Materials Chemistry and Physics 147 (2014) 884–894

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Assessing changes on poly(ethylene terephthalate) properties after recycling: Mechanical recycling in laboratory versus postconsumer recycled material

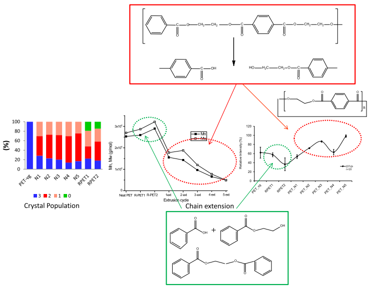
María del Mar Castro López [a], Ana Isabel Ares Pernas [a], Mª José Abad López [a],
Aurora Lasagabaster Latorre [a, b], J.M. López Vilariño [a], Mª Victoria González Rodríguez [a, *]

[a] Grupo de Polímeros, Centro de Investigacións Tecnolóxicas (CIT), Departamento de Física, Escuela Universitaria Politécnica, Universidade de A Coruña, Campus de Ferrol, 15403 Ferrol, Spain
[b] Departamento de Química Orgánica I, Facultad de Óptica y Optometría, Universidad Complutense de Madrid (UCM), Arcos de Jalón 118, 28037 Madrid, Spain

HIGHLIGHTS

- Combination of multiple techniques to characterize the effects of recycling in PET.
- Cleavage of ester bonds reduced viscosity, Mw, toughness in mechanical recycled PET.
- Virgin, mechanical recycled and commercial recycled PET differ in crystal populations.
- Cyclic oligomers $[GT_c]_n$ and $[GT_c]_n$-G increase from the fourth extrusion cycle onwards.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 March 2014
Received in revised form
20 May 2014
Accepted 15 June 2014
Available online 4 July 2014

Keywords:
Polymers
Ageing

ABSTRACT

Keeping rheological, mechanical and thermal properties of virgin poly(ethylene terephthalate), PET, is necessary to assure the quality of second-market applications. A comparative study of these properties has been undertaken in virgin, mechanical recycled and commercial recycled PET samples.

Viscoelastic characterization was carried out by rheological measurements. Mechanical properties were estimated by tensile and Charpy impact strength tests. Thermal properties and crystallinity were evaluated by differential scanning calorimetry and a deconvolution procedure was applied to study the population of the different crystals. Molecular conformational changes related to crystallinity values were studied by FTIR spectroscopy. Variations in average molecular weight were predicted from

---

Abbreviations: a_{cU}, Charpy impact strength; CI, carboxyl index; DEG, diethylene glycol units; DHB, 2,5-dihydroxybenzoic acid; σ_B, the stress at the break point; σ_y, the stress at the yield point; E, Young modulus; ESI, electrospray ionization; ε_B, the strain at the break point; ε_y, strain at the yield point; $G(t)$, stress relaxation modulus; G', storage modulus; G'', loss modulus; $[GT_c]_n$-G, cyclic oligomer with a glycol unit; H-$[GT_L]_n$-GA, linear oligomer with a glycol-aldehyde unit; LVE, linear viscoelastic region; Me: MeOH, Methanol; Mn, number average molecular weight; MS, mass spectrometry; MW, molecular weight; MWD, molecular weight distribution; Mw, weight average molecular weight; η^*, complex viscosity; PET, poly (ethylene terephthalate); PET_N1 to PET_N5, reprocessed PET samples (being N from 1 to 5 the number of reprocessing cycles suffered by the material); PET-vg, virgin bottle-grade poly (ethylene terephthalate); RPET1 and RPET2, two commercial recycled PET samples; T-$[GT_c]_n$, cyclic specie bearing one extra terephthalic unit; T_c, crystallization temperature; TFA, trifluoroacetic acid; T_g, glass transition temperature; T_m, melting temperature; TTS, time–temperature superposition; %T, fraction of *trans* conformer; α, crystallinity degree; ΔH_c, crystallization enthalpy; ΔH_{cc}, cold crystallization enthalpy; ΔH_m, melting enthalpy; $\nu_{(CH)}$, aliphatic C–H stretching vibrational mode; $\nu_{C(=O)-O-}$, carboxyl stretching vibrational mode; $\nu_{(OH)}$, hydroxyl stretching vibrational mode; $\omega(CH_2)$, CH_2 wagging vibrational mode; (ω), frequency.

[*] Corresponding author. Tel.: +34 981 337 400 3051, +34 981 337 400 3485; fax: +34 981 337 416.
E-mail addresses: quimcl02@udc.es (M.M.C. López), aares@udc.es (A.I. Ares Pernas), mjabad@udc.es (M.J. Abad López), aurora@quim.ucm.es (A.L. Latorre), iquimica@udc.es (J.M. López Vilariño), victoria.gonzalez.rodriguez@udc.es (M.V. González Rodríguez).

http://dx.doi.org/10.1016/j.matchemphys.2014.06.034

Mechanical properties
Thermal properties
Chemical techniques

rheology. Besides, the presence-absence of linear and cyclic oligomeric species was measured by mass spectrometry techniques, as MALDI-TOF.

