

Reactive-Extrusion Route for the Closed-Loop Recycling of Poly(ethylene terephthalate)

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Received 22 August 2006; accepted 20 October 2006

DOI 10.1002/app.25795

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The effectiveness of the reactive extrusion technique was investigated for poly(ethylene terephthalate) to promote the concept of closed-loop recycling, that is, the reuse of waste material in the initial application. More specifically, a chain-extender system, consisting of pyromellitic dianhydride, polyol, and a catalyst, was employed, and its efficiency regarding the improvement of the recycle quality was evaluated. Accordingly, rheological and thermal characterizations were performed and used as criteria of the modification induced in the polymer molecular structure during processing due to the counteracting degradation and chain-extension reactions. In particular, the molecular weight, related to intrinsic viscosity and melt flow rate measure-

ments, of modified poly(ethylene terephthalate) samples was found to increase with the additive content. Simultaneously, a decrease in the crystallinity was observed, attributed to the branching effect of the chain extender, which restricted the ability of the macromolecules to organize in the crystal structure. Beyond a critical concentration of the additive system, the molecular weight of the treated samples started to decrease again, and this was accompanied by a small increase in the crystallinity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1671–1678, 2007

Key words: degradation; polyesters; reactive extrusion; recycling

INTRODUCTION

Poly(ethylene terephthalate) (PET) is one of the most important engineering polymers with recognized properties in terms of processability, thermal stability, chemical resistance, and mechanical strength. These characteristics permit the commercial use of PET in a variety of applications, such as textile fibers, photographic films, tire cords, strappings, films for food packaging, insulators for capacitors, and mainly beverage bottles.^{1,2}

In the past few years, the importance of the recycling of plastics has been highlighted for several ecological, economical, and energy-related reasons, and significant efforts are being attempted with respect to the pertinent issues. On the basis of economic viability and effectiveness, recycling techniques may be considered successful especially when the virgin material can be substituted by a recycle satisfying the requirements of the original application (closed-loop recycling).^{3–8} In that respect, the use of recycled PET as a packaging material consists of a primary recycling target. However, thermal, oxidative, and hydrolytic degradation, occurring during the manufacturing

process of PET bottles and throughout their subsequent service life, causes a pronounced deterioration of the material properties and thus impedes their potential reuse in the initial application.^{9,10}

To compensate for polymer degradation, the use of so-called chain extenders has been proposed in many studies as a very effective method of increasing the polymer molecular weight. Generally, chain extenders are low-molecular-weight, multifunctional compounds capable of a rapid reaction with the polymer end groups, leading to the coupling of macromolecules. Various organic substances have been used for the PET chain-extension process and are mentioned in the literature, such as diepoxides, diisocyanates, dianhydrides, carbodiimides, and bisoxazolines. Among these reported chain extenders, pyromellitic dianhydride (PMDA) increases significantly the intrinsic viscosity (IV) of PET, thus allowing the manufacture of bottles.^{11–14}

On this basis, two major techniques have been proposed and depend on whether chain extension occurs in the solid state [solid-state polymerization (SSP)] or in the melt phase [reactive extrusion (REX)]. The former involves heating the prepolymer in an inert atmosphere or *in vacuo* at a temperature well above its glass-transition temperature (T_g) but below the melting point (T_m), resulting in a significant increase in the degree of polymerization. The main disadvantages of SSP are its slow rate and the requirement of large-scale supplementary equipment.^{15–20}

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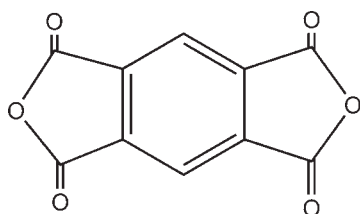


Figure 1 Chemical structure of PMDA.

On the contrary, REX, that is, the use of an extruder as a chemical reactor, offers a viable recycling solution because it is a very fast and flexible technique that can be easily applied during conventional melt processing. In reactive processing, two distinct processes take place simultaneously: chemical modification through the introduction of the chain extenders and shaping into a finished plastic product. In this way, specialty polymers, which are uneconomical to produce in large-scale operations, can be tailor-made easily by a single procedure.^{21–23} The key issue in this case is to control the extent of the reaction through the optimization of the operation parameters. These are principally the polymer (type, grade, molecular weight, number, and chemical structure of the end groups), the concentration of the chain extender, the residence time of the polymer in the extruder, and the working temperature profile. Fluctuations in the aforementioned variables are the main reasons for thermal, hydrodynamic, and chemical turbulence, leading to an instable operating system.^{24,25}

