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# Thermo-mechanical degradation and stabilization of poly(butylene succinate)

Ioanna-Nektaria Georgousopoulou [a], Stamatina Vouyiouka [a, *], Patrice Dole [b], Constantine D. Papaspyrides [a]

[a] *Laboratory of Polymer Technology, School of Chemical Engineering, National Technical University of Athens, Zographou Campus, 15780 Athens, Greece*
[b] *ACTIA, CTCPA Centre Technique de la Conservation des Produits Agricoles, Bourg-En-Bresse, France*

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ABSTRACT

The thermo-mechanical degradation and recyclability of poly(butylene succinate) (PBS) have been investigated by means of consecutive extrusion cycles under different temperature profiles, in order to simulate reprocessing intensive conditions. Herein it was found that PBS, when reprocessed at temperatures higher than 190 °C, suffers from branching/recombination degradation reactions, resulting in extrudates of higher solution viscosity, and of bimodal distribution of molar masses. When typical stabilizers (Irganox® 1010, Irgafos® 168) were added, the thermo-mechanical degradation of PBS was significantly suppressed, revealing the radical character of the pertinent degradation reactions. The incorporation of stabilizers at the level of 0.1% efficiently maintained polymer properties through reprocessing, while the higher concentration of 0.5% had a negative impact on extrudates quality. On thermal properties basis, degraded and stabilized PBS exhibited similar melting and degradation points compared to virgin material, showing its possibility for mechanical recycling. However, the induced degradation resulted in accelerated melt crystallization and lower degree of crystallinity, which might be attributed to the nucleating effect of the formed branches. The addition of stabilizers restricted the increase of the melt crystallization rate, and the relevant melt behavior was found similar to virgin material.

## 1. Introduction

Thermoplastic polyesters represent a wide class of polymeric materials carefully tuned to meet the needs for applications such as fibers, films, coatings, food and beverage packaging [1]. Currently, the majority of these materials are derived from fossil-based resources, which along with their non-degradable character intensify the problem of plastic waste accumulation and petrochemical feedstock depletion [1–3]. As a result, much attention has been paid to biodegradable polyesters, such as poly(lactic acid) (PLA), polycaprolactone (PCL) and poly(butylene succinate) (PBS) [4,5]. Among them, PBS is anticipated to be broadly commercialized in the near future, since it presents mechanical properties similar to those of polyethylene, and a much more flexible structure ($T_g = -32$ °C) compared to PLA ($T_g = 50$ °C) with higher toughness [6–11]. PBS boost will be also supported by the sustainability of its monomers, i.e. the high potential for production of bio-based succinic acid (SA) and 1,4-butanediol (BDO) [12–14].

Different studies exist on PBS degradation, such as hydrolytic [15–18], enzymatic [19–23], biological [24–26] and weathering [27], which are correlated to a number of polymer characteristics, such as molecular weight and distribution, crystallinity, lamellar thickness, copolymer composition, and macroscopic shape of articles, as well as to degradation conditions [9,10]. Thermal and thermo-oxidative stability is also important for PBS processing, application and reuse/recycling. A number of works have been made up-to-day [19,28–31], showing that PBS is stable under flowing nitrogen at temperatures below 220 °C with the rate of mass loss reaching a maximum at ca. 390 °C [27,30,32], presenting higher stability than PLA (max at 365–368 °C). More specifically, PBS thermal degradation studied under nitrogen flow in the range of 250–260 °C involved chain scission reactions with anhydride (dominant gas), olefin, esters (such as methyl ester) and carbon dioxide being the main evolved gases [28,30,31]. The presumed degradation reactions involved the β-hydrogen bond scission of the

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* Corresponding author.
*E-mail address:* mvuyiuka@central.ntua.gr (S. Vouyiouka).

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ester groups, along with the breaking of the weak O–$CH_2$ bond and the formation of succinic acid and/or chains terminated with alkenyl moieties and carboxylic end groups. The succinate end group further decomposed to anhydride functional species via dehydration. Thermo-oxidative degradation of PBS studied under atmospheric air in the range of 170 °C was also found to involve a significant reduction of the polymer molar mass, promoting the formation of PBS oligomers with different end groups [28]. An α-H abstraction mechanism has been proposed leading to the rate-determining step of the formation of hydroperoxide intermediates (ROOH), which further decomposed to hydroxyl ester (ROH), peroxy (ROO•), alkyl (R•) and alkoxy radicals (RO•). Three degradation pathways have been suggested with different induction periods and resultant oligomer species.

Especially for recycling purposes, apart from thermal and thermo-oxidative degradation, the thermo-mechanical stability upon reprocessing is also crucial, since it is known that polymers degrade during the re-melting process due to temperature, shear and the unavoidable presence of small amounts of oxygen [33]. Multiple extrusion processes are usually performed to evaluate melt processing stability as well as the efficiency of selected process stabilizers (e.g. antioxidants, hydrolytic agents) so as to establish an appropriate remelting-restabilization recycling technique [33–41]. During reprocessing, chain scission radical and/or non-radical reactions have been found to occur in the case of polypropylene (PP) [42–44], PET [45], PLA [46–48], and poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [49], resulting in decrease of molecular weight and consequent increase of crystallinity and opacity, with a deterioration of mechanical properties. Especially, in previous studies of the same group [39–41], post-used PP chairs were examined during extrusion reprocessing and the observed chain scission degradation reactions were efficiently restricted via the addition of three stabilization systems (Recyclostab 451®, Recyclossorb 550®, Recycloblend 660®).

