

Chain Extension Reaction in Solid-State Polymerization of Recycled PET: The Influence of 2,2'-Bis-2-oxazoline and Pyromellitic Anhydride

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ABSTRACT: Conventional and chain extended-modified solid-state polymerization (SSP) of postconsumer poly(ethylene terephthalate) (PET) from beverage bottles was investigated. SSP was carried out at several temperatures, reaction times, and 2,2'-bis-2-oxazoline (OXZ) or pyromellitic anhydride (ANP) concentrations. The OXZ was added by impregnation with chloroform or acetone solution. Higher molecular weights were reached when the reaction was carried out with OXZ, resulting in bimodal distribution. The molecular weights of the flakes reacted at 230°C for 4 h were 85,000, 95,000, and 100,000 for samples impregnated with 0, 0.5, and 1.25 wt % OXZ solution, respectively. In the

case of reactions with ANP, branched chains were obtained. The thermal and thermal-mechanical-dynamic properties of these high-molecular-weight recycled PET were determined. For OXZ-reacted samples, the reduction of crystallinity was observed as the reaction time was increased, becoming evident the destruction of the crystalline phase. The chain extended samples did not show changes in thermal relaxations or thermal degradation behavior. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 3177–3188, 2010

Key words: PET; chain extender; oxazoline; pyromellitic anhydride; solid-state polymerization; recycling

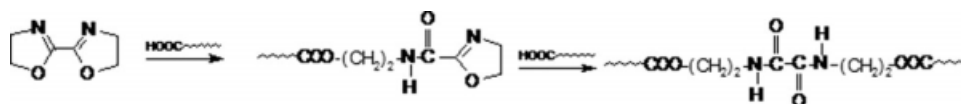
INTRODUCTION

The use of chain extenders to increase the molecular weight of condensation polymers by the reaction between reactive end groups is extensively reported in the literature.^{1–5} Several authors^{6–13} have synthesized new molecules or used commercial chemicals as chain extenders for poly(ethylene terephthalate) (PET), nylon, and other commercial polymers. Some chain extenders generate by-products and others promote chain extension without any by-products, if a ring-opening reaction takes place. It is the case of 2,2'-bis-2-oxazoline (OXZ), which can react with two carboxylic end groups of PET without by-product formation, improving the hydrolytic resistance by the decrease of the concentration of these carboxyl PET end groups (Scheme 1). Differently of OXZ reaction, the reaction between PET and pyromellitic anhydride (ANP) can produce branched structures (Scheme 2) because carboxylic groups generated from anhydride ring opening can react with another polyester molecule.

Literature reports that the chain extension reaction can be performed in solution or in the molten state in a mixer chamber or by extrusion. The last approach is more attractive, because it is easier to extrapolate the process to an industrial plant due to the high process speed and the absence of large solvent volume. However, to carry out the reaction by extrusion, some disadvantages appear such as the need of a specific extruder design capable of promoting ideal combination between the homogenization/mixing and appropriate residence time to reach the optimum molecular weight. Because of high temperatures used in the extrusion, some chain extenders can degrade and side reactions can lead to lost of the polymer optical properties, even in a very short residence time.

PET is one of the most important plastics with wide use particularly as packaging. Its annual world consumption is over 10 million tons, which makes the recycling a relevant subject considering environmental protection aspects. The application of chain extension and solid-state polymerization (SSP) has been cited as good methods to improve the quality of recycled PET.^{12–19} Thus, in this work, a new method that can be applied to PET recycling is introduced. The method combines a SSP process of PET flakes previously impregnated with chain extenders (modified chain extended SSP).

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Scheme 1 PET chain extension reaction with 2,2'-bis-2-oxazoline (OXZ).

The literature¹⁴ mentions the need of a drying/crystallization step before SSP process to avoid particles sticking and polymer hydrolysis. As amorphous phase is reduced, the stick tendency decreases either.

It is expected that, during the modified SSP, both esterification and transesterification reactions take place and the ultimate molecular weight is the result of all reactions, including degradation, polymerization, and chain extension. In addition, these reactions can be indirectly affected by the crystalline morphology and diffusion effects. These two factors are introduced because of the solid nature of the reactive environment. The influence of crystalline morphology is related to the assumed hypothesis that the condensation reactions only occur in the amorphous phase²⁰ and involve the end groups, which are chains defects expelled from crystalline phase. As esterification and transesterification are reversible reactions, producing volatile by-products, the diffusivity plays an important role on the rate of polycondensation. So that, there are technologies^{21–23} of conventional SSP developed to improve the reaction rate by using PET particles with larger surface area, like porous pills or pellets with special shapes. Considering this approach, the use of flakes instead of pellets is suitable to improve both the diffusivity of by-products and the absorption of chain extender, in the case of the modified SSP.

Others factors that affect the global reaction rate in the conventional SSP process are the initial molecular weight of the prepolymer, the concentration and type of end groups, the catalysts used, the technique applied to remove the by-products, the residence time, and the reaction temperature.¹⁴

Therefore, it was the aim of this work to investigate the mentioned chain extended-modified SSP. PET flakes, either nonimpregnated or impregnated or extruded with two chain extender (OXZ and ANP), were submitted to SSP in different temperatures and residence times. The molecular weight, thermal properties, and structural characterization of the samples were achieved with the purpose to compare the samples. A comparison between impregnation by solution with ANP and extrusion process is discussed. In this case, the SSP initial materials have different forms and molecular weights. A preliminary study using only pure flakes was done with the aim of investigating the SSP process conditions. The influence of residence time, temperature, nitrogen flow, and flakes crystallization condition was investigated.

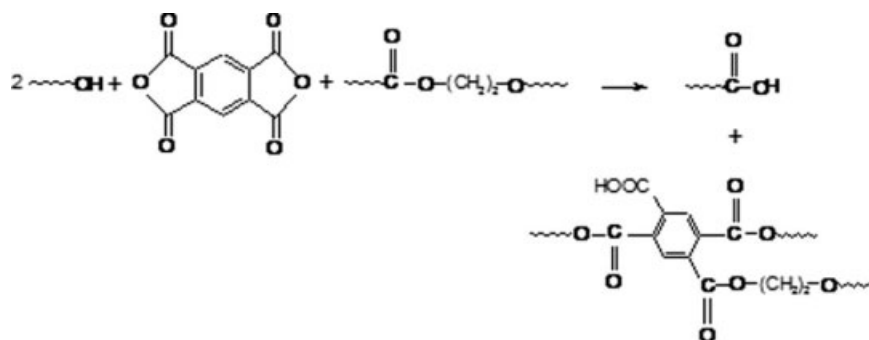
EXPERIMENTAL

Materials

Flakes of PET were obtained by grinding postconsumer 2 L bottles without caps and labels. 2,2'-Bis(2-oxazolona) and pyromellitic anhydride from TCI were used as received. Acetone and chloroform (Vetec, Brazil) were dried over molecular sieves.