In this study, our interest was focused on investigating the effectiveness of the REX process in the case of PET recycling and more specifically in the case of industrial scrap PET and postconsumer bottle-grade PET. Accordingly, a chain-extender system, consisting of PMDA, polyol, and a catalyst, was employed, and its efficiency regarding the recycle quality was evaluated on the basis of the melt strength and melt viscosity increase at different additive concentrations. From the perspective of the reuse of the modified material in the initial application (closed-loop recycling), the primary objective was the improvement of its quality to match the properties of the virgin polymer. Consequently, rheological and thermal characterizations were conducted and used as criteria of the modifications induced in the molecular structure due to the competitive degradation and chain-extension reactions occurring during processing.^{26–29}

EXPERIMENTAL

Materials

The study was conducted with three PET grades:

1. Virgin PET, under the trade name Voridian Aqua PET 20837, supplied by Eastman Chemical Co.

(San Roque, Spain) in the form of pellets, was used as a reference material. The resin is considered to be linear, with a nominal IV of 0.76 dL/g.

2. Scrap PET, the same grade as the virgin PET, came from the processing waste of a bottle manufacturing company (Plastiko, Ltd., Loutraki, Greece). The material was in the form of flakes, and its nominal IV was reported to be 0.74 dL/g.
3. Post PET (postconsumer bottle-grade resin) had an IV of 0.65 dL/g. The material was collected, cleaned, and adjusted into pellets for recycling purposes by the same company. The age of the collected postused bottles was estimated to be approximately 6 months.

To investigate the optimum chain-extension recipe for upgrading the quality of the aforementioned PET grades, a chain-extender system, kindly prepared by Ciba Specialty Chemicals, Ltd. (Lampertheim, Germany), was employed. This additive system was used in the form of a master batch at a concentration of 20% of active ingredients with PMDA as the main chain-extending substance, whereas PET was used as a substrate. PMDA is a tetrafunctional reactive agent capable of a fast reaction with the PET end groups and generating no byproducts (Fig. 1). The master batch contained furthermore a minor amount of pentaerythritol (Fig. 2), which acted as a moderator for the PMDA reaction, and, additionally, a phosphonate, which is known to act as a transesterification catalyst during the extrusion reaction. This additive system was selected because it is a ready-to-use chain extender, physically stable up to 60°C and chemically stable up to 320°C. Furthermore, it is completely compatible with the common PET grades, and contrary to pure PMDA, it has been reported to prevent crosslinking even at high concentrations.³⁰ Heavy crosslinking leads to extensive gel formation, which affects negatively the mechanical properties and thermal stability of PET.⁹

Reactive processing

Considering the problems arising from the limited hydrolytic and thermal stability of the PET melt, drying is regarded as a vital step in REX; to restrict the impact of hydrolytic degradation on the viscosity, the minimization of the moisture content has been proved essential. Thus, before processing, the

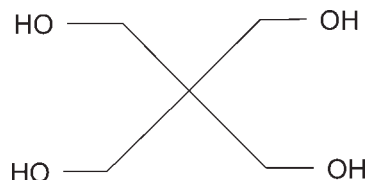


Figure 2 Chemical structure of pentaerythritol.

samples were dried at 120°C for 18 h *in vacuo* after four nitrogen purges. Subsequently, they were kept in a desiccator for 2 h, above P₂O₅, to reach room temperature.

The melt modification of the three PET grades comprised dry blending, extrusion, pelletizing, and drying of the extrudates. The chain-extender master batch was used at selective concentrations according to the quality of the PET grade; the prepared samples had an additive concentration of 0, 1, 2, or 5 wt % for the virgin PET, 0, 2, 3, 4, or 5 wt % for the scrap PET, and 0, 4, 5, or 6 wt % for the postconsumer PET. The overall procedure in each grade case was repeated for reproducibility reasons.

The reactive processing of the PET samples was conducted in a single-screw laboratory extruder (PLE 330 plasticorder, Brabender). The screw length was 500 mm, and the diameter at the feeding port was 20 mm, providing an effective length-to-diameter ratio of 25. The temperature settings along the four zones, at the barrel and the die, were 240, 270, 280, and 280°C, whereas the screw rotation speed was kept constant at 30 rpm. Under these conditions, the average residence time of the samples in the extruder was measured at 130 s, as described elsewhere.²⁵

Characterization

To detect the structural changes induced during REX, the prepared samples were characterized through solution rheology, melt rheology, and thermal analysis.

