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**THERMAL ANALYSIS AS A QUALITY TOOL FOR ASSESSING THE
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Abstract

Mechanical recycling of poly(ethylene terephthalate) (PET) was simulated by multiple processing to characterize the effects of thermo-mechanical degradation, and characterized using rheological and thermal analysis techniques. Thermo-mechanical degradation under repeated extrusion induces chain scission reactions in PET, which result in a dramatic loss in the deformation capabilities and an increase in the fluidity of the polymer under reprocessing, reducing its recycling possibilities after four extrusion cycles. Multiple reprocessing severely affects the storage modulus and the microstructure of recycled PET, both in the amorphous and crystalline regions. Multimodal melting behavior is observed for reprocessed PET, indicating heterogeneous and segregated crystalline regions. A deconvolution procedure has been applied to individually characterize each crystalline population in terms of lamellar thickness distribution and partial crystallinity. Thermal analysis techniques such as differential scanning calorimetry (DSC) and dynamic-mechanical analysis (DMA) have proved to be suitable techniques for the quality assessment of recycled PET, giving unequivocal information about its degree of degradation compared to the common technological measurements of melt-mass flow rate (MFR) or oxidative stability (T_{ox}).

Keywords

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Thermal analysis; recycling; poly(ethylene terephthalate) (PET); quality assessment; degradation.

Introduction

Poly(ethylene terephthalate) (PET) is a well established engineering and commodity polymer which has registered an important increasing production trend during recent years [1, 2]. The associated problem related to PET waste disposal is, however, not satisfactorily solved yet; according to recent statistics [3], only 35% of all PET bottles in Europe were recovered in 2005 through re-using, mechanical recycling, feedstock recycling or energy recovery. Among all recovery methods, mechanical recycling represents one of the most successful processes and has received considerable attention due to its main advantages, since it is environmentally friendly, relatively simple, requires low investment and its technological parameters are controlled [4]. Moreover, recent life cycle assessment studies have pointed out that mechanical recycling is the most preferable recovery route for relatively clean and homogeneous waste streams in terms of energy saving and emission of gases contributing to global warming [5].

However, mechanical recycling is still far away from being fully deployed; in general, recycling industries are characterized by a low degree of knowledge about plastic products and their properties. Recycled plastics usually come from unknown origins, they may be subjected to degradation processes, and they may have been contaminated during previous usage [6]. Polymers are subjected to the influence of degradative agents such as oxygen, light, mechanical stresses, temperature and water from which, separately or in combination during its life cycle (synthesis - processing - service life - discarding - recovery), arise chemical and physical changes that alter its stabilization mechanisms and long-term properties [7]. These degradation processes may modify the

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structure and composition of PET and, consequently, change the thermal, rheological and mechanical properties of recyclates [8-14]. The assessment of the degradation state is therefore necessary to determine the quality of recycled PET and to guarantee its further performance in second-market applications. Simulation of mechanical recycling by multiple processing has been widely employed to mimic the effects of thermo-mechanical degradation on polymers [15-18].

Traditionally, the evaluation of the melt flow rate (MFR) and the mechanical properties of the recyclates have been the only properties that are determined in the specification sheets of the final recycled material, but such analyses may give misleading information about the properties and long-term performance of recycled products in new applications [6]. Fast, cost-effective and reliable characterization procedures for plastic recyclates should be developed and implemented in the recycling facilities to guarantee their quality properties. Thermal analysis techniques have been successfully used in our group to monitor and control the degradative effects on the macroscopic properties of polymers submitted to different environments, including degradation in soil, photo-oxidation, hydrolysis and thermo-oxidation [19-20].

The aim of this work is to mimic the microstructural changes that PET suffers through thermo-mechanical degradation during mechanical recycling using thermal analysis techniques and compare the obtained analytical results with those given by the technological quality properties usually measured in large-scale mechanical recycling facilities. Semicrystalline PET was subjected to multiple processing up to six cycles and the changes in melt-mass flow rate, oxidative stability, morphology and mechanical

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properties were correlated with reprocessing cycles to model the degradation influence on recycled PET.

Experimental

Materials and sample preparation

Virgin poly(ethylene terephthalate) (PET), commercially labeled as Laser+ Melinar, (AdvanSa Limited, United Kingdom) was employed as reference material in this study. Previous to the mechanical recycling simulation process, it was put in a forced ventilation oven, Heraeus D-6450 (Heraeus GmbH, Germany), at 160 °C for 4 hours, and afterwards kept in a desiccator to avoid hydrolysis reactions that can produce molecular weight reduction [21].

Mechanical recycling was simulated following the scheme shown at Figure 1. Multiple reprocessing up to six times was performed by using a Brabender Plasticorder PL2000 co-rotating twin-screw extruder with 2.2 cm diameter and a L/D ratio of 16 (C.W. Brabender Instruments, NJ, USA). The temperature profile at the extruder was 250-260-270 °C from the feeder to the mouth of the extruder. After each reprocessing step, the material was cooled by air, ground and sieved. Some material was taken as a sample and placed again in a desiccator to prevent it from hydrolysis caused by environmental humidity until further analysis; the rest was reintroduced into the mechanical recycling simulation process. Rectangular sheets with dimensions 72 mm x 72 mm x 0.5 mm were obtained from the extracted samples by compression molding at 270 °C and 180 bar employing a hot-plate press (0230H Press, Pasadena Hydraulics Inc., CA, USA).

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Melt mass-flow rate (MFR)

Melt mass-flow rate (MFR) measurements of virgin and reprocessed PET material were carried out on a Melt Indexer CFR-91 (Campana Srl., Italy) according to ISO 1133:1999 standard. The test temperature was set at 270 °C and the nominal load was 1,2 kg. Measurements on each sample were repeated six times and the average was considered as the characteristic value.

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) was employed to evaluate the influence of reprocessing on the crystallinity, the melting behavior and the oxidative stability of virgin and reprocessed PET samples. Analyses were carried on a Mettler Toledo DSC 820° instrument (Columbus, OH) calibrated with indium. All experiments were carried out with a common heating rate of 10 K·min⁻¹. Approximately 10 mg of sample was weighed and placed in 40 µL aluminum pans, which were sealed and pierced to allow the gas flow (of 50 mL·min⁻¹).

In order to assess the oxidation temperature (T_{OX}), samples were heated from 25°C up to 400 °C under an oxygen atmosphere. T_{OX} was obtained from the onset point of the oxidation curve shown by the calorimetric analysis. Each sample was run three times and the average was assumed as the characteristic value.

