesting that the reaction of Scheme II takes place. Intrinsic viscosity measurements reveal the decreasing molecular weight (Table I), whereas intrinsic viscosity values comparable with starting ones (not processed materials) were obtained when processing is carried out in the presence of BO.

Curves of melt viscosity vs. shear rate at 280°C are reported in Figure 1. They show that the treatment with BO leads to an increment in melt viscosity, as a consequence of the chain-extension reaction, the increasing being much more evident for F + 2BO. It is reasonable to gather that a stoichiometric quantity of a chain extender is not sufficient to react with additional carboxylic groups formed during processing as a consequence of reaction of Scheme I and, thus, to efficiently counteract degradation. On the other hand, when BO concentration exceeds twice the carboxyl concentration, most likely, its reaction is incomplete and unreacted BO may act as an internal lubricant.

With the aim to verify if the average residence time in the extruder (about 3 min) is enough to bring the chain-extension reaction to completeness, variations of melt viscosities as a function of time were studied. To do this, polymer pellets obtained after extrusion were charged in the capillary rheometer, and melt viscosity values at 280°C and con-
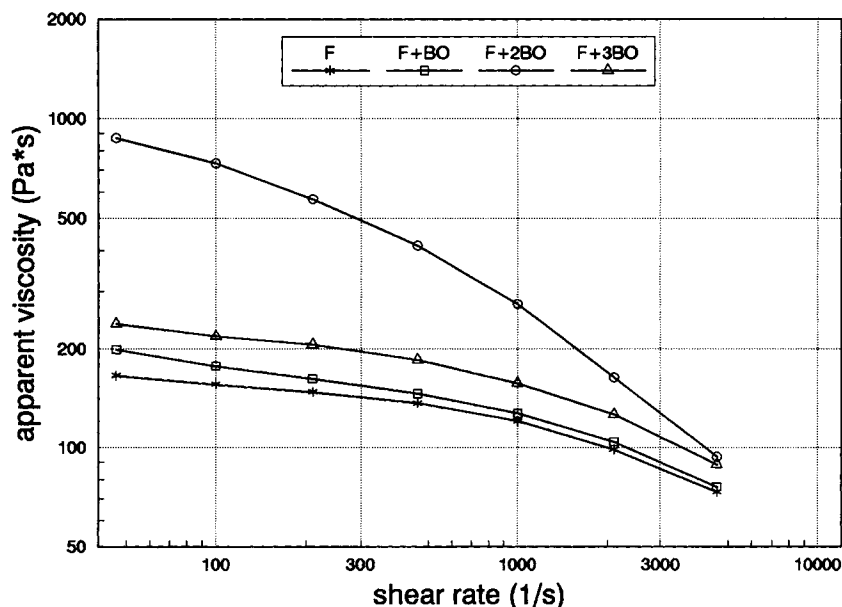

Figure 1 Melt viscosities vs. shear rate at 280°C of F, F + BO, F + 2BO, and F + 3BO.
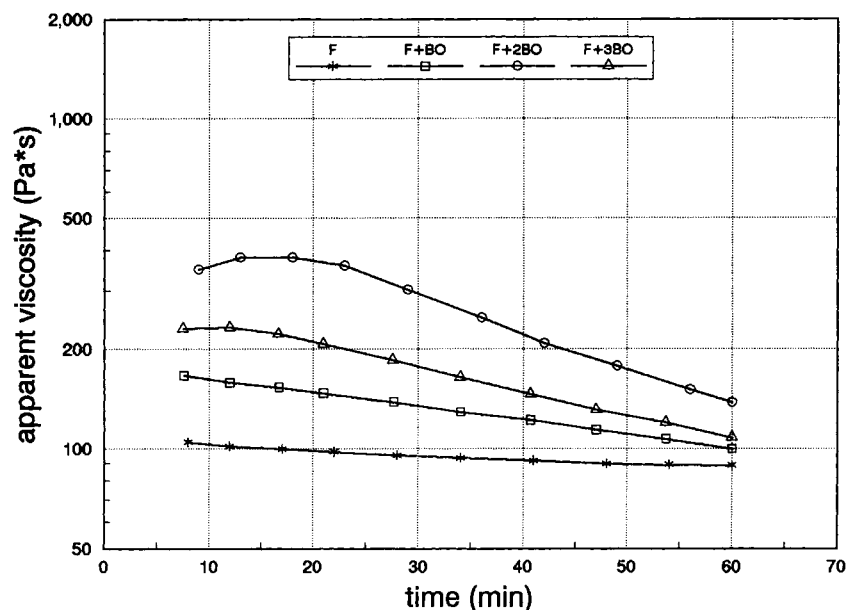
Figure 2 Melt viscosities vs. residence time at 280°C and 100 1/s shear rate of F, F + BO, F + 2BO, and F + 3BO.

stant shear rate were measured every 10 min. The analysis was carried on for the duration of 1 h, obtaining results reported in Figure 2.