Solution rheology

The dilute solution viscosity measurements were performed at a 0.5 g/100 mL polymer concentration in a mixture of phenol and 1,2-dichlorobenzene (50/50 w/w) at 25 ± 0.1°C with an Ubbelohde viscometer (ISO/DIS1228). The intrinsic viscosity IV was evaluated with the Huggins equation. Each measurement was conducted twice for reproducibility reasons, and the coefficient of variation (standard deviation/average) in these experiments was always less than 1%. The viscosity data were correlated with the molecular weight (MW) with the Mark–Houwink–Sakurada relation, $IV = KM^\alpha$. The constants, as obtained from the literature,³¹ were $K = 4.69 \times 10^{-2}$ and $\alpha = 0.68$. This relation provides only an indication of the samples average molecular weight because its accuracy is restricted in the case of branched polymers.³²

Melt rheology

The effect of chain extension on the melt rheology of the extrudates was studied through the changes in an industrially important parameter, the melt flow rate (MFR). MFR is an empirical index of the poly-

mer fluidity and is defined as the polymer mass extruded from a device of known geometry under a given pressure generated from the imposition of a prescribed external load at a given temperature. In practice, it is reported as the grams of the polymer collected from the test apparatus in 10 min.

The MFR experiments were carried out according to procedure A of ASTM D 1238 with a Kayeness Co. model 4004 capillary rheometer. The temperature was fixed at 260°C, and the weight of the ram load was equal to 2.16 kg. To ensure complete melting, the material (~ 5 g) remained in the barrel for 180 s before the beginning of the measurement. In all cases, only average values were reported, and the coefficient of variation was less than 2%.

Thermal analysis

To study the influence of chain extension on the thermal transitions and crystallinity of PET, thermal analysis was performed with a PerkinElmer Pyris 6 differential scanning calorimeter with pure indium as a calibration standard. To restrict the thermal lag between the differential scanning calorimetry (DSC) furnace and the polymer sample, a sample weighing approximately 10 mg, placed in an aluminum seal, was used. Furthermore, all runs were conducted under a nitrogen flow of 20 cm³/min to limit thermooxidative degradation.

For each measurement, the sample was subjected to heating from 30 to 300°C at a scanning rate of 10°C/min, and it remained at this temperature for 5 min to erase its previous thermal history. After this period, the sample was cooled to 30°C at 10°C/min, and the values of the crystallization temperature (T_c) and enthalpy of crystallization (ΔH_c) were recorded. Finally, it was scanned again up to 300°C at the same rate to observe the subsequent melting behavior. From this scan, the melting point (T_m), the glass transition temperature (T_g), and the enthalpy of fusion (ΔH_m) were measured. The degree of crystallinity was calculated with the following equation:

$$\text{Crystallinity (\%)} = \Delta H_c / \Delta H_0$$

where ΔH_c is the enthalpy of crystallization of the PET sample and ΔH_0 is the enthalpy of crystallization of 100% crystalline PET, which is equal to 120 J/g.³³ All the reported data are the averages of values obtained from the thermal analysis of three samples.

RESULTS AND DISCUSSION

Effect of REX on the solution and melt viscosity of PET

The reactive modification of PET represents a set of two counteracting reaction mechanisms, degradation

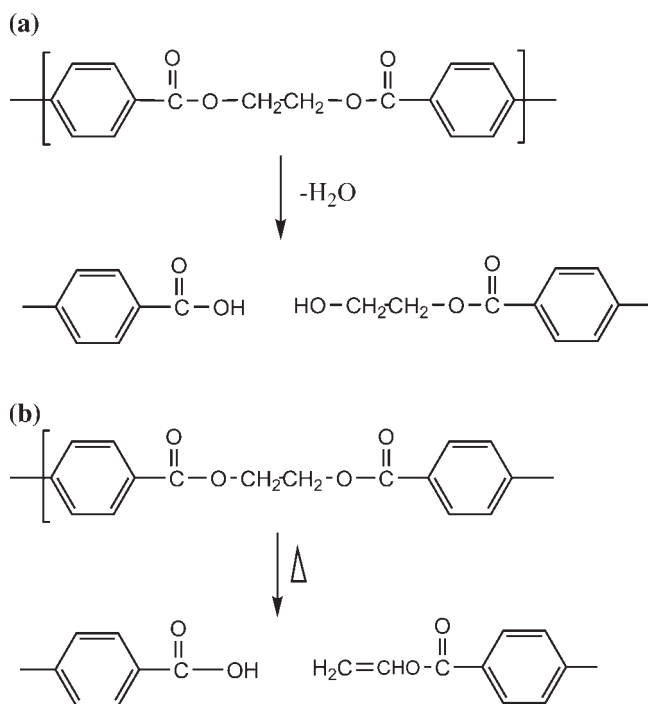


Figure 3 (a) Hydrolytic and (b) thermal degradation reactions of PET.