Similarly to PLA, PBS as an aliphatic polyester is susceptible to hydrolysis and thus is anticipated to present a chain scission degradation pattern upon reprocessing. However, two recent publications [50,51] dealing with PBS reprocessing by means of compression (140–200 °C) deviate from hydrolysis-based degradation mechanism; following PBS hydrolytic degradation, re-polymerization reactions were found to occur during reprocessing, leading to molecular weight recovery and increase of bending strength.

This PBS different behavior is really interesting to be studied in re-extrusion conditions, where mechanical shear and temperature are more intense compared to compression reprocessing; extrusion conditions strongly affect the thermo-oxidative reactions profile, such as the formation of alkyl radicals, while this high-shearing process simulates mechanical recycling in industrial scale. Therefore, in the current paper, the aim was to study for the first time the feasibility of PBS reprocessing for recycling purposes, via executing successive extrusions under elevated temperature and shear conditions and examine any effect on polymer structure and molecular weight including thermal properties. To this direction, a twin-screw co-rotating extruder was utilized to perform five consecutive extrusion runs. The use of primary and secondary antioxidants was also examined as a way to thermostabilize PBS, to induce melt processing stability and to understand the relevant degradation mechanism. The establishment of appropriate remelting-restabilization recycling route is anticipated to provide a practical, economically feasible and facile solution towards sustainable PBS plastic packaging.

## 2. Experimental

### 2.1. Materials

PBS resin (Natureplast PBE003, film grade) in the form of pellets (3 mm) was kindly provided by Natureplast (France) for the preparation of the degraded samples. Prior any characterization, PBS grades were dried at 80 °C for 5 h. The examined polymer antioxidants were Irganox® 1010 (I1010) and Irgafos® 168 (I168) kindly provided by BASF SE Ludwigshafen (Germany) and were added in the form of masterbatch in PBS at final concentrations of 0.1 and 0.5% (w/w).

Other reagents were chloroform (purity 99.5%) (Chem-Lab, Belgium), benzyl alcohol (BeOH) (Merck, Germany), tetra-n-butylammonium hydroxide (TBAH) (Alfa Aesar, Germany) and magnesium nitrate hexahydrate ($MgNO_3 \cdot 6H_2O$) (Merck, Germany).

### 2.2. Reprocessing

PBS was subjected to five successive extrusion cycles in a Haake Rheomex twin-screw co-rotating extruder ($L/D = 25$, $d = 16$ mm). Reprocessing temperature was set at 190, 200 and 210 °C at constant rotation speed of 100 rpm. After each extrusion cycle, the extrudates were cooled in water bath, pelletized in 3 mm pellets and dried at 80 °C for 5 h.

Multiple extrusion was carried out on neat PBS, as well as on samples containing the stabilizers. To examine the effect of storage and drying on reprocessing and to “simulate” typical storage environmental conditions, PBS sample was exposed for two weeks to 50.0 ± 3.5% RH environment [52] at fixed temperature of 25 °C. It was then dried (80 °C, 5 h) (prePBS: preconditioned PBS) and re-extruded according to the aforementioned procedure. The prepared PBS formulations and pertinent degradation conditions are presented in Table 1.

### 2.3. Characterization

#### 2.3.1. $^1H$ NMR and $^{13}C$ NMR

$^1H$- and $^{13}C$ NMR spectra were recorded at room temperature on a Varian Gemini 2000 300 MHz spectrometer, using $CDCl_3$ as solvent.

#### 2.3.2. FT-IR ATR and Raman analysis

FTIR spectra were acquired directly on PBS films of 0.05 mm thickness, within the wavelength range of 600–4000 $cm^{-1}$ using a FTIR spectrometer model Perkin Elmer Spectrum 100. The FTIR spectra were obtained using attenuated total reflectance (ATR) with a ZnSe crystal of 2.4 refractive index. The scans were run at a resolution of 4 $cm^{-1}$ and 16 scans were taken for each spectrum.

Raman spectra were measured on the same PBS films (0.05 mm thickness) using a Ranishaw invia confocal Raman microscope system with two lasers emitting at 532 nm/633 nm with a charge coupled device (CCD) detector. 532 nm laser was chosen for emission in 10%. Prior any measurement, crystal silicon with fixed peak position at 520 $cm^{-1}$ was used to calibrate the Raman shifts. The spectra were collected in WIRE3 workstation in extensive mode ranging from 100 to 3200 $cm^{-1}$.

#### 2.3.3. Solution viscometry

The intrinsic viscosity (IV, dl $g^{-1}$) was measured in chloroform at concentration of 0.2 g $dl^{-1}$ in an Ubbelohde 0c capillary viscometer at 25 ± 0.1 °C. All samples were dissolved at room temperature and filtered prior measurement using a disposable membrane. Measurements were performed in duplicates and IV values were determined using the Solomon–Ciuta equation (eq. (1)) [53]: