Ellagic acid as stabilizer in the thermo-oxidative degradation of thermoplastic polyurethane

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ABSTRACT

Ellagic acid (EA) is a plant polyphenol with strong antioxidant properties. The stabilizing effect of EA on the thermo-oxidative degradation of the commercial thermoplastic poly(ester-ether urethane) (TPU) was studied for the first time and compared with effect of kraft lignin (KL), butylated hydroxytoluene (BHT) and pentaerythritol tetrakis (Irganox 1010). TPUs doped with antioxidants (*ca.* 20,000 ppm), were analysed for their oxidation induction time (OIT) at 200 °C and the oxidation onset temperature (OOT). The extent of TPU degradation with and without addition of antioxidants was studied by head space-gas chromatography-mass spectrometry (HS-GC-MS) at 200 °C under aerobic atmosphere. The highest stabilizing effect of EA was attributed primarily to its stronger antioxidant capacity when compared to KL and synthetic polyphenolic antioxidants (BHT and Irganox), which was corroborated by antiradical power studies with 2,2-diphenyl-1-picrylhydrazyl (DPPH). The analysis of the volatile products released under thermo-oxidative degradation showed the suppressive effect of EA on the thermally induced depolymerization of TPU occurring *via* homolysis. Furthermore, it has also been proposed that EA affects TPU degradation with the cleavage of urethane bonds in carbamates due to eventual coordination with the intermediate cyclic intramolecular transition complex involved in thermally induced depolymerization. Further studies in this area can prompt the performance improvements of TPU products, allowing them to be used in a wider range of durable goods applications.

1. Introduction

The aging of polymers is the main reason for the decrease of their performance properties [1–6]. Among the various aging mechanisms (chemical, mechanical, thermal, photochemical, etc.), thermo-oxidative degradation stands out, since it manifests itself already in the production of polymeric goods by thermal processing, not to mention during their shelf life [1–6]. The addition of different antioxidants, mainly of phenolic origin, is a common way to prevent the thermo-oxidative degradation of polymers [1–4]. Sterically hindered phenols inhibit oxidation by competing with polymeric substrate for oxygen-centered active radical species thus shortening the kinetic chain length of the radical propagation reactions [5,6]. However, synthetic polyphenolic

antioxidants (SPAs) from fossil resources are not only harmful to the environment, but they can also be hazardous, which is especially important, for example, for food packaging and biomedical applications [7,8]. In this context, the application of natural polyphenolic antioxidants (NPAs) for the protection of polymeric matrices seems particularly attractive [9].

Despite several environmental and safety advantages of NPAs over SPAs, the former have several shortcomings that limit their wide applications. Thus, the most effective NPAs in stabilizing polymers, such as flavonoids and lignins, are even more efficient than the SPAs used in industrial practice [9–12]. Furthermore, the efficiency of some NPAs can be greatly improved through relatively simple structural modifications [9,12]. However, many of these NPAs have relatively low degradation

temperatures, are poorly soluble in polymeric matrices, may cause coloration, have irregular composition and/or purity, and can be expensive [9]. These features impose serious constraints on NPAs in polymer stabilization applications and need further refinement. A plausible solution could be to find widely available, mixable with polymeric matrices, thermally stable NPA, with regular structure and highly efficient antioxidant activity. Among natural polyphenols, ellagic acid (EA) is one of the most abundant NPAs, having the highest antioxidant efficiency and broad potential in biomedical and technical applications [13]. Wide technical applications of EA are hampered by the lack of affordable high-quality products on the market with acceptable prices [13]. However, recent advances in the large-scale production of EA from industrial streams of sulphite pulping of wood can fill this gap [14]. Although a remarkable effect of EA in the composition of pomegranate peel extract on polyethylene stabilization has recently been reported, the uncertainty of the conclusions drawn about its long-term stability effect and the mechanisms involved have been explained, at least partially, by complexity of phenomena that occur with the mixture of NPAs of different origins [15]. Thus, the potential of pure EA in polymer stabilization has not been clearly disclosed.

This study intended to evaluate the effect of EA on the stabilization of commercial thermoplastic polyurethane (TPU) under thermo-oxidative degradation. The stabilizing effect of EA was compared with those of commercial kraft lignin (KL) and conventionally explored SPAs, such as butylated hydroxytoluene (BHT) and pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (Irganox 1010). The obtained results were explained by a comparative study on the antioxidant activities of the referred NPAs and SPAs, and evaluation of the polymer degradation products released during aging assays.

2. Experimental

2.1. Materials

Pearlthane® 11H94, a polycaprolactone-based thermoplastic polyurethane (TPU) containing BHT was supplied by Lubrizol Chem. Corp. Ellagic acid (98% purity) was supplied by Acros Organics Chem. Comp. (Geel, Belgium). The Irganox 1010 was supplied from BASF Chem. Comp. (Nienburg/Weser, Germany) and BHT from Acros Organics Chem. Comp. (Geel, Belgium). 2,2-diphenyl-1-picrylhydrazyl (DPPH) was purchased from Merck Chem. Comp. (Darmstadt, Germany). All used organic solvents were highly pure products of HPLC grade and applied as received: tetrahydrofuran (THF) and N, N-dimethylformamide (DMF) from Acros Organics Chem. Comp. (Geel, Belgium); methanol from Merck Chem. Comp. (Darmstadt, Germany).

The kraft lignin (KL) was supplied by The Navigator Comp. (Portugal) being isolated from black liquor of *Eucalyptus globulus* wood cooking by LignoBoost® procedure. The empirical formula per one phenyl propane unit (PPU) was $C_9H_{6.76}O_{2.95}S_{0.18}(OCH_3)_{1.41}$ (M_{ppu}= 211.4 g/mol). The weight average molecular weight (Mw) was 1415 Da [16]. The total amount of hydroxyl groups was 1.47/1PPU and the phenolic groups of 0.83/1PPU [16].