and chain extension. Degradation is responsible for the depression of the molecular weight and the corresponding deterioration of the polymer mechanical properties. The origin of this behavior is the well-known chain-scission mechanism; high shear forces and, to a lesser extent, oxidation at elevated temperatures cause carbon-carbon bond cleavage along the chain. Hydrolytic reactions, caused by the simultaneous presence of retained moisture and contaminants, result in shorter chains with acid and hydroxyl ester end groups [Fig. 3(a)], whereas the thermal cleavage

of the PET ester bond leads to the formation of carboxylic end groups and vinyl esters [Fig. 3(b)].^{9,21,34}

Regarding chain extension, a reaction mechanism between PET and PMDA, proposed by Khemami,³⁵ is shown in Figure 4. According to this mechanism, a first-step linear chain extension takes place when the PET hydroxyl end groups react with the anhydride functionalities, forming two carboxyl groups per incorporated moiety (coupling). Further esterification and transesterification reactions, which involve all four PMDA functional groups, lead to branched or even crosslinked structures. At this point, it should be mentioned that the chain extender used in this study resulted apparently in a branched structure because during solution viscometry, all samples were completely soluble in the solvent mixture; no insoluble gel was formed. The latter clarifies that the prevailing chain-extension reaction was branching because of the presence of the moderator pentaerythritol; the point of network formation and crosslinking was not reached.^{30,36}

The modification of the molecular structure during processing is reflected in the rheological characteristics of the PET samples, which are depicted in Table I. The reduction of the IV and increase in the MFR for the three untreated extrudates—0% virgin EXT, 0% scrap EXT, and 0% post EXT—are representative of the extended process-induced hydrolytic and thermal decomposition that the polymer suffers inside the extruder. On the other hand, when the chain extender is added, the effectiveness of REX is proved by the increase in the IV and MFR depression of the samples compared with those of the untreated extrudates.

Turning to the effect of the additive concentration, we found that the viscosity of the modified samples increased with the chain-extender content up to a

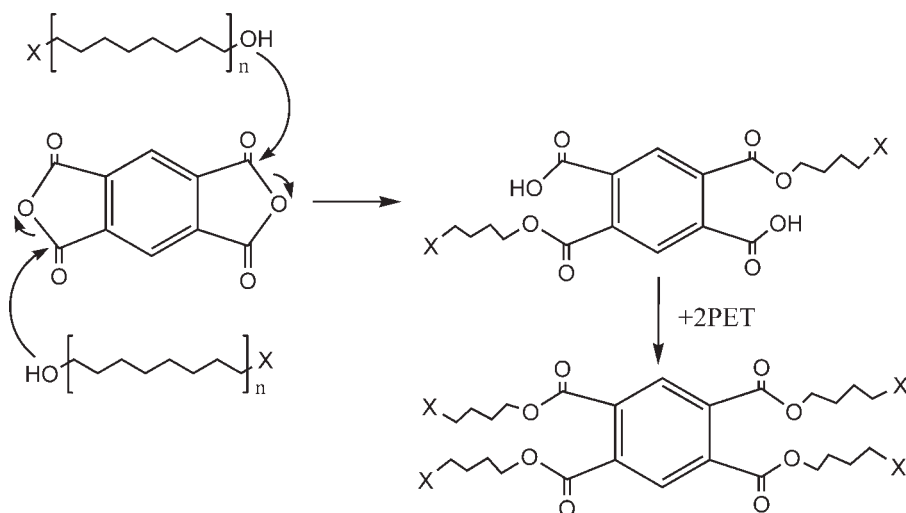


Figure 4 Reaction mechanism between PET and PMDA.