The curves are in the same relative order of those of Figure 1, i.e., the higher melt viscosity is exhibited by F + 2BO, while the lower one is exhibited by F. F + BO and F + 3BO curves stay in the middle. The order is maintained during the whole residence time in the rheometer. The chain-extension process seems to continue for the first 15 min of residence time, as displayed by the slight melt viscosity increase in the case of F + 2BO and F + 3BO. After this period, melt viscosities decrease. The curves are convergent and tend to approach that of F. This behavior may suggest some degree of thermal decomposition of oxamidic groups ($-$ NHCO-CONH $-$) formed in chain-extended polyesters.

Following the clues from the experiments with fiber-grade PET, extrusions of recycled PET were carried out using amounts of BO equal to twice and thrice the stoichiometric amount (Table II). The effect of the chain-extension reaction was showed by the head pressure of the melt during extrusion, which was 11 bar for R and about 20 bar for R + 2BO and R + 3BO. Accordingly, intrinsic viscosity of PETR falls to 0.63 after extrusion, while it remains unchanged in the presence of BO and carboxylic group concentration is double when BO is not used.

Melt viscosity vs. shear rate curves are reported in Figure 3. In agreement with observations made in the case of PETF, modified recycled PET possess higher melt viscosities than does R. The fact that melt viscosities of F and F + 2BO are higher than melt viscosities of corresponding runs for recycled PET (R and R + 2BO) could seem to be in contradiction to intrinsic viscosity data. This behavior may be interpreted as admitting that molecular weights of recycled samples obtained immediately after preparation are higher than are molecular weights of corresponding PETF (hence, the intrinsic viscosities trend). Then, as soon as polymer pellets are

Table II Chain-extension Reaction of PETR with 2,2'-Bis(2-oxazoline); Stoichiometric Ratio of Reagents, Intrinsic Viscosities (IV), and Carboxylic End-group Concentration (COOH)

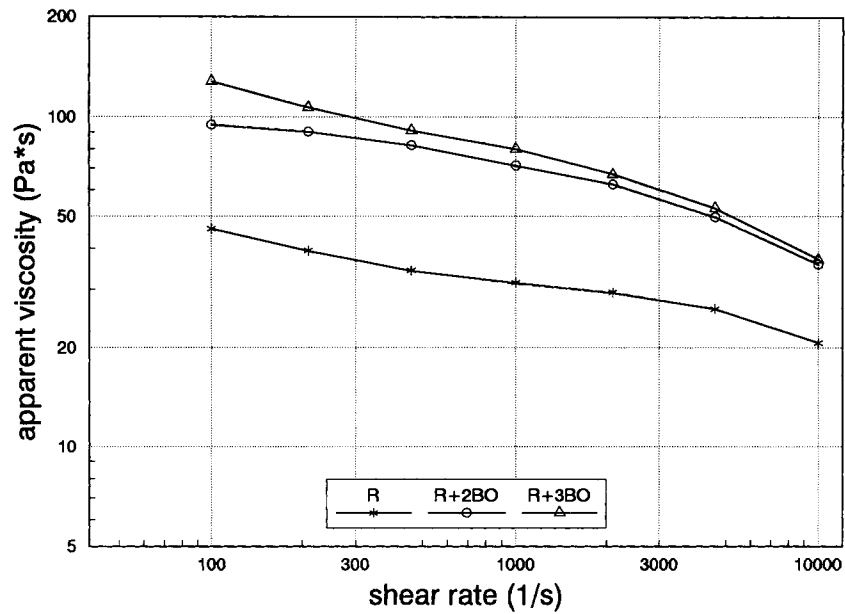| Run	eq BO / eq COOH (Starting)	COOH (meq/kg)	IV (dL/g)
PETR (starting)	—	26	0.70
R	0	41	0.63
R+2BO	2	17	0.71
R+3BO	3	21	0.70

Figure 3   Melt viscosities vs. shear rate at 280°C of R, R + 2BO, and R + 3BO.

charged in the rheometer for flow curve measurement, they quickly fall, because the charging of pellets requires a few minutes. The viscosity drop is much more evident for recycled samples, where degradation is stronger; very likely, the beginning of melt viscosity measurement takes place only when

molecular weights of recycled samples have become rather low.