2.2. Procedures

The antioxidants (EA, KL, BHT and Irganox 1010) were introduced in TPU in solution. In a typical trial, the estimated quantity of antioxidant (*ca.* 20,000 ppm) was dissolved in 2.0 ml of 0.1 M LiCl DMF solution and added slowly under stirring to TPU solution in THF (liquid-to-solid ratio of 50). After pre-evaporation of the obtained solution under stirring in fume hood, it was transferred into glass petri plates and dried for 48 h in the dark under room temperature in fume hood. The films, obtained by casting, were finally dried in the vacuum oven VacuTherm™ (Thermo Fisher Scientific, Waltham, Massachusetts, USA) at 35 °C, over one week. This procedure ensured the complete elimination of THF, but not of DMF, which has a very high boiling temperature (153 °C). The

obtained films were kept at room temperature, in the dark, inside a desiccator. The films were mechanically cut into particles of *ca.* 0.5 mm that were further used for thermal analyses. At least two sets of films were prepared with the same antioxidant and the samples obtained were homogenized. The TPU blank sample was prepared by the same methodology, but without the addition of antioxidants. All the films were visually homogeneous.

2.3. Analyses

2.3.1. Analytic pyrolysis and head space analysis of thermo-oxidative degradation

Around 0.10 mg of sample was weighted and analyzed using an analytical pyrolysis devise (Py) coupled to a gas chromatograph (Agilent 7890B) and mass detector (Agilent 5977B) designated as Py-GC-MS analysis. The samples were pyrolyzed at 550 °C for *ca.* 1 min in a platinum coil Pyroprobe connected to a CDS 5150 valve interface coupled to the GC-MS system equipped with a fused-silica capillary column (ZB-1701: 60 m x 0.25 mm i.d. x 0.25 μm film thickness). The chromatographic conditions used were as follows: 40 °C (held for 4 min), then increased at 20 °C·min^{-1} to 100 °C, and at 6 °C·min^{-1} to 270 °C (held for 5 min). The injector and MS interface temperatures were 270 and 280 °C, respectively, and the electron ionization energy (EI) of the mass detector was 70 eV. Helium was the carrier gas with a flow rate of 1 mL/ min. The compounds were identified by comparison of their mass spectra with databases (Wiley and NIST2014) and literature [17]. The total area of the chromatogram was obtained automatically, and the percentage area of each identified compound was calculated. The results of analyses of two samples were averaged. The typical total ion chromatograms (TICs) are presented in Figure S1 (Supplementary materials) and the detected products listed in Table S1 (Supplementary materials).

The head space (HS) analysis of TPUs was carried out using *ca.* 0.200 g of a homogeneously disintegrated sample in 20.0 ml glass vial purged with oxygen before the assays. The vial was placed in the 7694E head-space sampler with oven temperature of 200 °C keeping it for equilibration for 15 or 30 min. After vial equilibrium, the injection time was 1 min with a total GC cycle of 40 min. The injector temperature was 240 °C (split ratio 1:5.1). The separation of gaseous products was carried out on a gas chromatograph of Agilent 6890 series equipped with HP-5MS fused silica capillary column (30 m x 0.25 mm i.d. x 1 μm film thickness) coupled to the mass detector (HP 5973 series). The chromatographic conditions used were as follows: 40 °C (held for 4 min), heating ramp of 15 °C·min^{-1} to 295 °C and 4 min held at final temperature. Helium was the carrier gas with a flow rate of 1.5 cm^3/min. The BHT from commercial TPU detected in the gaseous phase was used as an internal standard for the normalization of the chromatograms in the HS-GC-MS analysis. The typical TICs are presented in Figure S2 (Supplementary materials) and the detected products listed in Table S2 (Supplementary materials).

2.3.2. Analysis of thermo-oxidative degradation

The oxidation induction time (OIT) of materials was determined by thermogravimetric analyses-differential scanning calorimetry (TGA-DSC), following the ASTM D 3895 – 07 methodology using a LABSYS evo STA analyzer (Setaram, Caluire, France, Setaram) in triplicate. The samples (*ca.* 18 mg) were heated in open aluminum pans at a constant rate of 10 °C·min^{-1} in an inert gaseous environment (nitrogen). When the specified temperature was reached (200 °C), the atmosphere was changed to oxygen, maintaining the same flow rate (20 cm^3·min^{-1}). The specimen was then held at constant temperature until the oxidative reaction started which was observed via the mass drop registered on the thermogram. The time interval from when the oxygen flow is first initiated to the oxidative reaction is referred to as the induction period (onset temperature).