TABLE I
Rheological Data for the Raw Materials and Modified PET Samples

Sample	IV (dL/g)	MFR (g/10 min)
Virgin PET	0.769	20.6
0% virgin EXT	0.707	36.7
1% virgin EXT	0.749	30.7
2% virgin EXT	0.843	7.4
5% virgin EXT	0.724	61.3
Scrap PET	0.747	24.8
0% scrap EXT	0.653	44.5
2% scrap EXT	0.688	25.1
3% scrap EXT	0.728	19.4
4% scrap EXT	0.778	5.9
5% scrap EXT	0.752	43.7
6% scrap EXT	0.709	86.1
Post PET	0.659	49.9
0% post EXT	0.567	128.1
3% post EXT	0.642	103.1
4% post EXT	0.659	90.2
5% post EXT	0.655	136.1
6% post EXT	0.616	239.2

critical value, suggesting dominance of the chain-extension reaction over degradation. However, a further increase in the additive concentration resulted in changing the prevailing mechanism from chain extension to degradation, as concluded from the depression of the viscosity of the extrudates. This trend is clearly illustrated also in Figure 5, where the sample molecular weight is shown to increase, reach a peak, and finally decrease with the additive content. A potential reason is the complexity of the system containing reactive components of different reactivities. At low concentrations, the chain-extending mechanism of PMDA seems to prevail. In contrast, at higher concentrations, chain scission by transesterification through pentaerythritol seems to overcompensate the PMDA effect.^{30,36} Therefore, a

potential solution would be to adjust the components of the master batch exactly to the starting material and the targeted application.

Regarding the concept of closed-loop recycling, the molecular weight, as indicated by the IV (Table I) of 2% virgin EXT (0.843 dL/g) and 4% scrap EXT (0.778 dL/g), is well above the value required for bottle manufacture (0.76 dL/g). On the contrary, the IV of postconsumer bottle-grade PET samples culminates (4% post: 0.659 dL/g) below that value, hampering the potential of the reuse in the original application. Nevertheless, it could be used for applications for which the requirements of the mechanical properties are less stringent.

The picture of chain extension is similar when we examine the MFR values, which follow the opposite trend of the IV values: as anticipated, the MFR of the three grades first decreases, shifts to a minimum, and finally increases with increasing additive content. These results might be a good indicator of the resins molecular weight but can be interpreted only in a comparative manner because of the different degrees of branching of the modified samples. Branched structures present increased resistance to flow as a result of entanglement couplings associated with the branches; this is the reason that samples of similar IVs do not present comparable MFR values.^{27,37} For example, the MFR of 1% virgin EXT (0.749 dL/g) was measured to be 30.7 g/10 min, whereas the MFR of 5% scrap EXT (0.752 dL/g) was 43.7 g/10 min.

Effect of REX on the thermal properties of PET

The degree of crystallinity and the corresponding thermal transitions are parameters of great technological importance that reflect the chemical structure

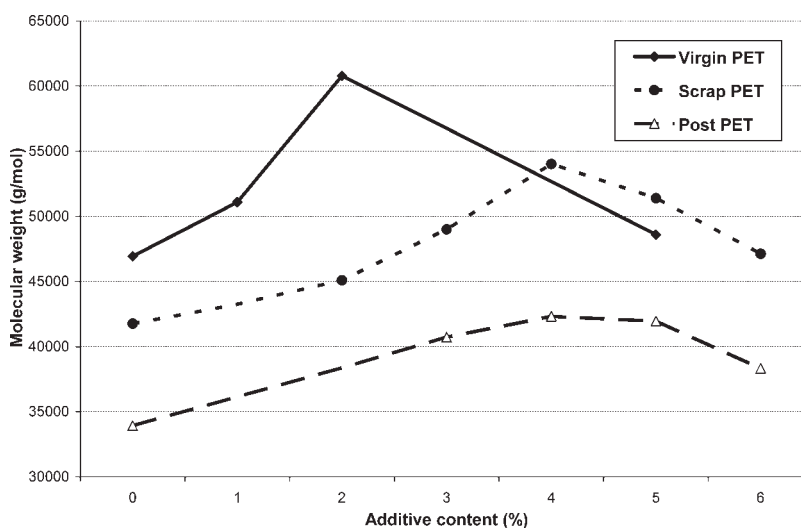


Figure 5 Molecular weight versus the additive concentration.