Melt viscosity vs. time curves reported in Figure 4 support this hypothesis: Although cautions must be taken about making such extrapolations, melt viscosities of PETR samples at 0 min of residence
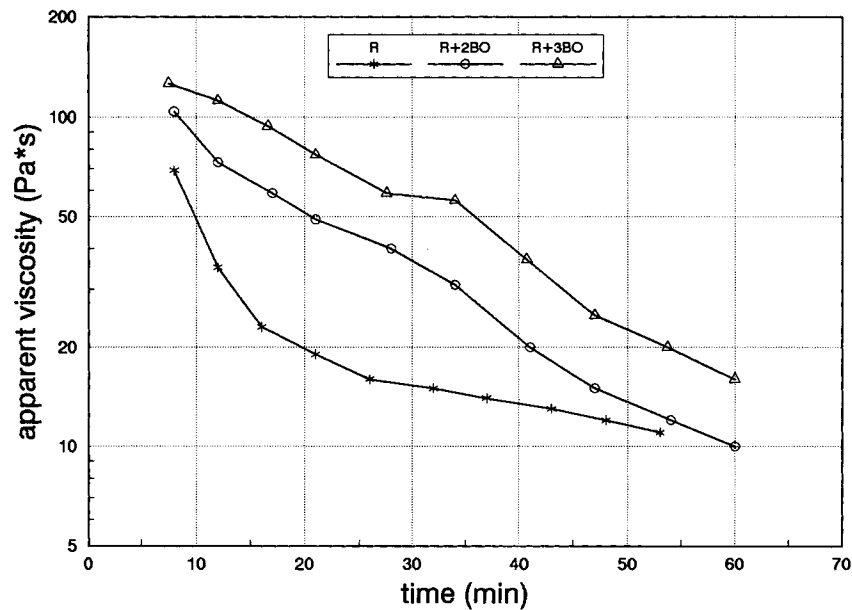

Figure 4   Melt viscosities vs. residence time at 280°C and 100 1/s shear rate of R, R + 2BO, and R + 3BO.
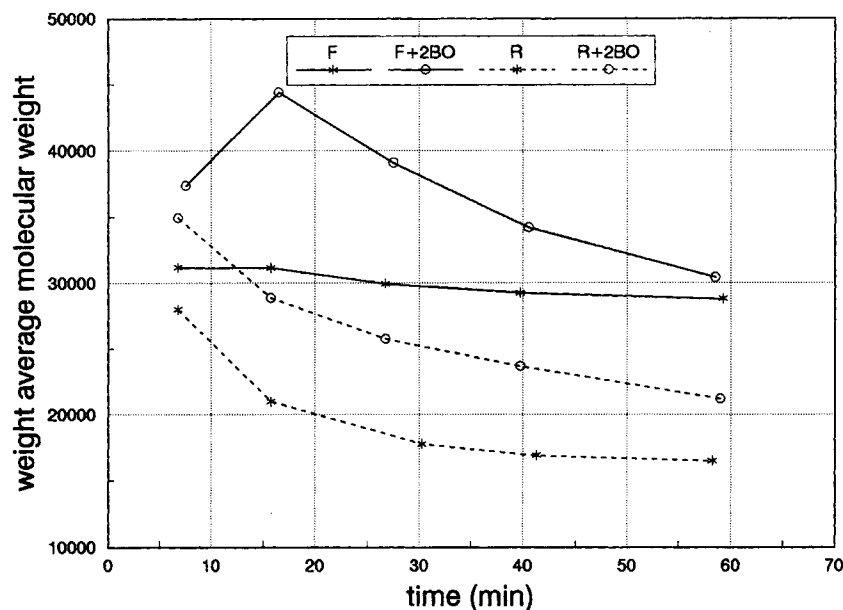
Figure 5 Average weight molecular weights vs. residence time at 280°C and 100 1/s shear rate of F, R, F + 2BO, and R + 2BO.

time appear higher than melt viscosities of PETF samples, in agreement with the intrinsic viscosities of Table I.