Oxidation onset temperature (OOT) of TPU derived samples was determined as onset degradation temperature from TGA analysis in
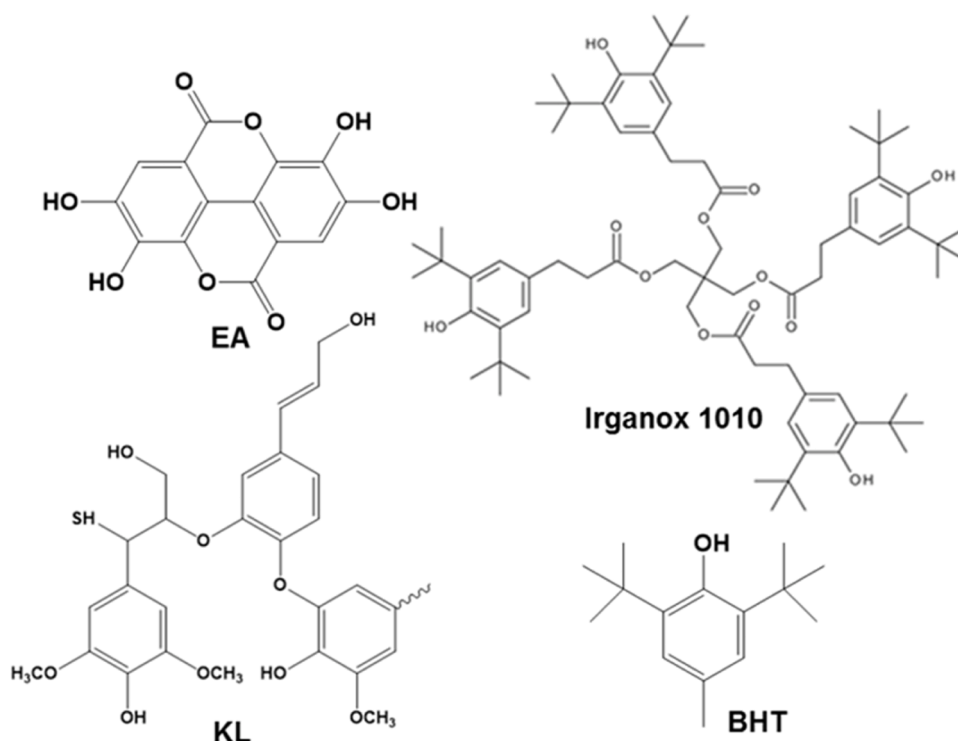
Fig. 1. Chemical structures of NPAs and SPAs used in the study. Schematic representation of the kraft lignin (KL) reflects the known structural features of *Eucalyptus* LignoBoost® lignin isolated from kraft black liquor [16].

oxygen atmosphere, carried out using a LABSYS evo thermogravimetric analyzer (Setaram, Caluire, France) from 30 to 700 °C, at a heating rate of 10 °C·min^{-1} and under oxygen flux (20.0 cm^3·min^{-1}).

Thermogravimetric analysis (TGA) of antioxidants was performed using a LABSYS evo thermogravimetric analyzer (Setaram, Caluire, France) from 30 to 700 °C, at a heating rate of 10 °C·min^{-1} and under nitrogen atmosphere.

2.3.3. Antioxidant activity via DPPH

DPPH reagent stock solutions of *ca.* 0.0989 mM were prepared by dissolving 0.0039 g of DPPH in 100 cm^3 of methanol. Antioxidants under study were initially dissolved in 2.0 ml of 0.1 M LiCl DMF and filled up to 100 cm^3 with methanol in order to address solubility issues while avoiding the use of solvents with inherent antioxidant capabilities (*e.g.*, dimethyl sulfoxide).

Spectrophotometric measurements at 515 nm were carried out on EvolutionTM 220 UV–Vis Spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) with Thermo Scientific INSIGHT software, used for the data processing. Calibration curves for DPPH were made in triplicate and the initial DPPH concentration was obtained from the following equation:

$$A_{515} = 1.09 \cdot 10^4 \cdot C_{DPPH} - 0.0301$$

A standard run followed an adapted protocol from Xie et al., 2014 [18]. 3.00 cm^3 of DPPH diluted solution (absorbance at 515 nm: 0.96 ± 0.03) was added to the 4-ml quartz cuvette in the reading slot. 30 μl of antioxidant solution, with [antioxidant]/[DPPH] ratios varying from 0.02 to 8.4 (depending on the run and target compound), were added to DPPH solution and rapidly mixed by aspiration in the pipette. At the same time, the timer was set to zero. The absorbance was recorded every 30 s for a total of 10 min. Simultaneously, a blank solution of DPPH was screened to estimate DPPH decomposition during the time of measurement. All measurements were made at 19 ± 1 °C, in triplicate. EC$_{50}$ values were determined according to Xie et al., 2014 [18] and anti-radical power (ARP) calculated according to Brand-Williams et al., 1995

Table 1
Basic characteristics of antioxidants.

Antioxidant	Molecular weight (M_r)	Degradation temperature (T_{deg}^0, °C)	Fusion temperature (T_f^0, °C)
EA	302.2	422±1	-**
KL	211.4*	225±2	-**
BHT	220.4	195±1	70±1
Irganox	1177.6	325±2	125±2

  * -Average phenyl propane unit (C$_9$H$_{6.76}$O$_{2.95}$S$_{0.18}$(OCH$_3$)$_{1.41}$) [16];.

  ** - Difficult or impossible to distinguish from T_{deg}^0, which was determined as onset degradation temperature from TGA analysis in nitrogen atmosphere; fusion temperature was determined under atmospheric pressure, T_f^0.

[19].

3. Results and discussion

3.1. Effect of antioxidants on the thermo-oxidative degradation of TPU

Two NPAs, ellagic acid (EA) and hardwood kraft lignin (KL), and two SPAs, butylated hydroxytoluene (BHT) and pentaerythritol tetrakis [3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] (Irganox 1010, or just simply Irganox) (Fig. 1), were introduced (*ca.* 20,000 ppm) in poly-caprolactone copolyester-based thermoplastic polyurethane (TPU) in order to assess their effect on its thermo-oxidative degradation.

According to established practice, referred TPU is commonly processed at 170–180 °C and needs to be doped with antioxidant to prevent excessive thermo-oxidative degradation. In this context, all preselected NPA and SPA stabilizers comply with the formal basic thermal resistance prerequisites (Table 1). KL and BHT were almost at the upper thermal limit, while EA and Irganox had a substantial margin. BHT and Irganox are fusible compounds while EA and KL had no clear fusion temperatures. Although EA is a crystalline compound [13,15], it was difficult to
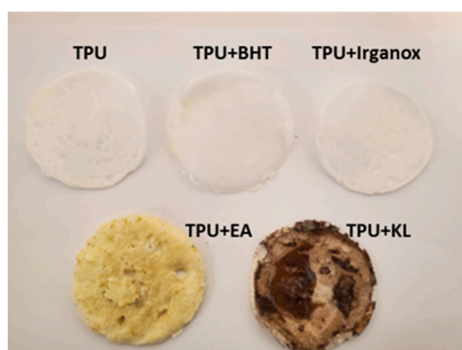
Fig. 2. Photos of TPU films obtained by casting. The sample without addition of antioxidants is designated as TPU and the samples with addition (*ca.* 20,000 ppm) of BHT, Irganox 1010, EA and KL designated as TPU+BHT, TPU+Irganox, TPU+EA and TPU+KL, respectively.