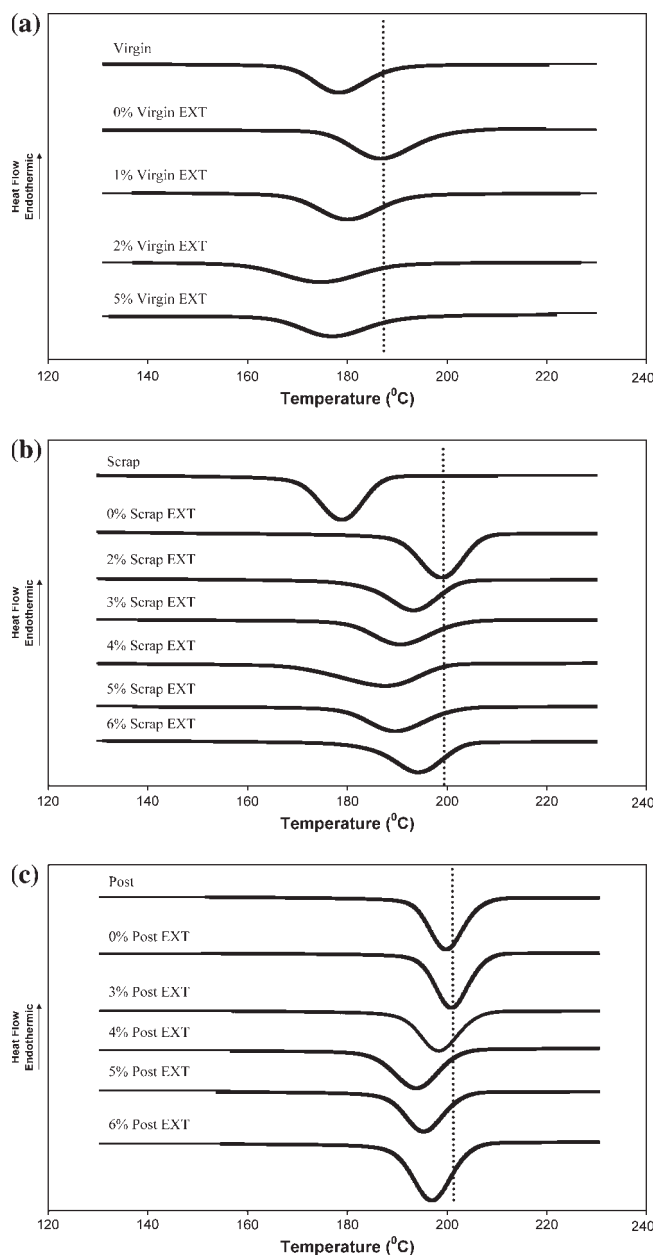


Figure 6 DSC cooling scans: (a) virgin PET, (b) scrap PET, and (c) postconsumer PET.

of the polymer and can be correlated with its mechanical properties. In this study, the thermal analysis of the reactive extruded samples was conducted through DSC, and the obtained cooling and subsequent heating curves of the virgin, scrap, and postconsumer PET samples are shown in Figures 6 and 7, respectively.

There is a distinct exothermic crystallization peak in all the cooling scans. Regarding the heating curves, the virgin PET extrudates demonstrate a single melting peak, whereas two endotherms are shown in the case of the chain-extended scrap PET samples and, more intensively, in the case of the postconsumer PET samples. An explanation of the

double melting is given, according to Medellín-Rodríguez et al.,³⁸ in terms of dominant and subsidiary crystals. The lower, less intense endotherm represents the melting of imperfect or smaller crystals with partially extended chains (secondary crystallization), whereas the higher one is assigned to the melting of the primary folded chain crystals. In that respect, the presence of the single melting peak for the virgin PET samples is indicative of their more homogeneous crystal structure.²⁸

The various parameters determined from the DSC curves are presented in Table II. T_c reflects the overall crystallization rate associated with the complex