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The crystallinity and the melting behavior were studied by means of calorimetric scans under a nitrogen atmosphere. A heating/cooling/heating program was performed in a temperature range between 25°C and 290°C. The samples were analyzed by triplicate and the glass transition (T_g), melting (T_m) and crystallization (T_c) temperatures, as well as melting (ΔH_m) and crystallization (ΔH_c) enthalpies, were calculated and averaged to obtain the representative values.

Differential Mechanical Thermal Analysis (DMTA)

Rectangular strips (35 mm x 1 mm x 0.5 mm) were cut from the pressed sheets and employed as test specimens. Samples were tested in a DMA Q800 (TA Instruments, DL, USA), employing a single-cantilever clamping geometry with a load of 0.001 N and 1 Hz frequency. Samples were stabilized at 35 °C for 5 minutes and then heated to 180 °C. Storage modulus and loss modulus were recorded as a function of temperature and time. Only samples up to the fourth recyclate could offer complete DMTA scans, due to the brittleness caused by the recycling procedure on the samples from the fifth and the sixth recyclates.

Results and discussion

Melt-mass flow rate (MFR)

The processability of polymer recyclates in large-scale mechanical recycling facilities is usually assessed using melt-mass flow rate (MFR) experiments. Figure 2 shows the evolution of MFR with reprocessing steps; a continuous and exponential increase of the MFR parameter can be observed with consecutive reprocessing cycles, which is almost fourfold after the sixth recycling step. This increase in the fluidity of reprocessed PET may be related to progressive diminution of the molecular weight through multiple processing; thermo-mechanical degradation at the extruder may induce chain scission reactions within the polymeric chain that contribute to this reduction [13].

Oxidative stability

The oxidation temperature (T_{OX}) as calculated using differential scanning calorimetry is a standardized parameter, employed to assess the oxidative stability of commercial polymeric materials. The initial extrusion steps are responsible for dramatic decrease of the T_{OX} parameter, with a reduction of approximately 30% of the initial value after 2 processing steps (Figure 3). From the third reprocessing step on, no significant differences are noticed, since the parameter reaches an almost constant value. It is supposed that the oxidative stability is mainly affected by thermo-mechanical degradation only during the first steps of extrusion and further reprocessing cycles would not alter that trend. Contradictory information is therefore shown: on the one

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hand, MFR increases almost exponentially with increasing reprocessing cycles; on the other hand, the oxidative stability is mainly affected during the first processing step, but subsequent reprocessing steps slightly modify the stabilization properties. Further analyses are therefore required to evaluate the degradation effects and the quality of in-plant recycled PET.

Dynamic-mechanical-thermal analysis (DMTA)

The influence of multiple processing on the dynamic-mechanical properties of PET was evaluated using DMTA tests. The storage (E') and loss modulus (E'') were recorded for PET reprocessed samples and their evolution as a function of temperature is displayed in Figure 4. Reprocessing induces a progressive increase of the storage modulus of PET up to four extrusion cycles, both below and above the glass transition region (Figure 4a). No spectra could be obtained for PET samples submitted to more than four reprocessing cycles, due to the brittleness induced by reprocessing and the loss of its plastic properties. The mechanical and plastic performance of in-plant recycled PET in second-market application may be therefore only guaranteed up to four processing cycles. The higher storage modulus of PET through repeated extrusion may be caused by chain scission reactions induced by thermo-mechanical degradation, which produce progressively shorter polymeric chains that have the ability to crystallize more freely during cooling after each extrusion, leading to the embrittlement of the material and the decrease of its deformation capacity [9, 22].

A prominent viscoelastic relaxation in the loss modulus can be observed for virgin and reprocessed PET between 70 and 100°C, which is assigned to the glass transition of PET chains (Figure 4b). In general, reprocessed samples exhibit a broader loss modulus peak displaced to higher temperatures, compared to virgin PET. A deeper analysis on the influence of multiple processing on the glass transition relaxation was performed by fitting the experimental loss modulus values as a function of temperature to the empirical Fuoss-Kirkwood model (Figure 5), as reported in previous studies [16].

$$E''(T) = \frac{E''_{\max}}{\cosh\left(m_{FK} \cdot \frac{E_a}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{\max}}\right)\right)}$$

E''_{\max} is the maximum of the loss modulus; m_{FK} is the Fuoss-Kirkwood parameter; E_a is the activation energy of the relaxation process; R is the ideal gas constant; T is the temperature; T_{\max} is the temperature of the maximum of the loss modulus, which is related to the glass transition temperature at a frequency of 1 Hz. The fitted values of T_{\max} and the dispersion parameter $m_{FK} \cdot E_a \cdot R^{-1}$, which is inversely related to the width of the viscoelastic relaxation, are presented in Table 1 for virgin and reprocessed PET samples. The value of T_{\max} is higher for reprocessed PET compared to that of virgin PET, while the dispersion parameter decreases with consecutive extrusion cycles. The broadening and the shift of the relaxation curves towards higher temperatures with multiple processing may be explained as due to thermo-mechanical degradation effects on PET chains. Random scission of PET chain linkages caused by mechanical and thermal stress in the extruder may lead to a diverse distribution of polymeric chain lengths, which may crystallize forming heterogeneous crystalline domains. These more

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abundant and heterogeneously distributed crystalline regions may hinder the mobility of the amorphous regions within the glass transition relaxation, causing broader and less regular loss modulus curves through the temperature range, and displacement of the relaxation peak to higher temperatures.

Melting and crystalline behavior

The study of the melting and crystallization behavior using differential scanning calorimetry was performed to prove the hypotheses established in the discussion of the dynamical-mechanical analyses and to get a deeper insight into the microstructural changes caused by multiple processing. Parameters such as melting and crystallization temperatures and enthalpies, as well as the crystallinity degree, the lamellar thickness distribution and the glass transition temperature were the main focus of the study.

The influence of reprocessing on the crystallization behavior has been studied from the cooling thermograms (Figure 6a); the crystallization temperatures (T_C) and crystallization enthalpies (ΔH_C) could be recorded and are displayed in Table 2. Once the previous thermal history of the materials has been erased by the first heating scan, the chains are free to rearrange into a new crystalline stage. Cooling thermograms appear sharper and shifted to higher temperatures with every reprocessing cycle, indicating that the crystallization process occurs earlier and faster for samples subjected increased number of extrusion cycles.

Figure 6b displays the curves of the second heating scan for the study of the effects of reprocessing on the melting behavior. The melting temperatures (T_m), the melting enthalpies (ΔH_m) and the glass transition temperatures (T_g), have been directly calculated from the thermograms; the degree of crystallinity (X_c) could equally be calculated as:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0}$$

where ΔH_m is the melting enthalpy and ΔH_m^0 the theoretical melting enthalpy of the fully crystalline PET, assumed to be 140 J/g [23]. These results are fully presented in Table 2. In all cases, the degree of crystallinity (X_c) is higher for the reprocessed samples than for virgin PET, and also progressively increases with every reprocessing step. These results are in agreement with the dynamic-mechanical behavior and prove the hypotheses presented; chain scission caused by thermo-mechanical degradation at the extruder may produce an increase in crystallinity and, as a result, a loss of mechanical and plastic properties.