Preparation of flakes

Before grinding, selected bottles were washed with plenty of water and predried by ambient exposure. To avoid the interference caused by unknown factors, as different kinds of catalysts, comonomers, or contaminants, only one manufacturer supplied the bottles used. The manufacturer took the bottles from



Scheme 2 PET chain extension reaction with pyromellitic anhydride (ANP).

the market after the product has become unsuitable to consumption. The bottles were used to pack one kind of soft drink that never was consumed. The manufacturer informed that the bottles were produced with one grade of commercial resin. Clean and dried flakes were separated by size with a set of standard sieves. The use of recycled PET in a flake form was preferred in this work, because this form has a larger surface area than pellets, which improve the impregnation process, and an extrusion process step is avoided. The flake fraction with an average diameter of 2.4 mm was used in this study.

Conventional SSP

SSP reactions were carried out in a stainless steel reactor with controlled heating and nitrogen flow. Before the reaction, the flakes were dried/crystallized for 16 h in an oven at 150°C. The reaction time was varied in the range of 6–16 h. The influence of reaction temperature (190, 210, and 230°C) and nitrogen flow rate (2.4 and 1.1×10^{-4} m³/s) was studied. In some experiments, this procedure was carried out at 170°C for 16 h and 150°C for 4 h. For comparison, characterization was also performed in samples not submitted to SSP to verify the influence of drying/crystallization temperature.

Chain extended-modified SSP

Chain extended-modified SSP was carried out in the same stainless steel reactor used in the conventional SSP. The dried flakes were immersed in an acetone or chloroform solution of the chain extender, and the impregnation process was carried out overnight. After the contact time, the solvent was evaporated and the flakes were put immediately into the SSP reactor. The chain extender influence was studied using the following SSP conditions: (1) residence time: 2, 4, and 6 h; (2) reaction temperature: 190, 210, and 230°C; nitrogen flow rate: 1.1×10^{-4} m³/s; and crystallization/drying condition: 150°C/16 h. OXZ solutions with concentration 0.5 and 1.25% (w/v) were used in the impregnation. The ANP impregnation was only done with a 0.5% (w/v) chloroform solution. Some experiments were performed using PET flakes extruded with ANP in the concentrations of 0, 0.1, 0.5, and 1 wt %. The extrusion was carried out at 100–220–240–250°C profile, 40 rpm in a HAAKE Model TW 100 extruder (L/D ratio = 25). Dry acetone and chloroform (Vetec, Brazil) were the solvents used in these experiments.

Molecular weight determination

Size-exclusion chromatography (SEC) was carried out in a Waters system using a Waters 510 pump

and a Waters 410 differential refractometer, the Waters Millennium software, and two GMHXL TSK gel columns at 25°C. The eluent used was recently distilled 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The system was calibrated with monodisperse poly(methyl methacrylate) standards. Because of the difference between hydrodynamic volumes of PET and PMMA in HFIP, molecular weights were corrected by a method described in literature.²⁴ An average curve from at least three analyses of each sample was considered.

The intrinsic viscosity $[\eta]$ determination was carried out at 30°C using an Ubbelohde 1B viscometer and phenol/tetrachloroethane (60 : 40 v/v) as solvent. The method is described in ASTM D 4603-91.

Differential scanning calorimeter

The thermal behavior of the samples was investigated using a differential scanning Perkin Elmer model DSC 7 calorimeter, under nitrogen atmosphere, in the following sequence: (1) first heating run from 25 to 300°C at 10°C/min, T_m and ΔH_m being determined; (2) fast cooling from 300 to 25°C; (3) second heating run from 25 to 300°C at 10°C/min, T_{ch} , T_m , ΔH_{ch} , and ΔH_m being determined; (4) second cooling run to 25°C at 10°C/min, for the determination, T_{cc} and ΔH_{cc} . The degree of crystallinity (X_c) was calculated by the equation: $X_c = \Delta H_m / \Delta H^o$, where $\Delta H^o = 32.5$ cal/g²⁵ and ΔH_m is the total melting enthalpy in the run.

Thermal gravimetric analysis

The thermal stability of a sample that reacted with the chain extender was compared with another one that was submitted to SSP, without the chain extender. The analysis was carried out in a Perkin Elmer TGA 7 using the temperature range: 30–700°C, heating rate: 10°C/min, under N₂ atmosphere.

Dynamic mechanical thermal analysis

Transitions and relaxations of the materials before the reactions were determined using a Rheometric Scientific Model MK dynamic mechanical thermal analyzer. The properties were determined using the bending mode. Samples used were 2 cm × 1 cm sheets with 2 mm thickness prepared by compression molding of flakes. The lost tangent ($\tan \delta$) was determined. The analysis was performed at temperature range: –120 to 180°C, heating run: 2°C/min, frequency: 1 Hz, and amplitude: 30 μ m.

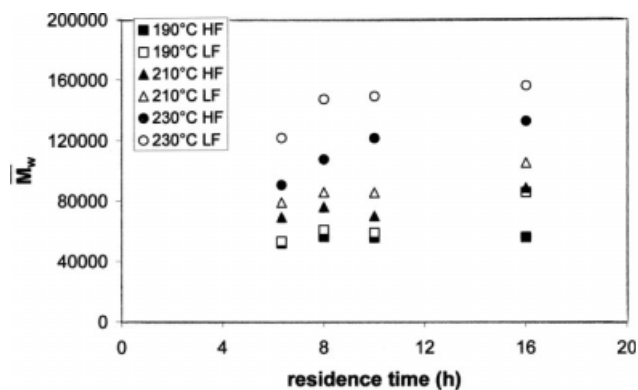


Figure 1 Reaction temperature, residence time, and nitrogen flow rate influence on molecular weight (\bar{M}_w) of PET flakes crystallized at 150°C/16 h, submitted to SSP. HF and LF are 2.4 and 1.1×10^{-4} m³/s nitrogen flow rates, respectively.

Infrared spectroscopy

A Perkin FTIR 1720-X Elmer spectrometer was used in this analysis. Some reacted samples were dissolved in HFIP and polymer films formed over KBr plate. The analysis was performed using the following conditions: resolution: 2 cm⁻¹; run number: 10; wave number range: 4000–400 cm⁻¹.

Rheological characterization

Rheological analysis was done with the aim to characterize branched structures formed when ANP was used. A cone-plate Ares rheometer (Rheometric Scientific) was used, and the analysis was performed under nitrogen flow at 280°C. The viscosity and the first normal stress difference were determined using a permanent shear procedure, with a shear rate range of 0.001–100 s⁻¹.