Melt viscosity of R decreases dramatically from 70 to about 20 Pa·s after 20 min. It should also be noted that although in PETR strong degradation occurs, masking in part the effect of BO, rheological curves of R + BO and R + 2BO, however, stay above that of the unmodified one. Also, in these cases, at the beginning of the experiment, melt viscosity drops fairly, while after 50 min, viscosity values are almost the same of the not-chain-extended PETR.

In the case of F, F + 2BO, R, and R + 2BO, simultaneously to viscosity measurements, samples

of melt polymer were discharged at fixed times from the rheometer and characterized by solution techniques, e.g., GPC and intrinsic viscosity. In this way, more direct and reliable parameters associated to degradations were measured. Molecular weights are reported in Figure 5; molecular weight distributions are reported in Table III together with intrinsic viscosities.

Molecular weights and intrinsic viscosity values are in very good agreement with the rheological data. The shape of the curves resembles very closely the shape of melt viscosity vs. time curves of Figures 2 and 4. Noteworthy, also in this case, is that the increase of molecular weight after 15 min of residence

Table III Intrinsic Viscosities (IV) and Index of Polydispersity (MWD) vs. Residence Time at 280°C and 100 1/s Shear Rate of F, R, F+2BO, and R+2BO

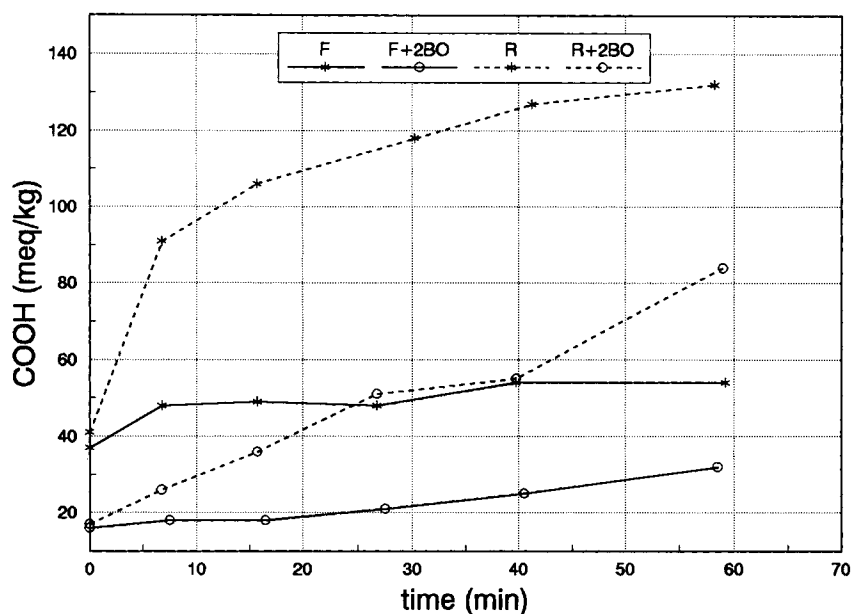| Residence Time (min)	F IV (dL/g)	F MWD	F+2BO IV (dL/g)	F+2BO MWD	R IV (dL/g)	R MWD	R+2BO IV (dL/g)	R+2BO MWD
0	0.56	—	0.63	—	0.63	—	0.71	—
7-8	0.57	2.5	0.68	2.4	0.52	2.3	0.57	2.2
16-17	0.57	2.4	0.75	2.3	0.43	2.3	0.53	2.2
27-28	0.55	2.4	0.72	2.4	0.38	2.2	0.49	2.2
40-41	0.57	2.4	0.68	2.3	0.35	2.2	0.45	2.2
58-59	0.57	2.5	0.62	2.4	0.31	2.2	0.41	2.2

Figure 6 Carboxylic end-group concentration vs. residence time at 280°C and 100 1/s shear rate of F, R, F + 2BO, and R + 2BO.

in the rheometer for PETF reacted with BO is evident.

Values of the polydispersity index lie between 2.2 and 2.5 and remain almost constant after 1 h at 280°C, suggesting a random scission mechanism for polymer chain degradation.[50]

Carboxylic end-group concentrations as a function of time are reported in Figure 6. The curves of modified polymers lie below the respective unmodified ones and that of R has a much greater slope than those of F, F + 2BO, and R + 2BO, reaching after 1 h very high values of carboxylic group con-

centration (130 meq/kg). The concentration increase of carboxylic groups of R + 2BO is greatly prevented by oxazoline and remains comparable with that of F even after 40 min at high temperature.