On the other hand, the melting curves increasingly spread out through the temperature region with every reprocessing step, which may suggest the modification of the crystalline population under repeated extrusion. The lamellar thickness (l_c) distribution was therefore studied applying the Hoffman-Lauritzen nucleation theory [24-26] to relate the evolution of the l_c distribution with the reprocessing simulation. The Thomson-Gibbs equation was employed to assess the evolution of the lamellar thickness distribution:

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$$l_c = \left[\left(1 - \frac{T_m}{T_m^0} \right) \cdot \frac{\Delta h_{mV}}{2 \cdot \sigma_e} \right]^{-1}$$

where T_m is the melting temperature; T_m^0 is the equilibrium melting temperature of an infinite crystal (564 K); σ_e is the surface free energy of the basal plane where the chains fold ($0.106 \text{ J}\cdot\text{m}^{-2}$); Δh_{mV} is the melting enthalpy per volume unit ($2.1 \cdot 10^8 \text{ J}\cdot\text{m}^{-3}$), both values obtained from *X.F.Lu* and *J.N.Hay* [27]. Figure 7 represents the l_c distribution for virgin PET and each reprocessed sample. In this figure, a prominent distribution related to the most probable lamellar size can be seen. The plots shift to higher l_c values with every reprocessing step, showing the continuous formation of crystalline zones with higher lamellae size. However, a closer inspection of the lamellar distribution curve revealed the presence of various small shoulders overlapped to the principal distribution which are more prominent with each reprocessing step. The chain scissions may enhance the crystallization and segregation of crystals with different crystalline sizes, highlighting the heterogeneity of this material.

In order to better understand the effects of the degradation process on the crystalline phase, the endothermic peaks of the second heating scan were carefully studied. A multimodal endothermic behavior, attributed to a segregation of the initial crystalline distribution into three main populations can be observed. A deconvolution procedure was applied to the melting thermograms in order to individually characterize the behavior of each population and their contribution to the overall effect using a partial areas study. The following expression was employed as deconvolution model:

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$$l_c(T) = \sum_i A_i \cdot \exp \left(\frac{-(T - T_i)^2}{\frac{w_i^2}{\ln(16)}} \right)$$

where T_i represents the average value of the temperatures range considered; A_i is the maximum intensity of the curve; w_i acts as a dispersion parameter. Figure 8 gives an example of the deconvolution model fitting to the experimental response. Populations have been labeled as I, II and III, from the higher to the lower peak temperature, and their melting enthalpies and temperatures are shown at Table 3. A shift of the T_m of approximately 5 °C for populations I and II and 20 °C for population III can be observed. The partial crystallinity of each population X_C^i has been calculated as $\Delta H_m^i / \Delta H_m^0$ (for $i=I, II, III$). Population III seems to be more affected by reprocessing operations, as X_C^{III} values reached doubled values from the third recycle on. Furthermore, in order to analyze the contribution of each partial crystallinity to the overall crystallinity, a new parameter (relative partial crystallinity) is calculated as $X^i = X_C^i / X_C$. This parameter clearly demonstrates that population I diminishes, population II does not show a specific variation trend, and for population III an overall increase of X^{III} is seen through the reprocessing cycles.

As it was discussed from the results of DMA, the increase in the degree of crystallinity may influence the values of glass transition temperature (T_g) calculated from the calorimetric scans (Table 2). The T_g values show small variations until the fourth reprocessing cycle, and continuously increases up to 6°C. As the amount of free chains induced by thermo-mechanical degradation is rising, the tendency of the smaller chains to fit among the larger ones facilitates the packing of these chains in crystalline

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domains, decreasing the amount of amorphous areas. Hence, more energy would be required to increase the mobility of the amorphous regions and to achieve the glass transition [28].

Conclusions

Multiple processing has been proposed to mimic the thermo-mechanical degradation effects on the microstructure and properties of poly(ethylene terephthalate) (PET) under mechanical recycling. The results of commonly-employed technological parameters, such as the melt-mass flow rate (MFR) and the oxidation temperature (T_{OX}), have been compared with the structural information provided by thermal analysis techniques such as dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC). It was demonstrated that the employment of MFR and T_{OX} parameters alone may induce misleading information when the degradation state and the quality of recycled PET is assessed.

Thermo-mechanical degradation causes deep changes in the microstructure and properties of PET under recycling. A dramatic increase in the degree of crystallinity is observed during consecutive extrusion cycles, leading to significant embrittlement of the recycled material and the complete loss of its plastic deformation properties after 4 reprocessing cycles. Chain scission reactions induced under thermo-mechanical degradation may result in a heterogeneous distribution of polymeric chain lengths in the melt state, altering the subsequent amorphous and crystalline microstructure in recycled PET after chain rearrangement during cooling. The existence of a multimodal melting

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distribution in reprocessed PET could be verified using DSC; the enhanced crystallization and segregation of these populations could be studied in detail employing a deconvolution procedure in terms of their partial degree of crystallinity and their lamellar thickness distribution.

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FIGURE CAPTIONS

Figure 1. Schematic representation of the mechanical recycling simulation procedure by multiple processing and analysis techniques employed (RPET-i: PET reprocessed “i” times).

Figure 2. Evolution of melt-mass flow rate (MFR) through reprocessing simulation.

Figure 3. Effect of reprocessing on the oxidation temperature (T_{OX}) of PET.