RESULTS AND DISCUSSION

Conventional SSP

For samples crystallized at 150°C for 16 h, using high and low nitrogen flow (2.4 and 1.1×10^{-4} m³/s, respectively), marked changes in weight-average molecular weight (\bar{M}_w) took place depending on reaction temperature (Fig. 1). It is expected that the increase in the nitrogen flow rate increases the molecular weight (\bar{M}_w), because of increase in the efficiency of by-products elimination. This effect may be noted up to a certain extent where the increase in the flow rate will produce no effect on the \bar{M}_w . However, better results were achieved when low nitrogen flow rate was used. This unexpected result might be attributed to differences in temperature profile inside the reactor that seems to be influenced by the nitrogen flow. This

TABLE I
Molecular Weight (\bar{M}_w) and Intrinsic Viscosity ($[\eta]$) of PET Flake Samples

Sample	\bar{M}_w	$[\eta]$ (dL/g)
Nonreacted flakes ^a	38,000	0.77
190°C, 4 h	46,000	0.85
190°C, 6 h ^b	57,000	1.21
230°C, 6 h	111,000	1.88
230°C, 16 h	132,000	2.30

^a Before crystallization.

^b OXZ/acetone (1.25% OXZ).

possibility could not be investigated because the reactor had only one point to take the temperature value.

The results of viscosity measurements in Table I corroborate the SEC results. The sample with highest molecular weight ($\bar{M}_w = 132,200$) showed an intrinsic viscosity of 2.3 dL/g, much higher than a commercial virgin PET sample ($\bar{M}_w = 46,000$ and $[\eta] = 0.85$ dL/g).

The effect of the temperature used in the drying/crystallization step on \bar{M}_w of solid-state polymerized flakes is shown in Figure 2. When crystallization was performed at 170°C, the efficiency of SSP decreased. The \bar{M}_w increases continuously with reaction time, even at the high temperatures and longer time used, which shows that degradation reactions were not significant in this conditions.

Some differences between the molecular weights of crystallized and noncrystallized samples were also observed (Table II), probably because of thermal and oxidative degradation during the crystallizing/drying step. In spite of the sample crystallized at 150°C for 4 h to show higher molecular weights, the crystallization at 150°C for 16 h was chosen for the further experiments with the chain extender because of the assurance of drying efficiency.

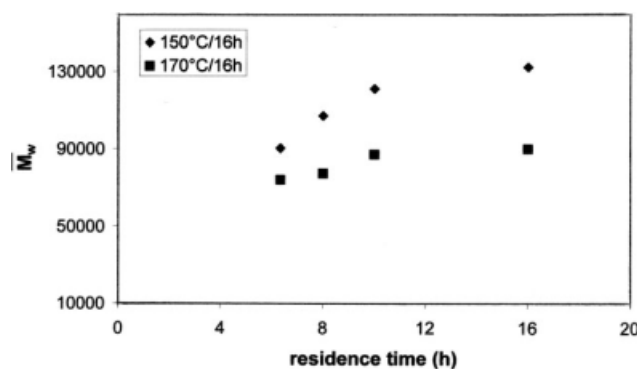


Figure 2 Molecular weight (\bar{M}_w) of flake samples crystallized at 150 and 170°C for 16 h, submitted to SSP at 230°C, under nitrogen flow of 2.4×10^{-4} m³/s, with different residence times.

TABLE II
Molecular Weights and Polydispersity of Crystallized Flake

Temperature and time of crystallization (°C/h)	Before crystallization			After Crystallization		
	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
150/6	17,000	38,000	2.0	15,000	33,000	2.0
170/6				13,000	28,000	2.0
150/4				17,000	35,000	2.0

SSP modified by OXZ

The modified SSP was performed with impregnated PET flakes, using OXZ/chloroform or OXZ/acetone solutions. The solvents were used because of the capacity to interact with PET, swelling the polymer chains, and helping the chain extender penetration. Tables III and IV show the molecular weights obtained with different residence times, reaction temperatures, and solution concentrations. In general, higher \bar{M}_w values were observed for samples impregnated with higher OXZ concentrations, comparing samples reacted in the same condition. As it is expected, increase of both time and temperature improved the molecular weight.

Because of its higher capacity to swell PET, chloroform makes possible a deeper permeation of the

TABLE III
Molecular Weight (\bar{M}_w) of PET Flake Samples Impregnated with OXZ/Acetone Solution in Different Reactions Conditions

Temperature (°C)	Residence time (h)	Solution concentration (%)	\bar{M}_w
190	2	–	44,000
		0.5	42,000
		1.25	47,000
	4	–	46,000
		0.5	47,000
		1.25	58,000
	6	–	52,000
		0.5	54,000
		1.25	57,000
210	2	–	39,000
		0.5	47,000
		1.25	52,000
	4	–	56,000
		0.5	56,000
		1.25	64,000
	6	–	63,000
		0.5	67,000
		1.25	67,000
230	4	–	85,000
		0.5	83,000
		1.25	84,000
	6	–	111,000
		0.5	74,000
		1.25	109,000

TABLE IV
Molecular Weight (\bar{M}_w) of PET Flake Samples Impregnated with OXZ/Chloroform Solution in Different Reactions Conditions

Temperature (°C)	Residence time (h)	Solution concentration (%)	\bar{M}_w
190	2	–	44,000
		0.5	43,000
		1.25	56,000
		–	46,000
		0.5	66,000
		1.25	65,000
	4	–	52,000
		0.5	75,000
		1.25	56,000
		–	39,000
		0.5	50,000
		1.25	54,000
210	2	–	56,000
		0.5	63,000
		1.25	74,000
		–	63,000
		0.5	78,000
		1.25	75,000
	4	–	57,000
		0.5	81,000
		1.25	72,000
		–	85,000
		0.5	95,000
		1.25	100,000
6	–	111,000	
	0.5	80,000	
	1.25	108,000	

chain extender, which would improve the reaction. As temperature or OXZ concentration increased, a secondary peak appeared in a higher molecular weight region of the SEC chromatogram (Fig. 3). This peak also appeared in some samples impregnated with acetone solution but, in this case, it had an insignificant size. However, in the case of samples impregnated with chloroform, this secondary peak became larger, particularly in samples reacted for 6 h. The critical cases were the samples reacted at 230°C for 4 and 6 h (Fig. 3), where a bimodal curve could be seen. In those cases, the \bar{M}_w values of the samples (Table IV) did not correspond to the total sample, because it was not possible to calculate the molecular weight of the secondary peak using the calibration curve plotted with commercial PMMA standards. As observed in the chromatograms (Fig. 3), the samples reacted with OXZ presented a higher molecular weight than the flakes reacted without any extender, regardless of the lower values showed in Table IV. These results suggest that the impregnation process did not induce a continuous variation of OXZ concentration inside PET matrix. The presence of two peaks instead of only one broader peak is an evidence that two different regions were formed in PET matrix: a surface