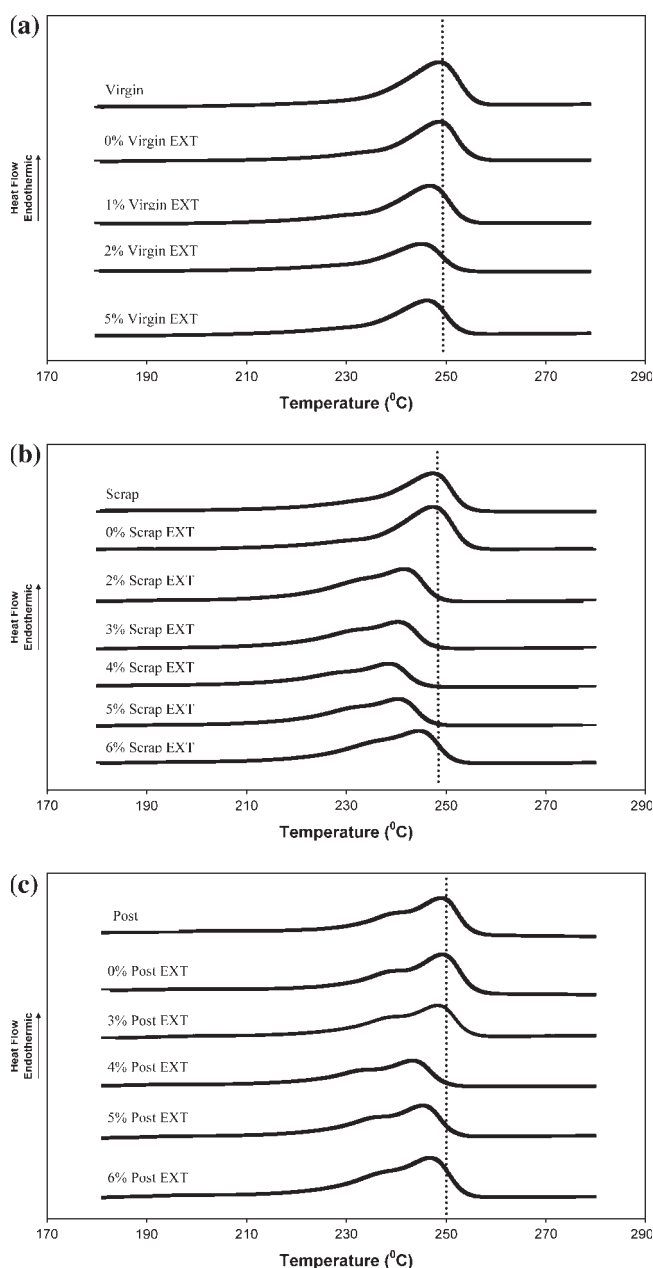


Figure 7 DSC melting scans: (a) virgin PET, (b) scrap PET, and (c) postconsumer PET.

TABLE II
Thermal Characteristics of the Raw Materials and Modified PET Samples

Sample	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	ΔT_c (°C)	ΔT_m (°C)	$\Delta H_c/\text{time}$ (J g ⁻¹ s ⁻¹)
Virgin PET	177.8	248.1	40.41	44.11	32	40	0.210
0% virgin EXT	183.0	248.5	43.26	44.41	32	42	0.229
1% virgin EXT	177.1	246.3	40.26	41.52	37	45	0.182
2% virgin EXT	175.6	246.1	35.30	37.35	45	48	0.130
5% virgin EXT	176.0	246.4	38.92	39.72	42	45	0.156
Scrap PET	180.8	247.4	44.79	45.29	32	42	0.233
0% scrap EXT	198.8	247.9	45.58	49.55	32	42	0.237
2% scrap EXT	191.9	242.7	38.81	43.52	35	45	0.185
3% scrap EXT	189.9	241.7	37.29	41.65	39	48	0.159
4% scrap EXT	187.2	239.9	36.60	39.53	42	50	0.145
5% scrap EXT	188.7	241.1	38.39	41.35	40	48	0.160
6% scrap EXT	192.4	244.9	39.95	42.24	35	45	0.190
Post PET	199.1	249.2	44.02	48.09	25	40	0.293
0% post EXT	200.2	249.4	45.05	50.53	25	45	0.300
3% post EXT	196.2	247.1	43.72	47.61	28	47	0.260
4% post EXT	193.5	245.4	42.14	45.09	30	50	0.234
5% post EXT	194.1	245.9	43.86	46.23	28	48	0.261
6% post EXT	195.8	246.7	49.29	51.09	25	45	0.328

phenomenon of nucleation and growth. The crystallization rate is defined as the enthalpy of crystallization divided by the time required from the onset to the completion of crystallization ($\Delta H_c/\text{time}$). Differences in ΔH_c and ΔH_m , as well as the crystallization (ΔT_c) and melting (ΔT_m) width, are assigned to the extent of crystallization and the homogeneity of the crystal structure.³⁹ T_g is not reported because it was found not to be significantly affected by the REX process, in accordance with the literature.^{25,28}

First, the effect of extrusion without the presence of the chain extender is examined through a comparison of the thermal characteristics of the extrudates (0% virgin EXT, 0% scrap EXT, and 0% post EXT) with those of the respective raw materials. On that basis, the values of ΔH_c and ΔH_m of the extrudates were found higher, indicating that the process-induced degradation facilitates crystallization. Further evidence to this is also provided by the increase in the crystallization rate. These results are in complete accordance with the findings of Silva Spinace and De Paoli,⁴⁰ according to which the chain scission, occurring during the processing of PET, seems to improve chain packing, increasing the crystallite size and consequently shifting T_m and T_c to higher values.