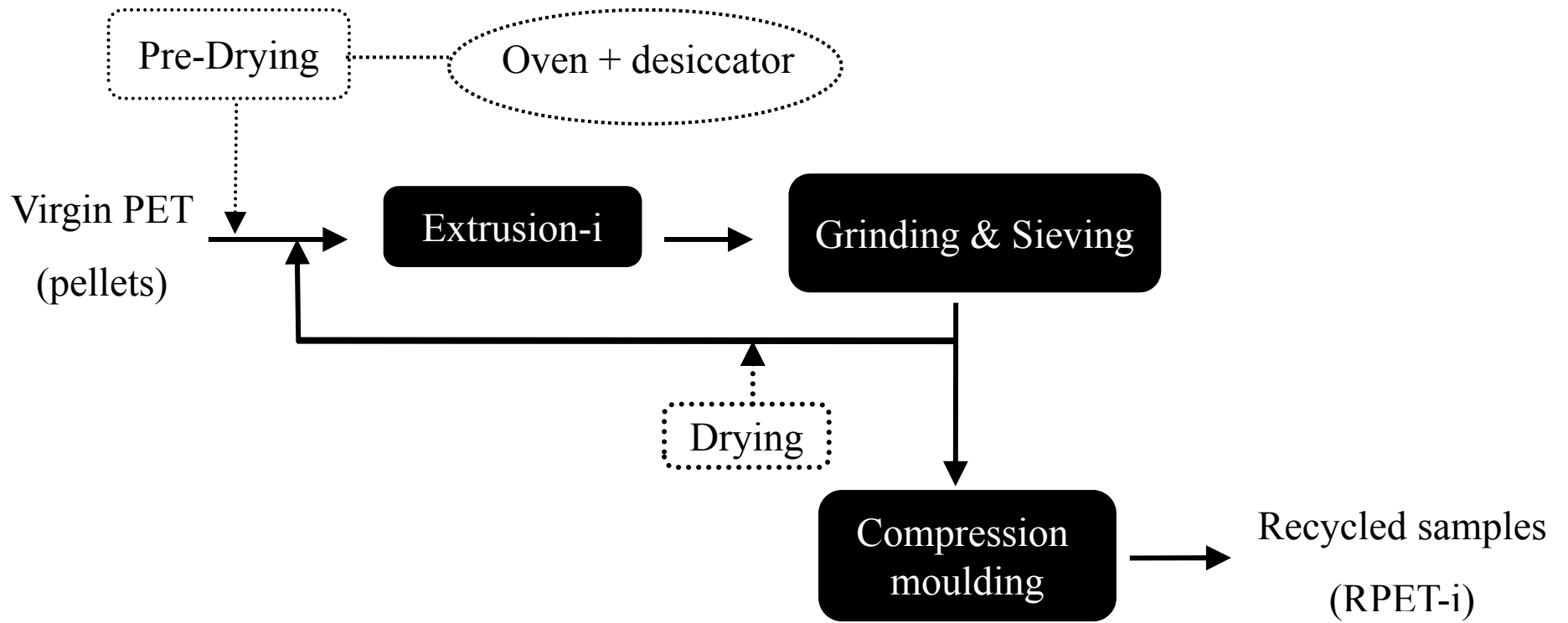
Figure 4. Reprocessing influence on the dynamic-mechanical behaviour of PET: a) storage modulus; b) loss modulus.

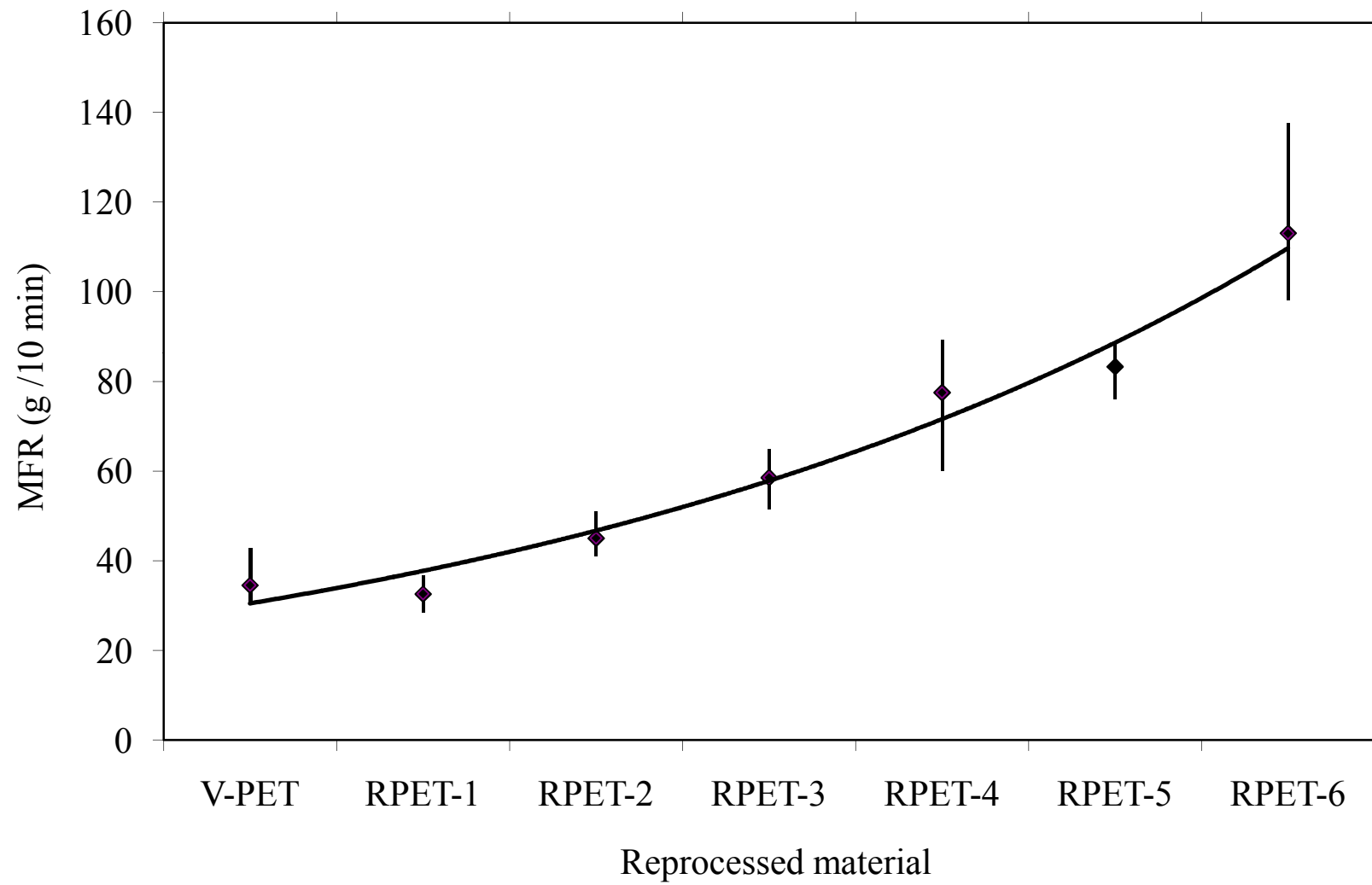
Figure 5. Loss modulus experimental data fitting to Fuoss-Kirkwood model for virgin PET (○: experimental data; □□ fitted function).