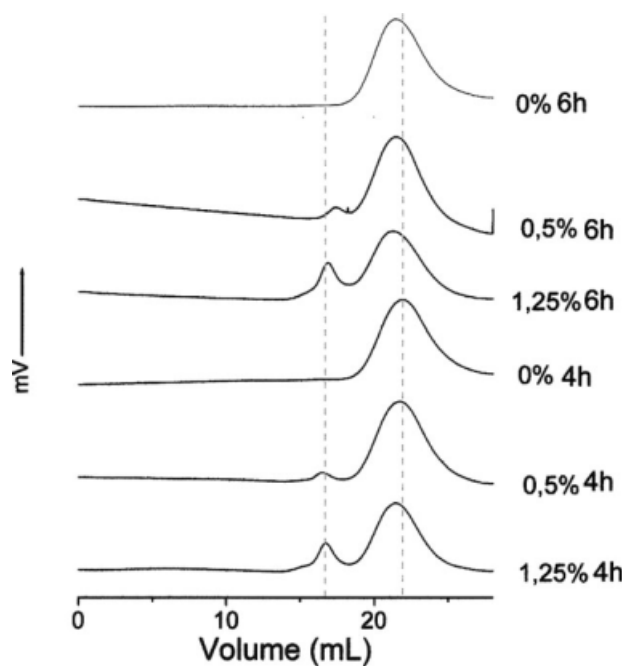


Figure 3 Chromatograms of OXZ/chloroform-impregnated samples reacted at 230°C for several residence times.

layer, with higher OXZ concentration, and a core with lower concentration. Probably, this effect can be due to the influence of the bioriented morphology of PET bottles, but it could only be verified comparing with an isotropic nonoriented PET matrix experiment. An external part of the sample reacted for 6 h

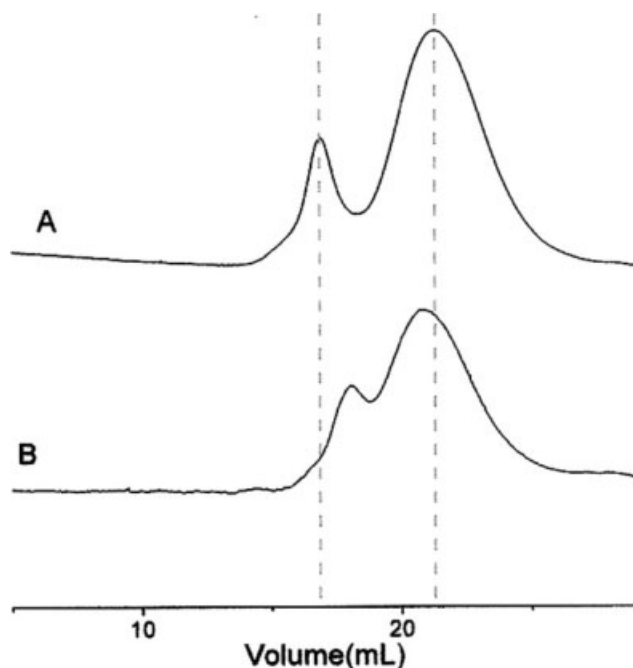


Figure 4 Chromatograms of 1.25% OXZ/chloroform-impregnated samples reacted at 230°C for 6 h. A: integral sample; B: surface part sample.

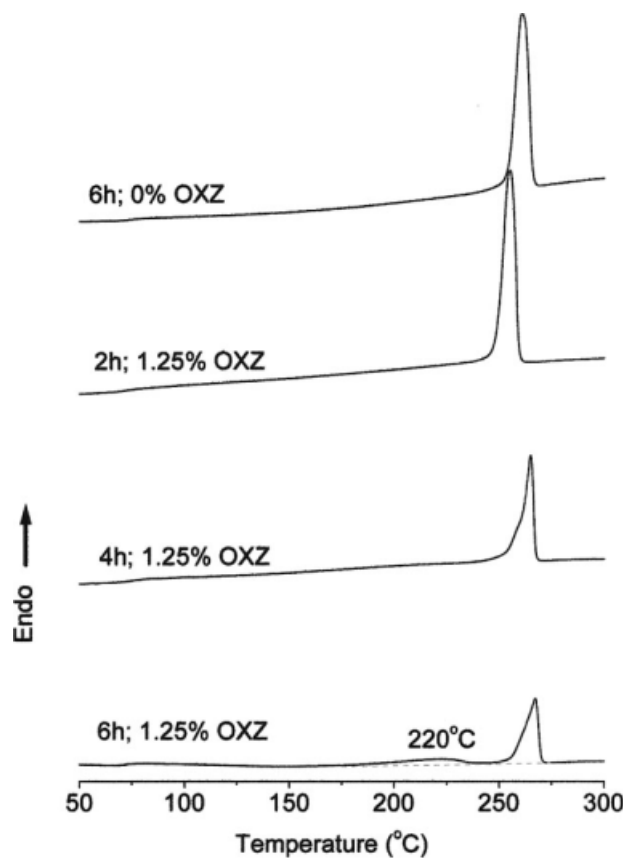


Figure 5 DSC first heating run of OXZ/chloroform-impregnated samples reacted at 230°C for several residence times.

and impregnated with a 1.25% OXZ chloroform solution was mechanically removed from the sample surface and dissolved in HFIP to be analyzed by SEC. A partial solubility was observed, without a gel formation, which indicated the high molecular weight of the sample and the absence of crosslinks. The comparison between the surface part sample and the whole one by chromatography was hindered by this solubility problem (Fig. 4), because the higher molecular weight part was excluded.

The increase of crystallinity occurs during a conventional SSP, because an annealing takes place simultaneously with the reaction. However, in the case of OXZ-reacted samples, the opposite was observed (Fig. 5). Chain extension reactions promoted the destruction of existing crystallites and the development of few imperfect crystallites with lower melting temperature. It is well known that the rise of molecular weight decreases the molecular mobility, and as a consequence, the decrease in the crystallization tendency in both, the cooling from the melt and on heating of quenched samples. This effect can be observed by either the rise of T_{ch} or the drop of T_{cc} . Moreover, the decrease in the crystallization peak area or, more precisely, the decrease in the heat of crystallization means that a smaller

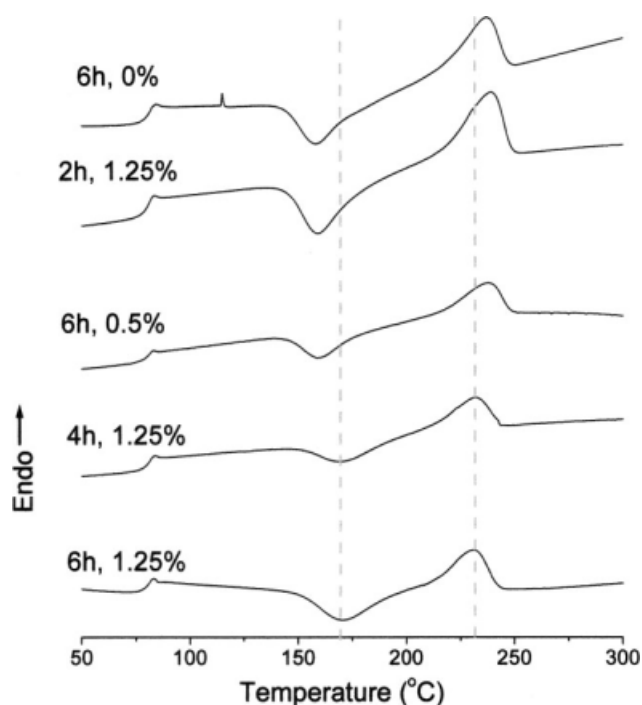


Figure 6 DSC second heating run of OXZ/chloroform-impregnated samples reacted at 230°C for several residence times.

amount of crystallites was formed. These effects are clearly observed in Figures 6 and 7. Both samples impregnated with 1.25 and 0.5% OXZ chloroform solution for 4 and 6 h, respectively, showed small tendency to crystallize when compared with the sample nonimpregnated with the chain extender and reacted for 6 h. These results corroborate the fact that the use of a chain extender impregnated in PET can improve so much the molecular weight in SSP that the residence time or temperature can be significantly decreased to obtain the requested molecular weight.