Table 2
Effect of antioxidants addition on the thermo-oxidative degradation of TPU.

Antioxidant added in TPU	OIT min	OOT °C	Time to 20% weight loss (t_{20}^w, min)
TPU (no additive)	2.3 ± 0.2	254±1	10.0 ± 0.1
TPU+BHT	2.6 ± 0.1	258±1	10.5 ± 0.3
TPU+Irganox	2.8 ± 0.1	260±2	10.8 ± 0.2
TPU+EA	4.6 ± 0.2	298±2	15.7 ± 0.1
TPU+KL	3.9 ± 0.2	279±3	13.4 ± 0.3

*- Oxidation onset temperature (OOT) was determined as onset degradation temperature from TGA analysis in oxygen atmosphere; t_{20}^w was determined from TGA analysis in oxygen atmosphere at 200 °C.

distinguish the melting point of the crystals from their degradation with formation of carbonized matter under aerobic conditions. TPU and TPU doped with BHT or Irganox showed the same light color, while TPU doped with EA or KL showed pale yellow and brown colours, respectively (Fig. 2).

The effect of the stabilizers was evaluated through the changes in the oxidation induction time (OIT) and the oxidation onset temperature (OOT) determined by TGA/DSC analysis (Table 2). The lowest effect from BHT addition is explained by its presence in the original commercial TPU samples (*ca.* 2000–5000 ppm), presuming that no significant synergistic or antagonistic effects with other antioxidants took place. Partial evaporation of BHT may be another factor to consider.

Special attention should be given to the substantial increase in OIT

and OOT with the addition of NPAs. It is also noteworthy that the stabilizing effect of EA was even more pronounced than that of KL (Table 2), already recognized for this purpose in previous studies. In fact, the stabilizing effect from lignin addition was previously reported for laboratory-produced TPU [12] and in poly(ethylene) blends [20] that showed even better polymer protection than such commercial SPAs as *tert*-butylhydroquinone (TBHQ) and Irganox 1010.

The basic antioxidant mechanism of lignin, like in other polyphenols, is usually associated with direct scavenging of reactive oxygen species (ROS) by hydrogen atom transfer (HAT), mainly from phenolic moieties [9,12,20]. In turn, HAT proceeds via proton-coupled electron transfer (PCET) or by sequential proton loss–electron transfer (SPLET) mechanisms in the case of ionized substrates (Fig. 3).

Direct electron transfer from the protonated polyphenol (electron transfer then proton transfer, ET-PT) is unlikely to occur [21]. Accordingly, the antioxidant capacity is frequently reported to be correlated with the number of phenolic groups and their bond dissociated energy (BDE), being the latter linked to the likelihood of cleaving the PhO—H bond *via* homolysis [21,22]. Among examined antioxidants, EA had the lowest BDE, followed by BHT and Irganox, which is associated to their TPU stabilization efficiency (Table 3). The lignin has no clearly defined BDE, but according to estimates made, based on different phenolic lignin model compounds [12], it should be between those of EA and SPAs (BHT and Irganox). Therefore, these observations are in line with the importance of the proposed PCET mechanism of HAT (Fig. 3). The remarkably higher stabilization effect of KL, when compared to BHT and Irganox, can be explained not only by its slightly lower BDE, which could be comparable for some lignin structural units with BDE of SPAs, but also due to the so-called charring mechanism [20,23]. The latter implies that the aromatic structures of lignin favor the formation of carbonization at high temperatures in polymeric matrices, which acts as a barrier to heat and mass transfer, thus hindering the diffusion of oxygen from the gaseous phase to the polymeric matrix [23]. In fact, the TGA analysis clearly showed the highest amounts of char matter exactly with the addition of lignin to the TPU (Fig. 4). It is noteworthy that the KL used in

Table 3
Basic thermal characteristics of antioxidants.

Antioxidant	BDE [12,22] (kJ/mol)	OH_{Ph} (mmol/g)	EC_{50} / OH_{ph} (μM) *	ARP **
EA	322.6	13.2	6.4/25.6	14.2
KL	325–339	3.9	69.7/57.9	1.3
BHT	334.3	4.5	344.8/344.8	0.3
Irganox 1010	335.0	3.4	41.7/166.8	2.2

* EC_{50} (DPPH) is the concentration of the substrate (or the phenolic groups in the substrate) that results in a 50% loss of [DPPH].
** Antiradical power (ARP) is defined as $1/EC_{50}$ (DPPH), where EC_{50} is expressed as [antioxidant]/[DPPH] ratio [19].
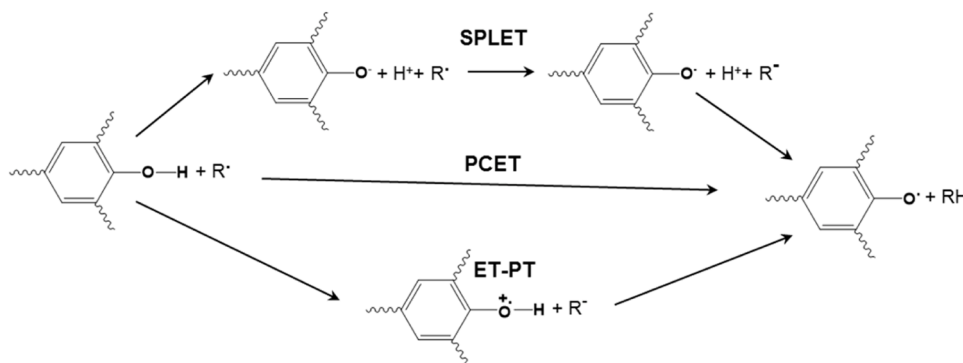