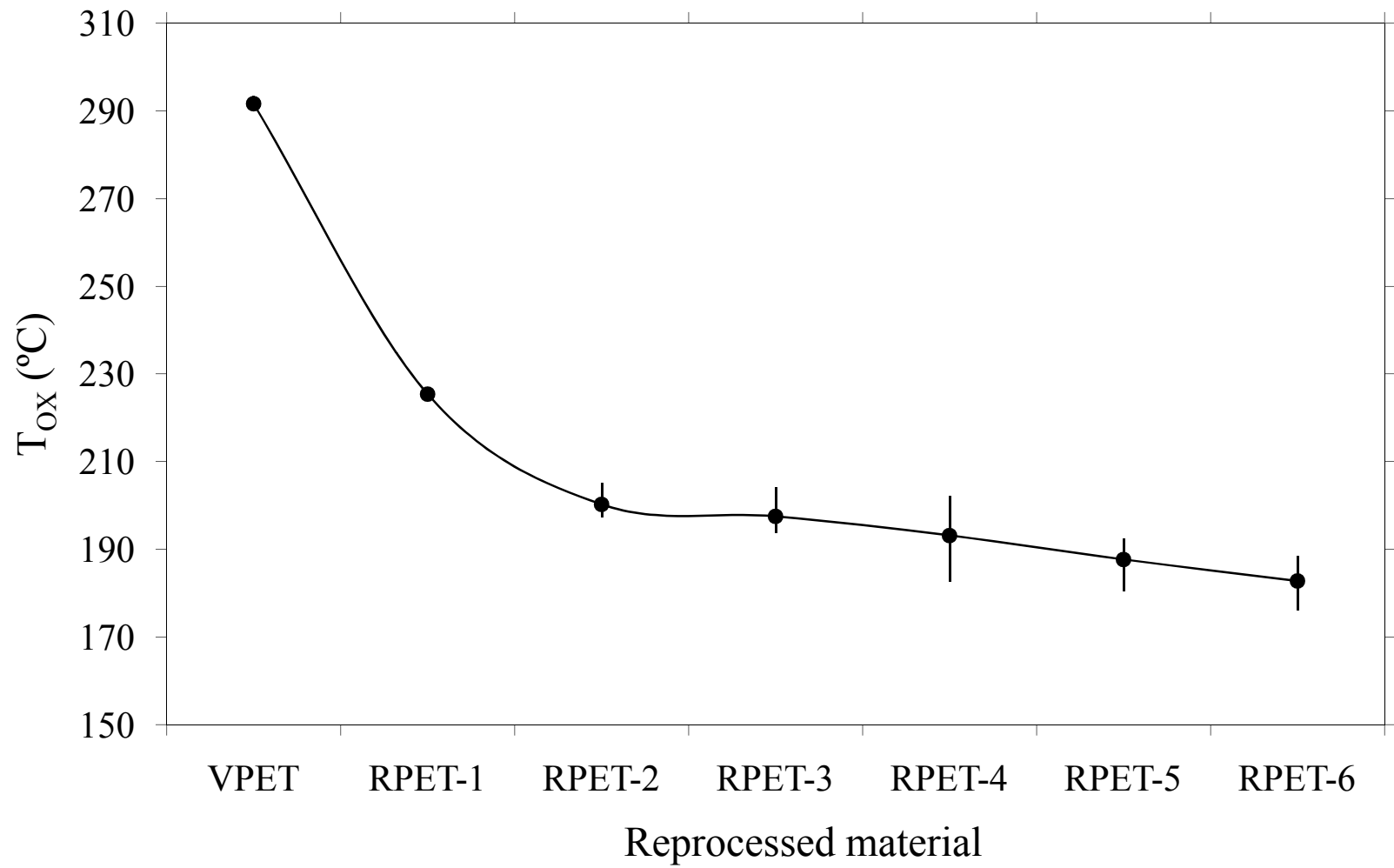
Figure 6. DSC thermograms for virgin and reprocessed PET: a) crystallization scan; b) second melting scan.

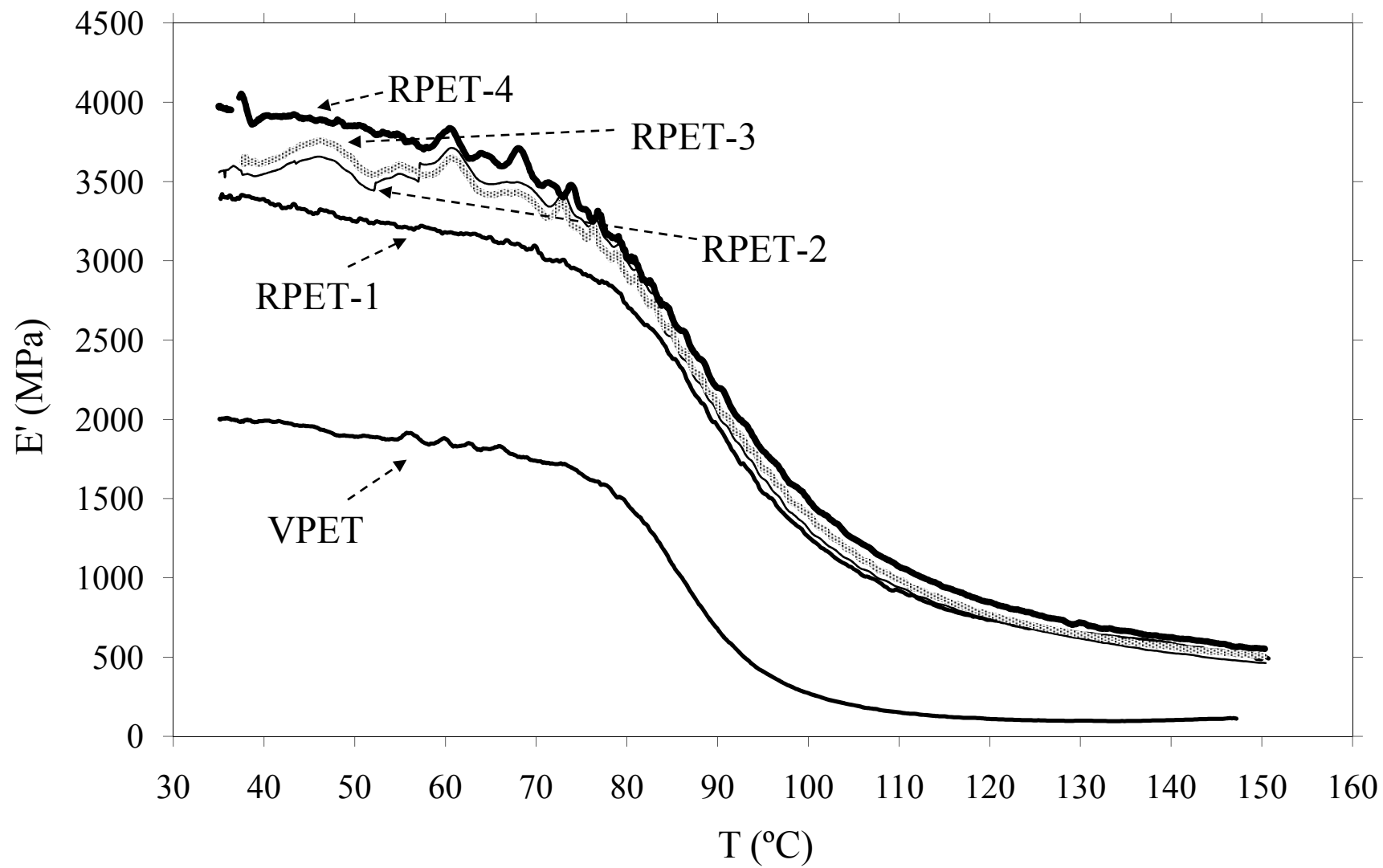
Figure 7. Lamellar thickness distribution evolution for virgin and reprocessed PET.