Comparing both the processes, the polydispersity of OXZ-reacted material would be also higher and its influence in process and products should be investigated.

No relevant changes in relaxations were observed for OXZ-reacted material (Fig. 8). The β -relaxation, which appears as small peak around -60°C , did not change either.

In the same way, the thermal stability of PET material was not modified as a consequence of the chain extension reaction. The TGA curve profile (Fig. 9) of OXZ-reacted material is characteristic of a typical PET sample.

Even in the sample impregnated with the OXZ solution of higher concentration, it was not found in the FTIR spectrum (Fig. 10) any band of C—N bond (e.g., 1635 cm^{-1}). It is probably due to the low amount of this linkage in the material; FTIR analysis is not sensible enough to detect it. The improbable

possibility that OXZ could polymerize over PET flakes was definitely rejected.

SSP modified by ANP

Two routes were used for modifying SSP with ANP: (1) impregnation of PET flakes using a 0.5% ANP/chloroform solution and (2) extrusion of PET flakes with ANP-generating pellets.

Samples extruded with ANP showed gel formation after dissolving in HFIP. Thus, the reaction with ANP took place in the extrusion step and the SSP initial material was already, in some degree, branched and crosslinked PET. The rise of molecular weight during the SSP could occur simultaneously with reactions, which generated new branches points, if the ANP has not been completely consumed during the extrusion. If most ANP has been consumed, linear chain growth of the initial branching structure was predominant in SSP.

In the case of impregnated samples, gel formation was observed only after SSP. In this case, the initial material is basically composed by linear chains and the majority of branches formed in SSP must be constituted by long chain segments whose size depends

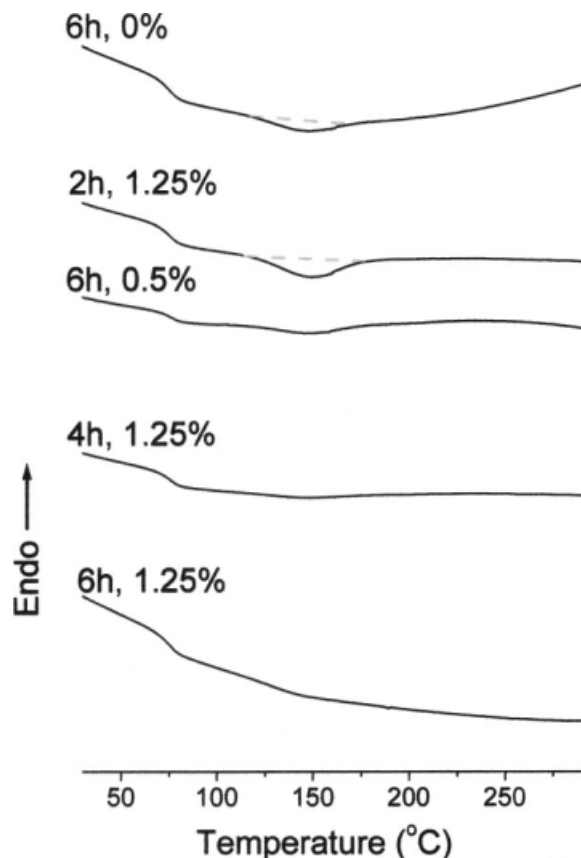


Figure 7 DSC second cooling run of OXZ/chloroform-impregnated samples reacted at 230°C for several residence times.

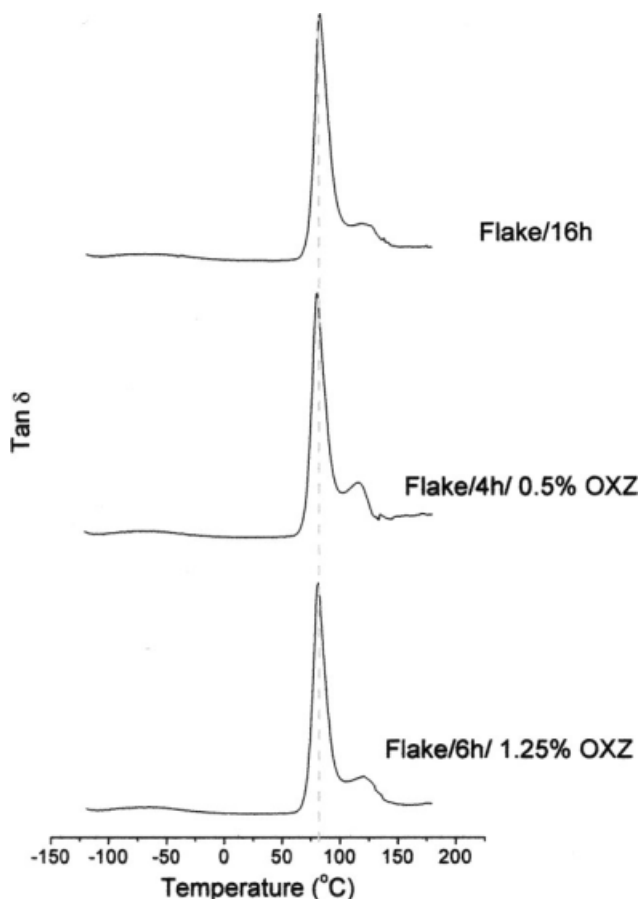


Figure 8 Loss tangent ($\tan \delta$) of pure and OXZ/chloroform-impregnated flake samples, reacted at 230°C for several residence times.

on position of the ester group reacted inside the molecule.

As linear standards were used in the SEC method, molecular weight determination of branched samples was inappropriate, besides part of the sample included in the gel cannot be analyzed by the method. The chromatograms of the soluble fraction of ANP-impregnated reacted samples are shown in Figure 11. The peak area decrease is more influenced by temperature than by the increase in residence time. Therefore, the branching process must have been stabilized in earlier stages of SSP. Obviously, the comparison between the elution volumes of samples reacted and nonreacted with ANP has no significance because the soluble part of ANP-impregnated reacted samples must consist of a mixture of branched and linear chains.

Considering that few and well-spaced branching points were formed, the long branched chains should crystallize in the same way of linear chains. Thus, the relation among T_{ch} , T_{cc} , and the heat of crystallization can be used to compare the drop of PET molecular mobility caused by chain enlargement and crosslinking points. Table V shows the

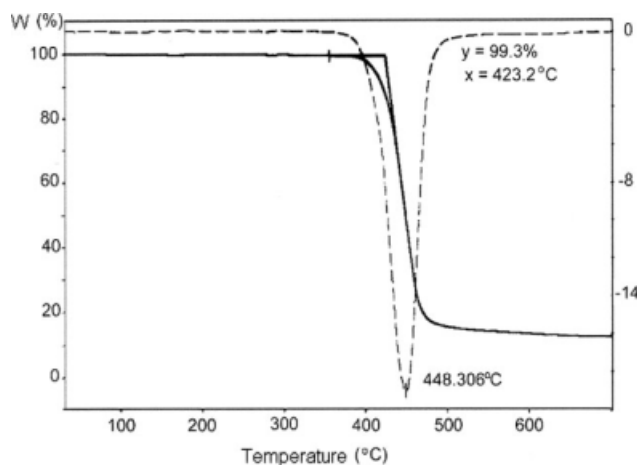


Figure 9 Weight loss (W) of 1.25% OXZ/chloroform-impregnated flake sample, reacted at 230°C for 6 h..

thermal properties and crystallinity of ANP-reacted and nonreacted samples. In the opposite of what was observed for OXZ-reacted samples, the crystallinity of ANP-impregnated samples increases as SSP residence time was increased. It is evident that chain extension reactions did not interfere on crystallization kinetics during SSP when ANP was used, in spite of the chain mobility lost caused by the

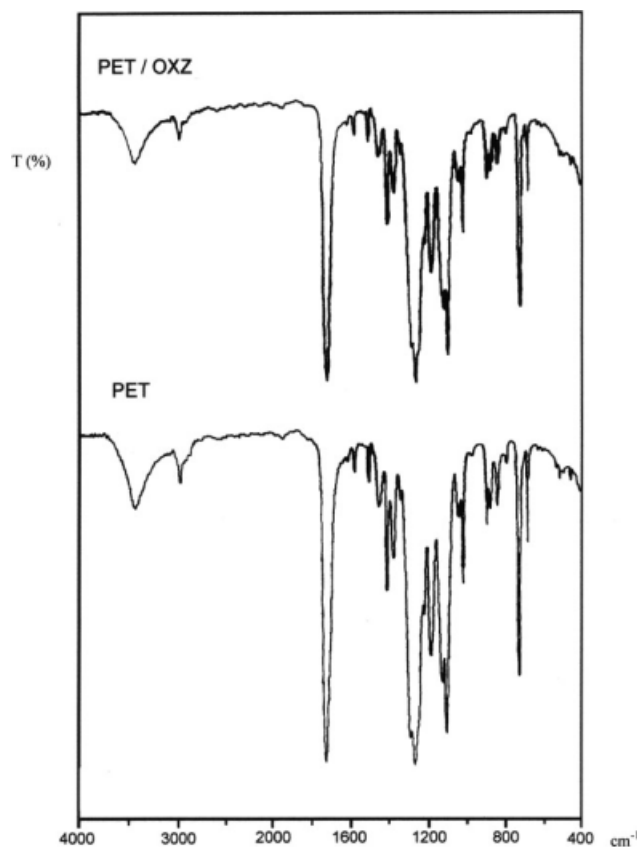


Figure 10 FTIR transmittance spectra of PET flake and 1.25% OXZ/chloroform-impregnated flake PET flake sample, reacted at 230°C for 6 h..

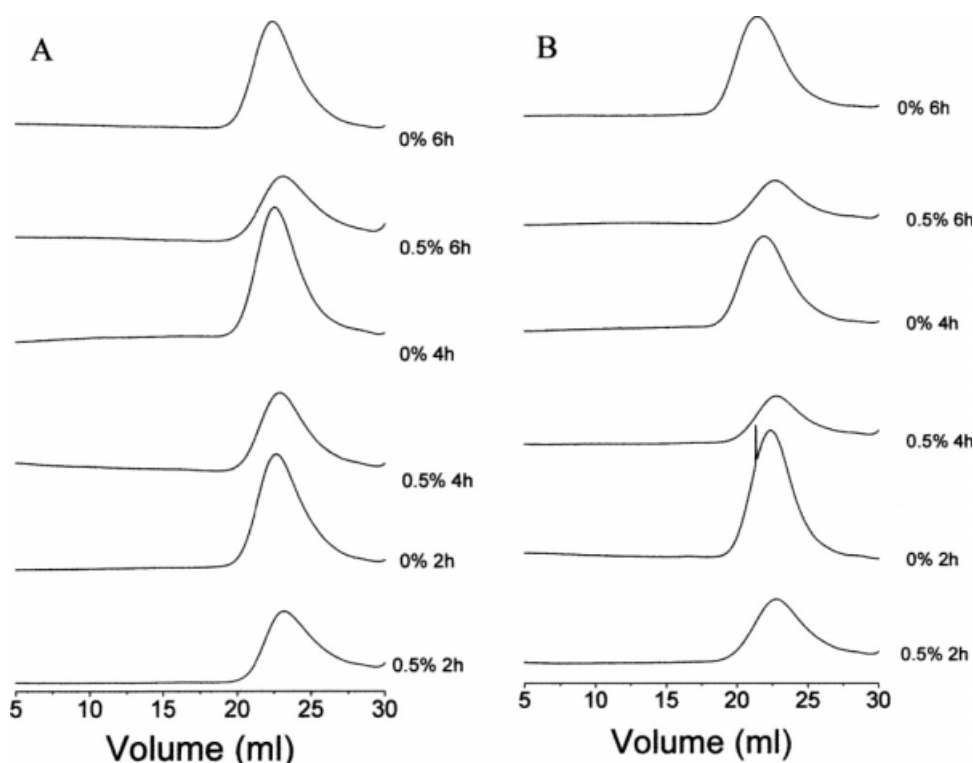


Figure 11 Chromatograms of ANP/chloroform-impregnated samples, reacted for several residence times. A: at 190°C; B: at 230°C.

crosslink's formation. No conclusive results were obtained by the comparison between T_{ch} and ΔH_{ch} tendencies, but the absence of a crystallization peak in the DSC cooling run suggests that extremely high molecular weights were achieved.

In the case of ANP-extruded and reacted samples, multiple melting peaks were observed in the first DSC heating run, showing that heterogeneous crystallites were formed in SSP. The total melting en-

thalpy showed a slight drop as the ANP concentration increased (Table VI). However, the thermal properties determined in the second heating and cooling run did not change significantly with ANP concentration, excepting for the sample reacted with 0.5% ANP, which showed an increase in T_{ch} and a decrease in T_{cc} .