Two aspects should be considered in explaining the strong tendency of recycled PET toward degradation: a kinetic factor and a thermodynamic factor. Looking at kinetics, the rate of ester bond hydrolysis depends on both the proton concentration and the amount of water.[29] The hydrochloric acid generated by PVC decomposition increases the hydrolysis rate[51-54] according to Scheme IV. Moisture
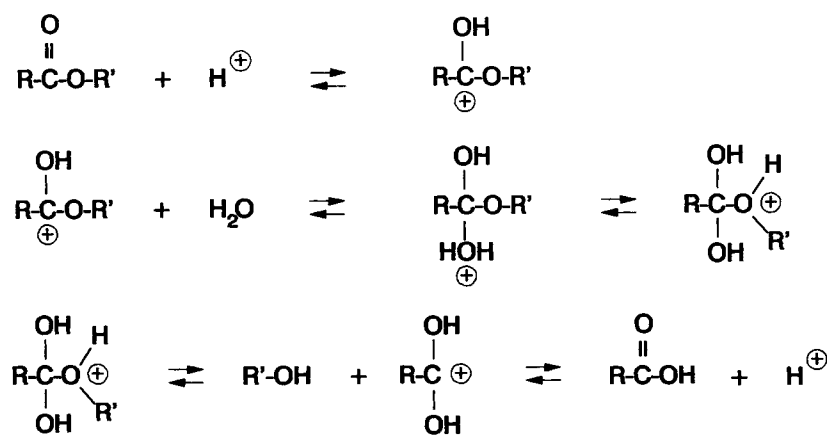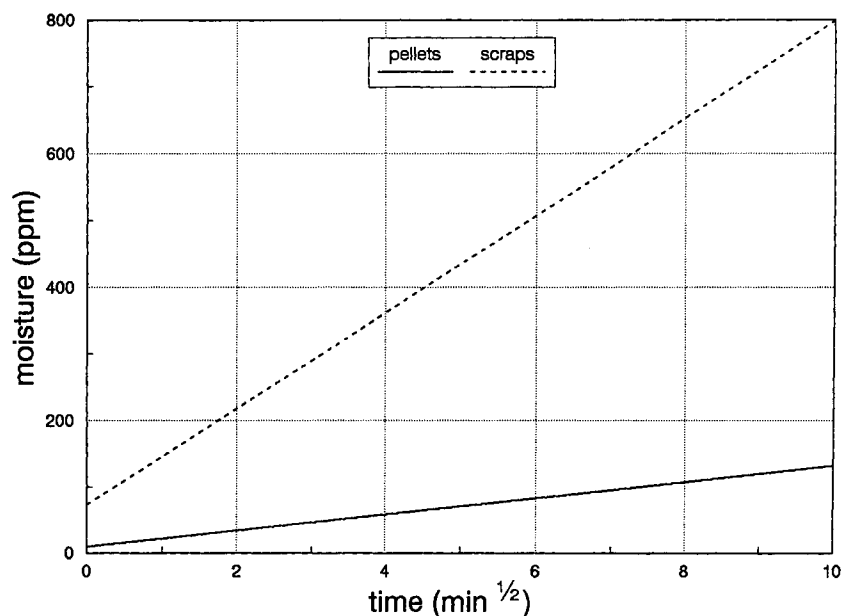

Scheme 4

Figure 7 Moisture content of dried (4 h, 180°C) PET pellets and scraps as a function of square root of exposure time in air (28°C, 50% RH).

influences the thermodynamic of hydrolysis, as well as the kinetics. The crystallinity and shape of material particles are very important in determining their hygroscopicity and, thus, their tendency to subsequent hydrolitic degradation. The specific surface of scraps is obviously much greater than that of pellets. Consequently, the moisture absorbed by scraps during the period needed for the mixing with the chain extender and the feeding to the extruder is expected to be higher than that of the pellets. Accordingly, in Figure 7, the moisture of PET pellets and scraps dried at 180°C and then exposed to air is showed. Performing all manipulations in a closed system under rigorously inert atmosphere, like in an industrial processing apparatus, should avoid these problems.

CONCLUSION

Rheological measurements, solution characterization, and carboxylic end-group titration results prove that impurities and the shape of particles can cause strong thermal and hydrolitic degradation of recycled PET in processing conditions. Degradative effects can be limited using 2,2'-bis(2-oxazoline), acting either as chain extender and COOH end-group controller.

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