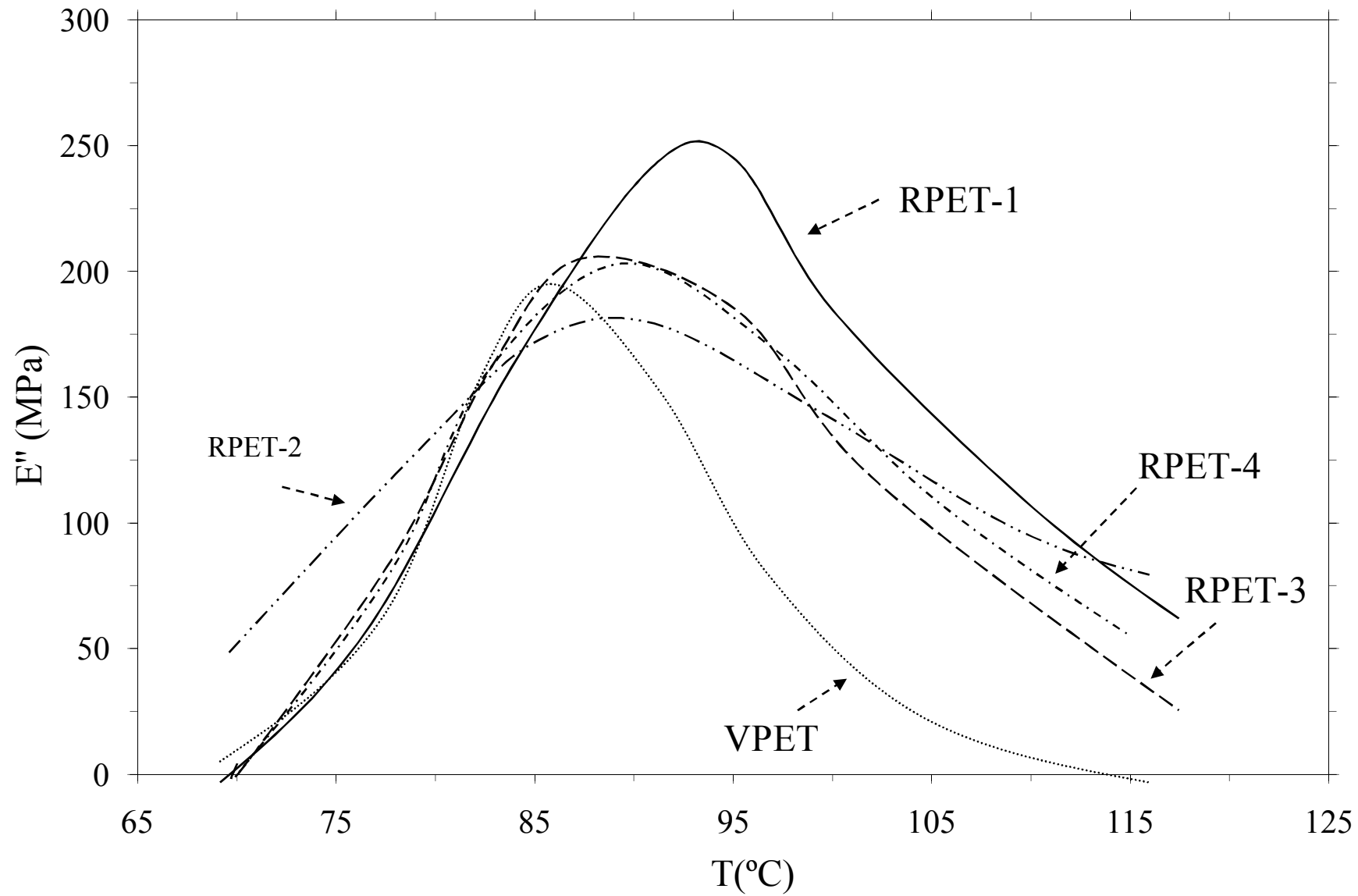
Figure 8. Deconvolution of the melting calorimetric thermogram into crystalline populations I, II, and III for PET reprocessed 4 times.