Similarly to OXZ-reacted samples, the ANP-reacted material showed a characteristic PET

TABLE V
Thermal Properties and Degree of Crystallinity (X_c) of PET Flakes Impregnated in a 0.5% ANP Chloroform Solution and Reacted at 230°C

Properties	Samples				
	Flake/ANP, reacted for 2 h	Flake/ANP, reacted for 4 h	Flake/ANP, reacted for 6 h	Flake, reacted for 6 h	Flake, reacted for 16 h
\bar{M}_w	—	—	—	111,000	132,000
First heating run	T_m (°C)	254	260	254	261
	ΔH_m (J/g)	37	48	59	59
	X_c (%)	27	35	44	44
Second heating run	T_{ch} (°C)	168	173	167	159
	T_m (°C)	234	232	233	237
	ΔH_{ch} (J/g)	−21	−13	−25	−23
	ΔH_m (J/g)	22	18	24	22
Second cooling run	T_{cc} (°C)	—	—	—	148
	ΔH_{cc} (J/g)	—	—	—	−6

T_m , melting temperature; ΔH_m , melting enthalpy; T_{ch} and ΔH_{ch} , crystallization temperature and enthalpy at heating; T_{cc} and ΔH_{cc} , crystallization temperature and enthalpy at cooling.

TABLE VI
Thermal Properties and Degree of Crystallinity (X_c) of PET Flakes Extruded with ANP and Reacted at 230°C for 6 h

Properties	ANP concentration (%)				
	0	0.1	0.5	1	
\bar{M}_w	49,000	–	–	–	
First heating run	T_m (°C)	257	253	254	237, 239
	ΔH_m (J/g)	60	59	54	40, 12
	X_c (%)	44	43	39	38
Second heating run	T_{ch} (°C)	138	137	140	136
	T_m (°C)	241	241	239	238
	ΔH_{ch} (J/g)	–25	–27	–26	–27
	ΔH_m (J/g)	30	30	26	30
Second cooling run	T_{cc} (°C)	176	176	167	174
	ΔH_{cc} (J/g)	–31	–33	–28	–35

T_m , melting temperature; ΔH_m , melting enthalpy; T_{ch} and ΔH_{ch} , crystallization temperature and enthalpy at heating; T_{cc} and ΔH_{cc} , crystallization temperature and enthalpy at cooling.

behavior in relation to thermal stability (Fig. 12) and relaxations temperatures determined by dynamic mechanical thermal analysis (Fig. 13). The literature²⁶ mentions the appearance of a relaxation at about 52–58°C below T_g , in PET samples reacted with a diepoxide chain extender. This relaxation was attributed to long chain branch motion. Nevertheless, this new relaxation was not observed for reacted samples neither impregnated nor extruded with ANP.

Rheological behavior of ANP-reacted PET

The polymer rheology is very sensible to changes on molecular weight, polydispersity, and long chain branches because of their influence in the viscoelasticity of polymer melt. The viscosity is affected by the polymer molecular structure and its value at Newton's plateau, which occurs at low shear rates, is influenced by molecular weight. For the same polymer, as the molecular weight rises the viscosity of Newton's

plateau rises too. On the other hand, the influence of long branches content is observed at higher shear rates, above 1 s^{-1} , for example. Branches alignment in the flow direction is noticed as a step in viscosity versus shear rate graph. It is due to an abrupt viscosity drop, which is not characteristic of linear chains. Besides, branches promote an increase of entanglements concentration and, therefore, in melt elasticity. This effect can be easily detected as a rise of the first normal stress difference.

The rheological behavior of samples nonreacted and reacted with ANP (extruded and impregnated)

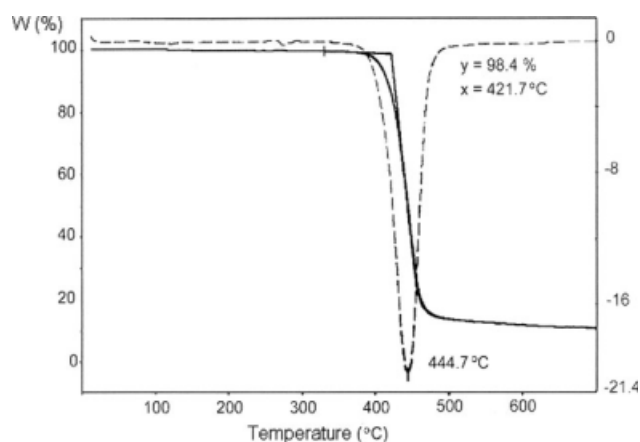


Figure 12 Weight loss (W) of 0.5% ANP/chloroform-impregnated flake sample, reacted at 230°C for 6 h.

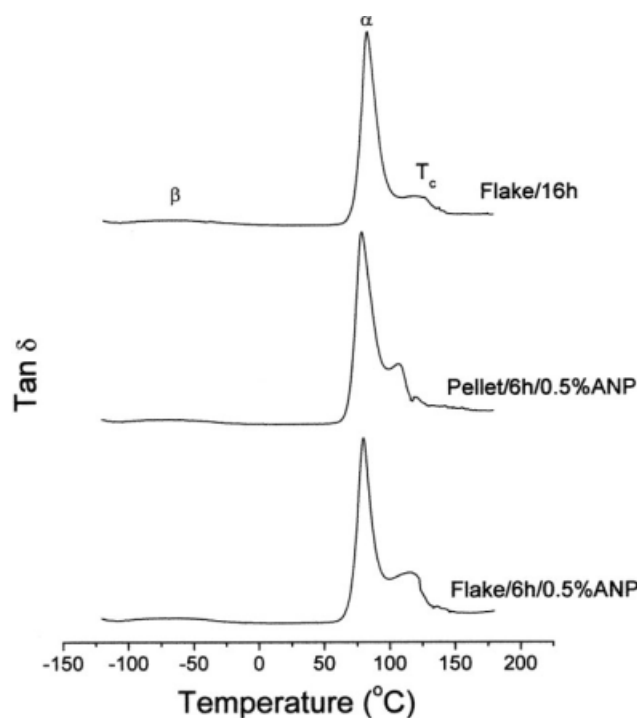


Figure 13 Loss tangent ($\tan \delta$) of pure flake, ANP/chloroform-impregnated flake, and ANP-extruded samples, reacted at 230°C for 16 and 6 h.