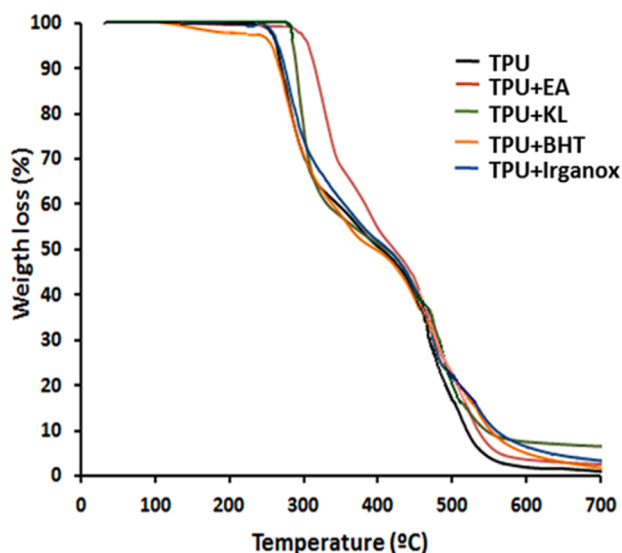**Fig. 3.** General mechanisms for hydrogen atom transfer from polyphenols.

Fig. 4. TGA curves of TPU with addition of antioxidants under oxygen atmosphere.
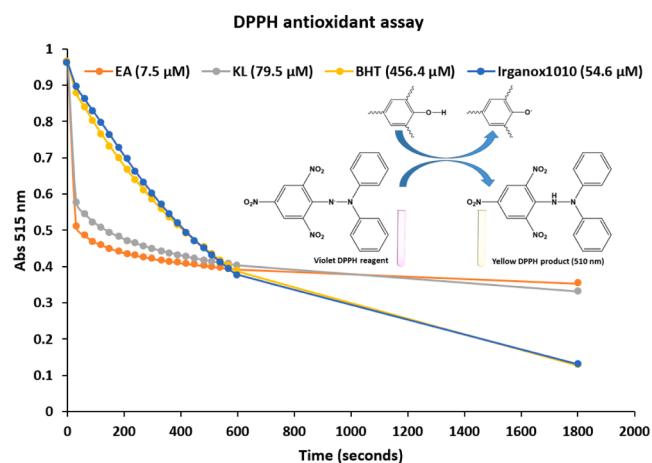

Fig. 5. Comparison of antioxidant activity of ellagic acid (EA), kraft lignin (KL), butylated hydroxytoluene (BHT) and pentaerythritol tetrakis (Irganox1010) evaluated by reaction with DPPH. The chosen runs for the comparative graphical representation had the closest concentrations of the antioxidants to theoretical EC_{50} while having the closest final absorbances by 10-minute mark.

this study contained small amounts of EA as a concomitant (*ca.* 5–7%) [16]. Hence, KL showed some collegial effect of combining antioxidant activities of different lignin substructures and polyphenolic concomitants.

The observed outstanding efficiency of EA in TPU stabilization (Table 2) is not only due to the highest abundance of phenolic moieties, which was 3–4 times higher than with other examined antioxidants (Table 3), but also due to their greater efficiency in hydrogen atom donating capacities as follows from the reaction with DPPH. In fact, at the EC_{50} of antioxidants, the efficiency of phenolic groups in EA was more than 2-fold *vs* KL and more than 13-fold and 6-fold *vs* BHT and Irganox, respectively (Table 3). The excellent radical scavenging properties of EA are also related to the extensive resonance stabilization of formed phenoxyl radicals, that provide appropriate conditions for radical inactivation [24]. Radical stabilization and ability for regeneration of hydrogen donating capacity are key characteristics of antioxidants [19]. Finally, the anti-radical power (ARP) of EA was almost 11 times greater than lignin and more than 6 times greater than Irganox

(Table 3).

At the same time, the kinetics of DPPH reaction with NPAs and SPAs were completely different. This is particularly visible at EC_{50} of antioxidants, which showed the DPPH depletion kinetics with NPAs much faster than those with SPAs (Fig. 5). This can be related to the fact that DPPH can be quenched by both electron and hydrogen atom transfer, however the latter mechanism is much slower and diffusion-controlled, whereas electron transfer is extremely fast, in the order of femtoseconds [25]. Another plausible explanation of overlapping tendencies in the DPPH assay of the referred NPAs and SPAs could be the steric hindrance effect in the latter due to bulky *tert*-butyl substituents at the *ortho* positions. SPAs such as BHT and Irganox are designed to decrease the rate of free radical chain reactions in the polymeric matrix, when due to stabilization, delocalization or/and steric hindrance of the phenoxy radicals formed, further activity in radical propagation reactions is hampered [2,5]. SPAs readily react with peroxy radicals, thereby inhibiting free radical oxidation of polymers. In addition, under thermal processing conditions, in the presence of antioxidants, the rate of radical chain transfer reactions responsible for branching or cross-linking of the polymer is decreased, thus improving the processability of polymers. However, the steric hindrance effect in SPAs is also a reason for the slowing down of their reaction with such bulky reagents as DPPH (Fig. 5). This must be one of the main reasons for the much slower reaction kinetics with DPPH of SPAs (BHT and Irganox) than of NPAs (KL and EA). However, the lifetime of referred SPAs is longer than that of NPAs.