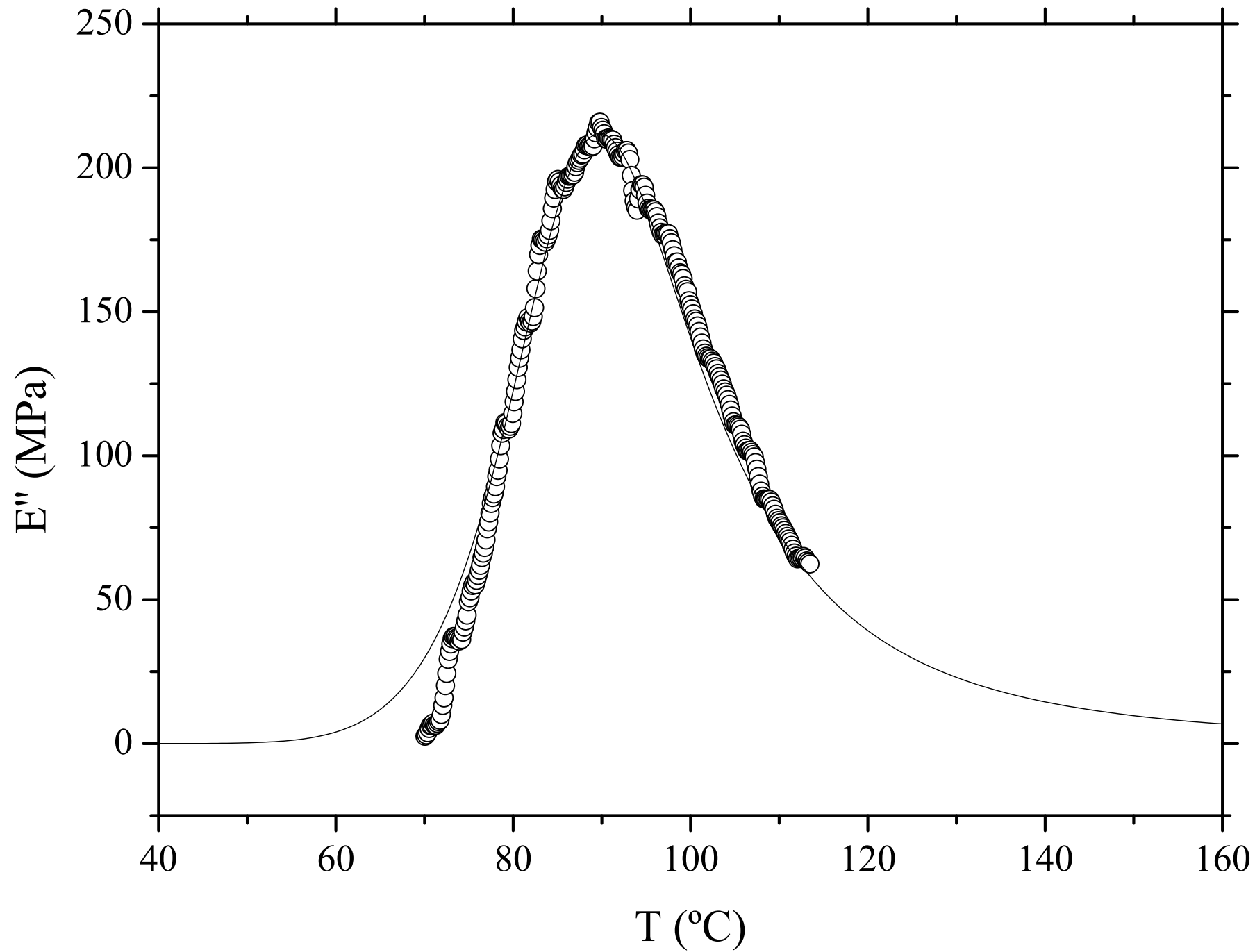


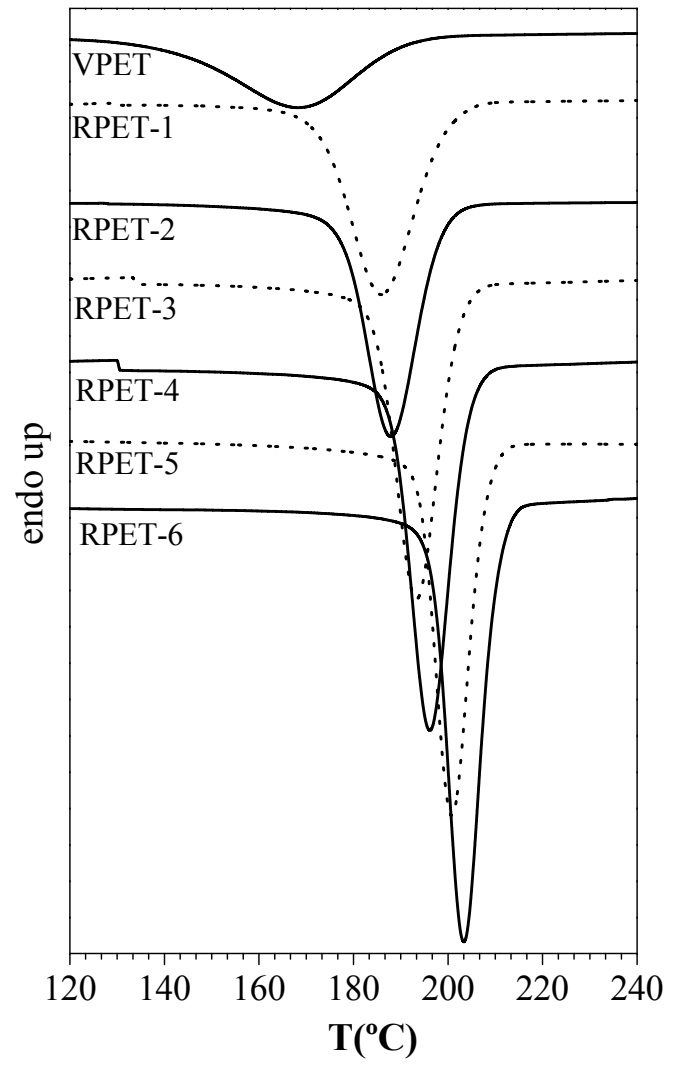


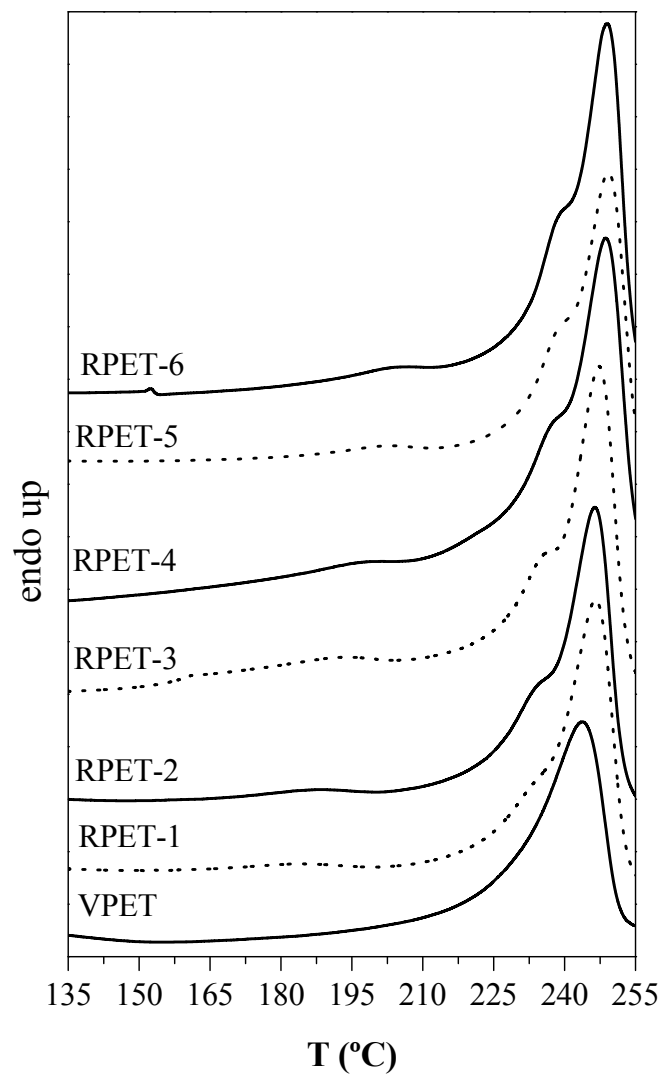


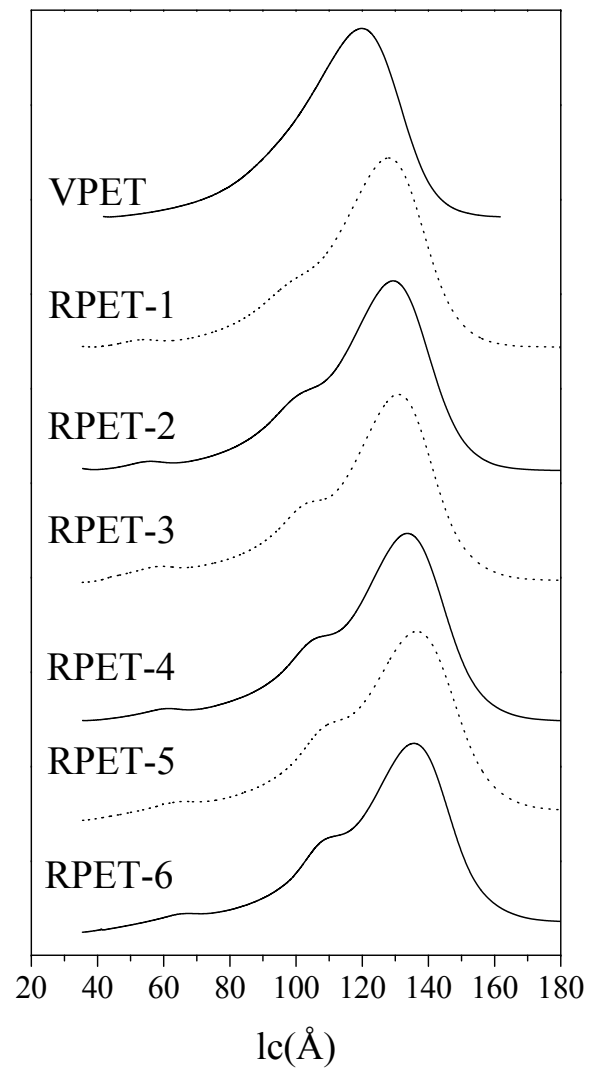


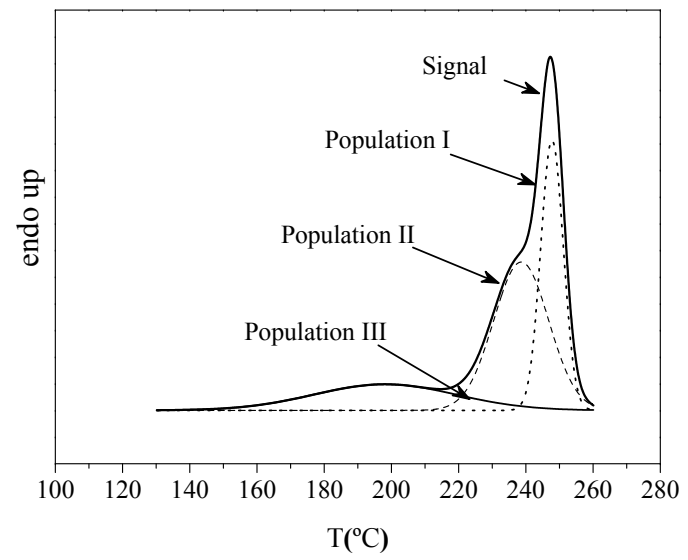












Badia, J. D., Vilaplana, F., Karlsson, S., & Ribes-Greus, A. (2009). Thermal analysis as a quality tool for assessing the influence of thermo-mechanical degradation on recycled poly (ethylene terephthalate). *Polymer Testing*, 28(2), 169-175.

TABLES

Table 1. Fuoss-Kirkwood parameters for virgin and reprocessed PET after loss modulus fitting as a function of temperature.

Table 2. Calorimetric parameters for virgin and reprocessed PET: crystallization temperature (T_C), crystallization enthalpy (ΔH_C), glass transition temperature (T_g), melting temperature (T_m), melting enthalpy (ΔH_m), and degree of crystallinity (X_C).

Table 3. Individual melting parameters and partial crystallinity for each population after deconvolution of the melting calorimetric thermograms for virgin and reprocessed PET.

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Table 1

Material	E'_{\max} (MPa)	T_{\max} (°C)	$m_{FK} \cdot E_a \cdot R^{-1}$ (K)	R^2 (fitting coefficient)
VPET	202.8	86.4	1310.6	0.994
RPET-1	254.3	92.4	1045.3	0.983