Mechanical recycled PET undergoes a significant decline in rheological, mechanical and thermal properties upon increasing the number of reprocessing steps. This is due to the cleavage of the ester bonds with reduction in molar mass and raise in cyclic oligomeric species, in particular $[GT_c]_n$ and $[GT_c]_n$-G type. Chain shortening plus enrichment in *trans* conformers favour the crystallization process which occurs earlier and faster with modification in crystal populations. Additional physicochemical steps are necessary to preserve the main benefits of PET.

1. Introduction

Due to the good barrier properties of blow-moulded containers made with poly(ethylene terephthalate) (PET), it has become a very important commercial plastic used in food packaging, films and carbonated soft drink bottles. PET presents good thermal and mechanical properties and is also used in reinforced plastics [1].

PET recycling process has received considerable attention as a result of societal pressure to reduce environmental pollution and to improve waste management. PET products have a slow rate of natural decomposition; therefore, recycling processes are the best way to economically reduce PET waste. Two major processes have been applied in order to recycle post-consumer PET, chemical and mechanical recycling. Although, both have been extensively studied, the disadvantage of chemical recycling is its high cost. Conversely, mechanical recycling is a relatively simple process that has received considerable attention as it is a successful route in terms of energy saving and emission of gases contributing to global warming. Mechanical recycling normally consists of contamination removal by sorting and washing, drying and melting processing [1,2].

Keeping high molar mass is necessary to assure the quality of second-market applications of recycled polymer. However, the exposure to several reprocessing cycles can modify the molecular structure and molecular weight (MW) of PET materials causing changes in their thermal, rheological and mechanical properties and thus, turning them useless for main commercial applications. Irreversible macromolecular changes generated by different chemical processes take place during PET mechanical recycling process. The main chemical reactions are chain scissions that predominate in “well-oxygenated” zones, but other minor modifications such as chain coupling can also take place in “poorly oxygenated” zones [2–4].

As result of chain-scission, ester-scission or auto-catalysed hydrolytic reactions, among others, the formation and disappearance of linear and cyclic oligomeric species have been identified in PET degradations studies [5]. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) has become a valuable technique to study the chemical degradation of PET [6], allowing a faster identification of the characteristic degradation products. Application of the MALDI technique opened new vistas in polymer degradation analysis since it allows desorption and ionisation of intact polymer molecules and their identification in well resolved mass spectra, especially in the lower molecular mass range (<10,000 Da) [7,8].

In addition, it has been reported that small amounts of cyclic low molar mass oligomers present in PET samples come from PET polymerization process as it is usual for polymers prepared by condensation polymerization [6,9]. In the same way, the relation between the percentage of individual cyclic oligomers formed in the polymer melt and the percentage of cyclic oligomers initially found in commercial PET has been reported [10].

With all this in mind, the oligomeric degradation products have been used to investigate the chemical degradation of mechanical recycled PET. Although the application of MALDI-TOF MS to analyse PET degradation is not new [4–6], the combination of this method with a wide range of characterization techniques in order to correlate the chemical degradation with declining in physical properties, critical for industrial processes, has seldom been published.

In the current work, several numbers of reprocessing cycles have been used to simulate the mechanical recycling of PET. The polymer degradation state for each reprocessing cycle has been characterized by measuring its rheological, thermal and mechanical properties and by FTIR spectroscopy. Furthermore, number average molecular weight (*M*n) and weight average molecular weight (*M*w) of the different reprocessed samples have been calculated from data obtained in the dynamic rheological tests. Finally, linear and cyclic oligomeric degradation species (100–10,000 Da) have been monitored by liquid chromatography coupled to mass spectroscopy (MS) and MALDI-TOF-MS. In the same way, two postconsumer recycled PET have been studied and compared with the mechanically recycled PET samples.

2. Experimental

2.1. Materials

Samples of virgin bottle-degree poly (ethylene terephthalate) (Seda PET SP04) were supplied by Catalana de Polimers S.A., Grup LaSeda (Barcelona, Spain) in the form of pellets (PET-vg). The Seda Pet SP04 consists of opaque semicrystalline granules with an Intrinsic Viscosity value (IV) of 0.8 ± 0.02 dL g^{-1} which corresponds approximately to 125 repeat units per molecule and an approximate MW of $2.53 \cdot 10^4$ g mol^{-1}. It has a melting point (T_m) is 245–250 °C and a service temperature range between -20 and $+70$ °C. Besides, two commercial recycled PET (RPET1 and RPET2) were provided from Nosoplas S.L. (A Coruña, Spain).

Methanol (MeOH) and dichloromethane HPLC-gradient for instrumental analysis were supplied by Merck (Darmstadt, Germany). Formic acid 98–100% puriss p.a. was from Sigma–Aldrich (Stockholm, Sweden). Water was purified using a Milli-Q Ultrapure water-purification system (Millipore, Bedford, MA, USA). MALDI-TOF MS matrix compound 2,5-dihydroxybenzoic acid (DHB) and trifluoroacetic acid 99% (TFA) were purchased from Sigma–Aldrich.

2.2. Polymer samples manufacture: reprocessing simulation

To simulate the mechanical recycling of PET, multiple reprocessing up to five times was performed using a corotating twin-screw extruder (DSE20, Brabender, GmbH & Co, Duisburg, Germany). Five reprocessing protocol was selected since the extrusion parameters were difficult to settle after the 5th step due to the low polymer viscosity; in addition, the resulting polymer strand was