Taking into account the efficiency of NPAs in the decreasing of TPU aging, their TPU formulations were analyzed for the release of characteristic volatile degradation products in order to study deeper the protective mechanisms.

3.2. Effect of natural antioxidants on the thermo-oxidative degradation products of TPU

The stabilization effect of NPAs was also assessed by comparing the volatile degradation products released under aerobic conditions similar to those applied for the determination of OIT (200 °C, 15 min) using a head space analysis (HS-GC-MS). Alternatively, the degradation of initial TPU and the TPU doped with EA or KL was evaluated under analytical pyrolysis conditions (flash pyrolysis) at *ca.* 550 °C (1 min). Both assays are complementary: the first allows to evaluate the primary volatile degradation products, released under thermo-oxidative degradation at moderate temperature under oxygen atmosphere, while the second reflects the intense thermal depolymerization of polymeric chains under pyrolysis in an inert atmosphere, being also the analytic tool to assess the polymer composition.

The main thermal degradation products of TPU under conditions of analytical pyrolysis were 2-oxepanone (ε-caprolactone), 1,4-butanediol (1,4-BDO), tetrahydrofuran (THF), 5-hexenoic acid and 4,4ʹ-methylene diphenyl diisocianate (4,4ʹ-MDI) (Fig. 6A).

2-oxepanone and 5-hexenoic acid are typical thermal degradation products of polycaprolacone (PCL) *via* radical unzipping depolymerization mechanism and *via* syn *Ei* intramolecular rearrangement mechanism, respectively [26,27]. 4,4ʹ-MDI arises during thermal degradation of carbamates *via* homolytic cleavage of the urethane linkage [28,29]. The detection of 1,4-BDO indicates that the polyester polyol used in the reaction with 4,4ʹ-MDI to obtain TPU was poly(ε-caprolactone)-b-poly (butylene oxide). As was previously reported, 1,4-BDO and 4,4ʹ-MDI or 4,4ʹ-diaminodiphenylmethane (4,4ʹ-DADM) are the main pyrolysis products of thermoplastic poly(ether urethane) produced from the reaction of poly(butylene oxide) (PBO) and 4,4ʹ-MDI [29–31]. In addition, the TGA analysis (Fig. S3, Supplementary materials) showed the typical two-step thermal degradation patterns, respective to each constituent polymer block (*ca.* 370 °C for PCL [32] and *ca.* 320 °C for PBO [33]), for this kind of polymer. This assumption allowed a better interpretation of the results of thermo-oxidative degradation of TPU at 200 °C.
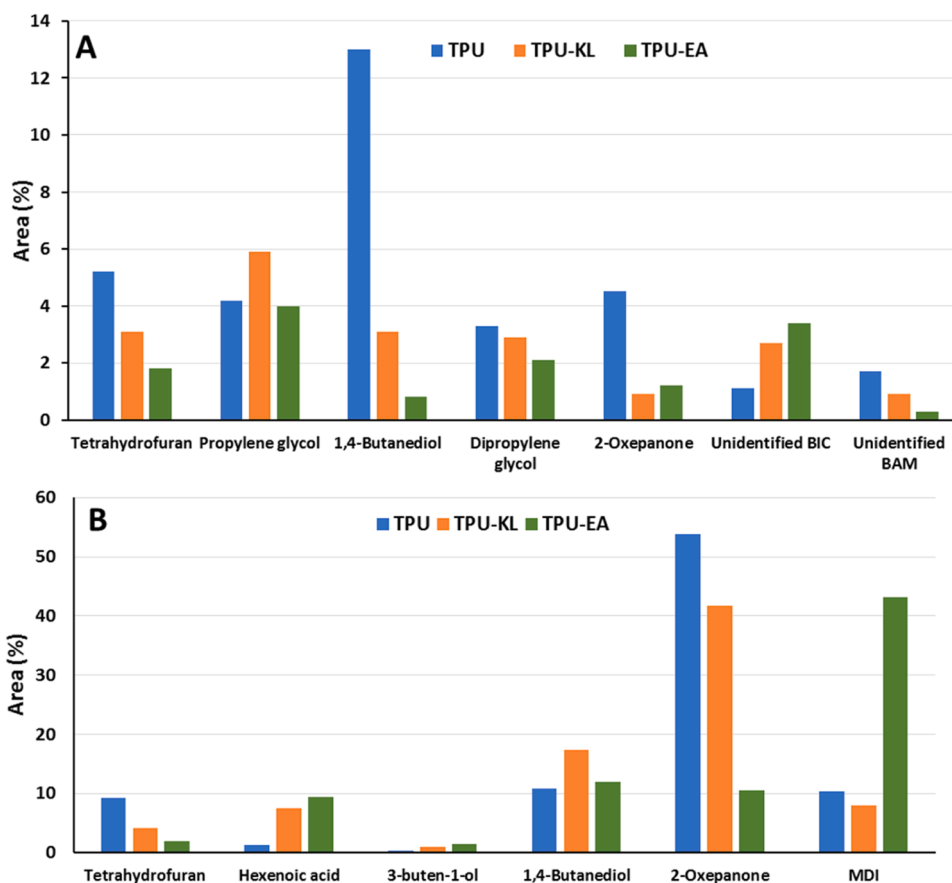
Fig. 6. Degradation products, of solely TPU and with addition (20,000 ppm) of ellagic acid (TPU+EA) or kraft lignin (TPU+KL), released during thermal treatment in aerobic atmosphere (200 °C, 15 min, A) and in flash pyrolysis assay (550 °C, 1 min, B). Abundances are expressed in relative area (%) of normalized chromatographic peaks (A) or as a relative area (%) of total detected products (B).
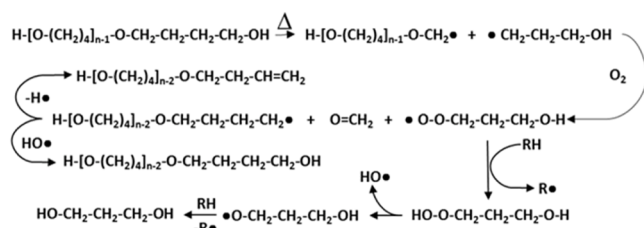

Fig. 7. The proposed thermo-oxidative degradation of poly(butylene oxide) through homolytic cleavage of C—C linkages leading to the formation of 1,3-propylene glycol.