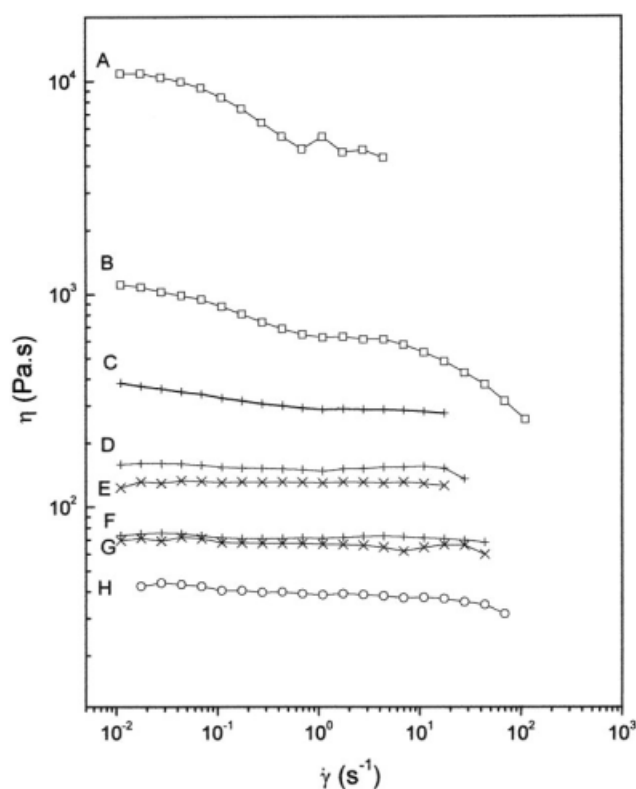


Figure 14 Viscosity (η) curves of reacted and nonreacted samples. A: Impregnated flake (0.5% ANP) reacted at 230°C for 6 h; B: pellet (extruded with 0.5% ANP) reacted at 230°C for 6 h; C: flake reacted at 230°C for 6 h ($\bar{M}_w = 111,000$); D: flake reacted at 230°C for 2 h ($\bar{M}_w = 57,000$); E: pellet reacted at 230°C for 6 h ($\bar{M}_w = 49,000$); F: nonreacted flake ($\bar{M}_w = 33,000$); G: nonreacted pellet ($\bar{M}_w = 26,000$); H: nonreacted pellet (extruded with 0.5% ANP).

was investigated, and viscosity variation as a function of the shear rate is presented in Figure 14. In the case of linear PET chains, the viscosities at Newtonian plateau showed a good agreement with mo-

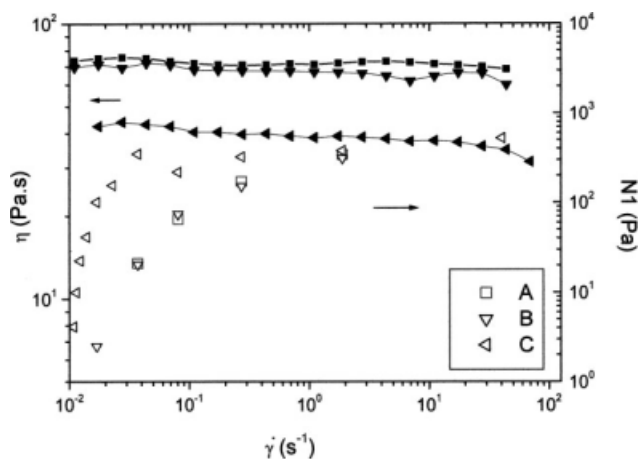


Figure 15 Viscosity (η) and normal stress (N1) curves of reacted and nonreacted samples. A: Nonreacted flake ($\bar{M}_w = 33,000$); B: nonreacted pellet ($\bar{M}_w = 26,000$); C: pellet extruded with 0.5% ANP. Open symbols: N1.

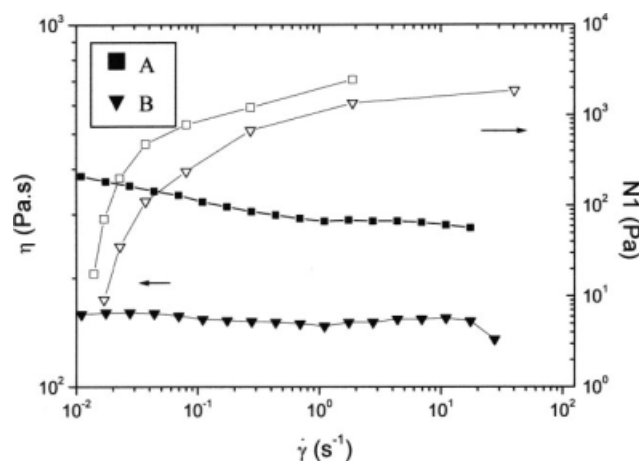


Figure 16 Viscosity (η) and normal stress (N1) curves of several reacted samples. A: Flake impregnated (0.5% ANP) and reacted at 230°C for 6 h ($\bar{M}_w = 111,000$); B: flake reacted at 230°C for 2 h ($\bar{M}_w = 57,000$). Open symbols: N1.

lecular weights tendency, even considering small differences, such as the nonreacted flakes and pellet samples (samples F and G, Fig. 14).

The sample impregnated and reacted with ANP (sample A, Fig. 14) showed extremely high viscosities, which disabled the rheometer at higher shear rates because the maximum torque was achieved. In spite of that, the characteristic viscosity drop due to branches alignment could be seen for this sample and for the sample extruded with ANP, both reacted for 6 h (A and B, Fig. 14). However, the difference between the viscosities levels of these two samples demonstrates that the impregnating process is much more effective than extrusion in promoting chain growth and/or crosslinking during SSP.

Despite gel formation in the ANP-extruded sample (before SSP), the expected viscosity drop was not observed (sample H, Fig. 14). The low viscosity value suggests that an intense chain cleavage took place during the extrusion process, and hence the main chain and branches must be so short that changes in viscosity could not be detected. However, higher values for the first normal stress differences of this sample were observed, in comparison with higher molecular weight linear chain samples (Fig. 15), which only can be due to a branching contribution to melt elasticity. Although the molecular weight increase of linear chains also promotes the increase in elasticity, because it always contributes to entanglements rise, branching influence is more significant on first normal stress differences (Figs. 15–17).

CONCLUSIONS

The chain extender impregnation before PET SSP is a versatile method to achieve a wide range of PET grades. Using this methodology, it is possible to

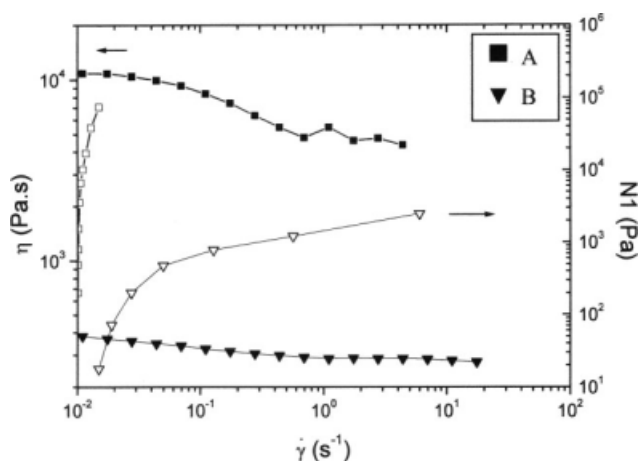


Figure 17 Viscosity (η) and normal stress ($N1$) curves of reacted samples. A: Flake reacted at 230°C for 6 h; B: flake reacted at 230°C for 6 h ($\overline{M}_w = 111,000$). Open symbols: $N1$.

synthesize linear bimodal or branched ultra-high-molecular-weight polyesters. The OXZ-reacted samples showed lower crystallization tendency than ANP or pure reacted samples. The samples reacted with ANP tend to produce branching structures both in extruded or impregnated samples. No relevant changes in relaxations or thermal stability were observed for OXZ- or ANP-reacted material.

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