As for the influence of REX on the thermal properties of the extrudates, an analysis of the experimental data shows that they are strictly dependent on the chain-extender content. In particular, with an increase in the additive concentration (0–2% virgin EXT, 0–4% scrap EXT, and 0–4% post EXT), a substantial shifting of ΔH_m , ΔH_c , T_m , and T_c to lower values can be observed, indicating that crystallization is hindered by chain extension. Moreover, ΔT_c and ΔT_m increase, and this proves the growing het-

erogeneity of shapes and sizes of the formed crystallites. The lower crystallization rates simply ascertain the reduction of the samples' crystallizability. Hence, it can be concluded that the ability of the polymer chains to crystallize in folded lamellae seems to be limited in the chain-extended samples, and this leads to the formation of smaller and less perfect crystallites. Based on the fact that branching is the prevailing chain-extension reaction, this can be attributed to the presence of branching points that distract the chain symmetry, restrict the segment movements, and act as crystal defects.⁴¹

As mentioned before, the degree of branching, indicated by the IV measurement, maximizes at a specific additive concentration (2% virgin EXT, 4% scrap EXT, and 4% post EXT), over which it decreases, possibly because of chain scission becoming the predominant reaction mechanism. This tendency is also illustrated by the crystallinity (Fig. 8) and the corresponding thermal characteristics of the modified PET samples. The depression of the branching points enhances the ability of the macromolecules for free rotation or translation to reorganize and form the crystal structure. Hence, ΔH_m and ΔH_c start to shift to higher values, and the same trend is followed by T_m and T_c . A sharpening of the melting and crystallization peaks is also reported, suggesting crystallites of better homogeneity.

CONCLUSIONS

In this study, the REX technique was applied for upgrading three PET grades: virgin, industrial scrap, and postconsumer bottle-grade PET. For this purpose, a chain-extender system consisting of PMDA,

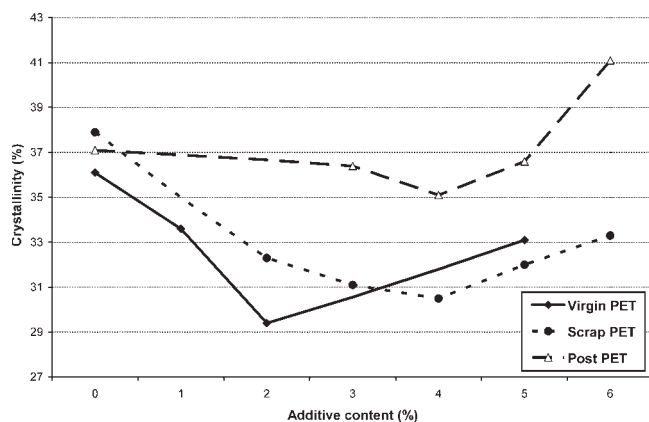


Figure 8 Crystallinity versus the additive concentration.

pentaerythritol, and a phosphonate catalyst was used, and its ability to improve the recycle quality was investigated. The reactive processing of PET represents a complex set of competing reactions, degradation and chain extension/branching. In that respect, rheological and thermal characterizations were performed and used as criteria of the modification induced in the polymer molecular structure during processing.

On the basis of the interpretation of the IV and MFR experimental data, the molecular weight of the modified PET samples was found to increase with the additive concentration. This increase was accompanied by an alteration of the crystallinity level and the crystallization rate of the treated extrudates. This is attributed to the branching effect of the chain extender, which restricts the motion of the polymer chains and their organization in the crystal structure, leading to the formation of less perfect and less uniform crystals. However, the results illustrate that there is a specific additive content at which the upgrading of the PET grades culminates. Over this concentration, the molecular weight of the modified samples starts to diminish, and this facilitates the formation of a more perfect crystal structure.

The authors thank D. Ntokos for his contribution to the Experimental section and Plastiko, Ltd., for the poly(ethylene terephthalate) grades. One of the authors (C.D.P.) also gratefully acknowledges Ciba Specialty Chemicals, Ltd., for its solid support of this project.

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