The thermo-oxidative degradation of TPU at 200 °C under aerobic conditions revealed, in addition to 2-oxepanone (2-OP), 1,4-BDO and THF, such oxidation products as 1,3-propylene glycol (PG), dipropylene glycol (DPG), benzene isocyanate (BIC) and benzene amine (BAM) derivatives of unidentified structure (Fig. 6B). Other degradation products of minor abundance ($\leq 1\%$) and BHT with its oxidation products were not considered for this comparative analysis (*e.g.*, acetone, propylene carbonate or 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde and 2,6-di-*tert*-butyl-*para*-benzoquinone, among others). Furthermore, the BHT from commercial TPU detected in the gaseous phase was used as an internal standard for the normalization of the chromatograms in the HS-GC/MS analysis. In addition, the release of DMF used for the primary dissolution of KL and EA, which was incompletely removed under vacuum during the preparation of TPU films, was also not considered for the comparative analysis.

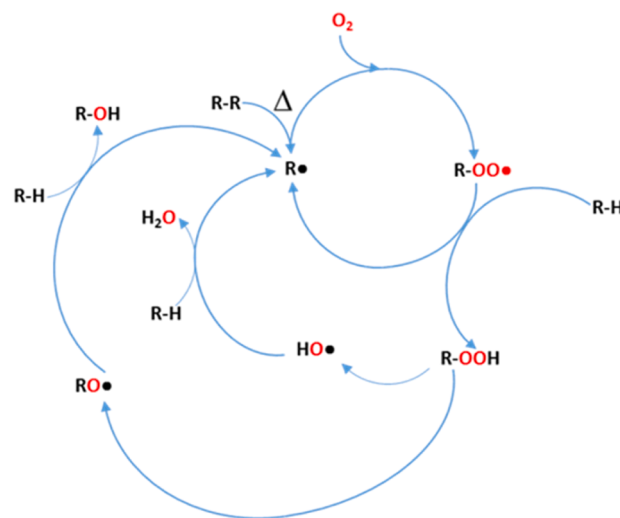The prevalence of 1,4-BDO and THF over 2-OP could be explained by

Fig. 8. Schematic representation of polymer thermal degradation under aerobic conditions, as adapted from [36]. Thermally induced homolysis is combined with free radical autoxidation stages.

easier thermal degradation of PBO in poly(ε-caprolactone)-b-poly (butylene oxide) of TPU under aerobic conditions and moderate temperature (200 °C), than of PCL counterpart. It is commonly assumed that these products are released from unzipping depolymerization occurring *via* homolysis [26–31]. The formation of DG and DPG could be the result of random homolysis of C—C bonds in PBO followed by oxidation with
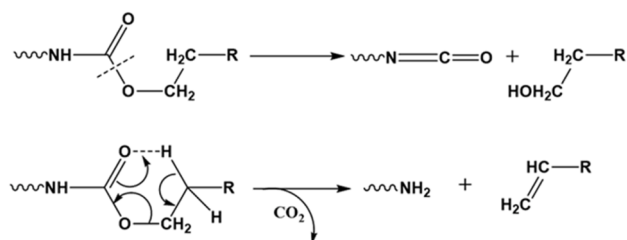
Fig. 9. Thermal degradation of urethane linkage in carbamate *via* homolysis (upper scheme) or *via* intramolecular cyclic mechanism (bottom scheme), as adapted from [28–30].

oxygen (Fig. 7).

According to common opinion, NPAs interrupt radical chain reactions *via* scavenging of free radicals, including ROS [34–37]. The decrease of the main degradation products, 1,4-BDO, THF and 2-OP, with the addition of NPAs (Fig. 5) clearly demonstrates their protective effect against radical depolymerization reactions induced by heat treatment. The EA effect was particularly notable for the protection of the more labile PBO counterpart of the TPU. A weaker effect of NPAs was detected on the release of PG and DPG from TPU during thermo-oxidative degradation (Fig. 6A). Apparently, oxidative degradation, characterized by greater radical reaction kinetic chain length than depolymerization *via* homolysis, leveled out the effect of NPAs. This fact, however, does not diminish the eventual importance of EA in the elimination of ROS responsible for radical propagation reactions. It is noteworthy that heat-induced radical depolymerization reactions and thermo-oxidative degradation are closely related (Fig. 8) and it is not easy to clearly define their interdependence at this point.

Special attention is warranted to the fact that TPU derived degradation products in the presence of EA were essentially of BIC rather than of BAM types. This is also visible in the analysis of TPU using analytical pyrolysis at 550 °C (Fig. 6B), showing a sharp increase in 4,4´-MDI release after the addition of EA to the TPU matrix. The prevalence of 4,4´-MDI or 4,4´-DADM among thermal degradation products of urethanes depends on the predominant mechanisms involved [28-31,36]. Thus, 4,

4´-MDI releases from thermal degradation of respective carbamates *via* homolysis of urethane ArNHC(O)-O linkage followed by the hydrogen radical transfer (Fig. 9), whereas the 4,4´-DADM releases during thermal degradation *via* intramolecular cyclic mechanism (intramolecular elimination). The latter presumes some coordination within the six-membered transition complex (Fig. 9). Speculating of known high chelating capacity of EA [13], it could be proposed that EA compete for the carbonyl group in the transition cyclic complex, thus shifting the thermal decomposition of urethane linkage *via* homolysis.