RPET-2	190.2	89.2	616.9	0.987
RPET-3	212.0	89.7	843.9	0.967
RPET-4	213.1	89.7	881.6	0.973

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Table 2

Material	Cooling scan		Heating scan			
	T _c (°C)	ΔH _c (J/g)	T _g (°C)	T _m (°C)	ΔH _m (J/g)	X _c (%)
VPET	170.3	-44.0	79.0	243.7	43.9	31.4
RPET-1	183.9	-57.5	79.1	246.1	57.7	41.2
RPET-2	188.2	-59.5	78.5	245.5	56.2	40.2
RPET-3	193.7	-66.8	78.3	247.0	67.6	48.3
RPET-4	196.5	-77.4	82.9	247.7	71.9	51.3
RPET-5	201.1	-67.4	84.9	248.7	59.6	42.6
RPET-6	202.9	-78.4	85.3	248.0	67.4	48.2

Table 3

Material	Population I				Population II				Population III			
	T _m ^I (°C)	ΔH _m (J/g)	X _C ^I (%)	X ^I (%)	T _m ^{II} (°C)	ΔH _m (J/g)	X _C ^{II} (%)	X ^{II} (%)	T _m ^{III} (°C)	ΔH _m (J/g)	X _C ^{III} (%)	X ^{III} (%)
VPET	243.7	43.9	31.4	-	-	-	-	-	-	-	-	-
RPET-1	246.1	23.3	16.6	40.3	235.9	27.8	19.8	48.1	184.3	6.7	4.8	11.6
RPET-2	245.5	21.4	15.3	38.0	236.7	28.0	20.0	49.8	189.4	6.9	4.9	12.2
RPET-3	247.0	22.6	16.1	33.2	236.9	28.9	20.6	42.6	195.4	16.4	11.7	24.2
RPET-4	247.7	25.0	17.9	34.6	238.2	33.9	24.2	46.9	197.3	13.3	9.5	18.5
RPET-5	248.7	19.6	14.0	32.8	240.7	27.7	19.8	46.6	204.3	12.3	8.8	20.7
RPET-6	248.0	22.3	15.9	34.1	240.7	29.7	21.2	45.4	205.3	13.4	9.6	20.6

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