The high sensitivity of transition cyclic complex, involved in thermally induced depolymerization of polyesters to Lewis's acid additives (*e.g.*, multivalent metal cations), was reported previously in the context of emerging depression in thermal degradation temperature and alternative homolytic backbone depolymerization pathways [27]. It has been suggested that the coordination of metal cations with carbonyl groups in polymer ester groups changes their thermal degradation rate and proportions of formed degradation products. Similarly, the eventual coordination of EA with carbonyl groups in carbamate moieties could be one of the reasons for detected changes in thermal degradation of urethane linked TPU counterparts. However, this proposition needs further experimental confirmation.

The general degradation products of TPU during thermal degradation at 550 °C and at thermo-oxidative degradation at 200 °C, under aerobic conditions, are summarized in Fig. 10. The presented degradation products do not take into account low-molecular weight products such as water and carbon dioxide, normally reported for poly(ester urethane) and poly(ether urethane) thermal degradation [30,36,37], that were not assessed in this study.

4. Conclusions

This study demonstrated the particularly high protection effect of ellagic acid (EA) in the thermo-oxidative degradation of the commercial thermoplastic poly(ester-b-ether urethane) (TPU) based on the analysis of OIT at 200 °C and the OOT of the doped polymer. This is directly related to the high antioxidant capacity of this natural polyphenol. The antioxidation activity of EA, expressed as EC_{50} in reaction with DPPH,
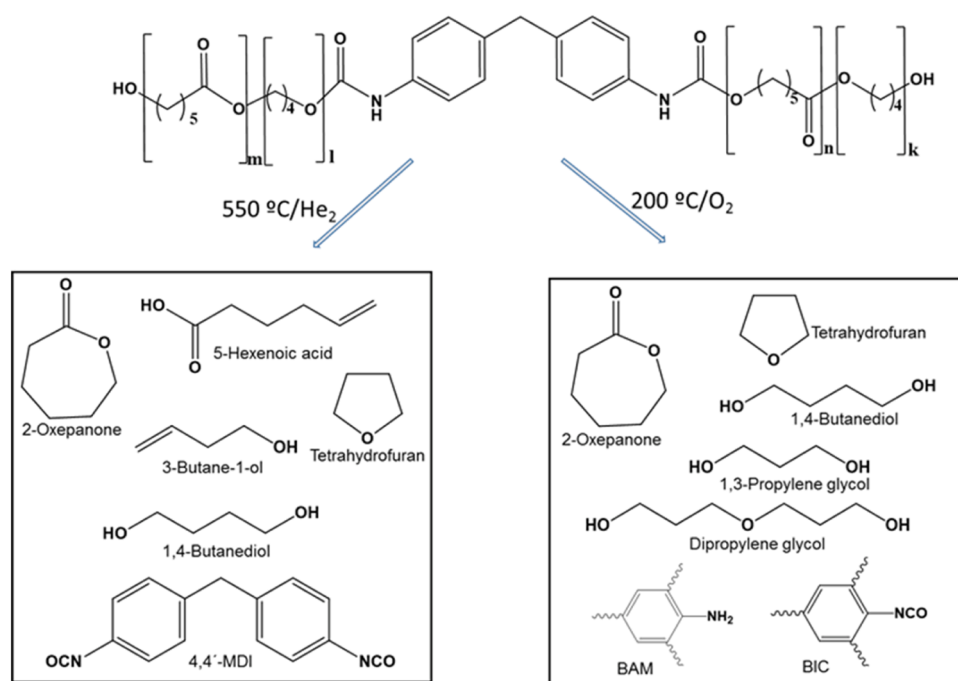

Fig. 10. Major volatile thermal degradation products released from thermoplastic poly(ester-ether urethane) (TPU) during thermal treatment in aerobic atmosphere (200 °C) and in flash pyrolysis assay (550 °C).

was even stronger than that of kraft lignin (KL) (almost 11-fold) and other examined synthetic polyphenolic antioxidants (BHT and Irganox 1010). This fact was assigned to the higher hydrogen atom donating capacities of EA in comparison to other referred polyphenol antioxidants. Although EA is a stronger antioxidant than BHT and Irganox 1010, the latter have a longer shelf life, as follows from reaction kinetics with DPPH. This fact mainly relates to the spatially hindered chemical structure of those synthetic polyphenolic antioxidants (SPAs). EA does not color the polymer matrix as much as technical KL and many other natural antioxidants and has a high thermal decomposition temperature (>400 °C), which allows it to be used in thermal processing of the widest range of polymers. The use of EA in polymer blends involved in the production of goods for food, pharmaceutical and cosmeceutical applications is safe due to the known health benefits of EA. In particular, the protection effect of EA in the thermo-oxidative degradation of TPU results in the suppression of radical depolymerization occurring *via* homolysis. It has also been proposed that EA can influence TPU degradation through its interaction with the intramolecular transition cyclic complex of the urethane moieties, thus affecting their thermal degradation pathways. Accordingly, in addition to the HAT mechanism, donor-acceptor interactions of EA with TPU could also contribute to its thermal degradation. However, further studies are needed to evaluate the effect of EA on the thermal processability of TPU and other polymers by extrusion and molding techniques.

CRediT authorship contribution statement

Nuno Gama: Investigation, Visualization, Writing – original draft. **Dmitry D. Evtyugin:** Methodology, Investigation, Visualization, Writing – original draft. **Ana Lourenço:** Methodology, Investigation, Validation, Writing – review & editing. **Célia Lopes:** Methodology, Investigation, Validation, Writing – review & editing. **Dmitry V. Evtyuguin:** Methodology, Conceptualization, Validation, Funding acquisition, Supervision, Resources, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.polymdegradstab.2023.110456.

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