Effect of additives on the thermal and thermo-oxidative stability of poly (ethylene furanoate) biobased polyester

Zoi Terzopoulou, Mohamed Wahbi, Nejib Kasmi, George Z. Papageorgiou, Dimitrios N. Bikiaris

ARTICLE INFO

Keywords:
- Poly(ethylene furanoate)
- Stabilizers
- Polycondensation
- Thermo-Oxidative stability

ABSTRACT

Polymers based on 2,5-furan dicarboxylic acid are a new class of biobased polymers with properties superior of those of their fossil-based homologues. However, similarly to poly(ethylene terephthalate) (PET), poly(ethylene 2,5-furan dicarboxylate) (PEF) degrades during its thermal processing and as a result its molecular weight drops, and discoloration occurs. This is mainly attributed to thermal and thermo-oxidative degradation reactions. The addition of several types of thermal stabilizers during the synthesis or the processing of thermoplastic polyesters is a common practice. In this work, a commercial phenolic antioxidant (Irganox 1098), and two phosphorus-containing thermal stabilizers (phosphoric acid and triphenyl phosphate) were added in PEF polyester during synthesis with the use of antimony acetate catalyst. The effect of these additives on the molecular weight, thermal properties, thermal, thermo-oxidative stability and physical aging of PEF was evaluated. It was found that all additives slightly improved the thermal stability of PEF, with phosphoric acid and mainly triphenyl phosphate being the most efficient ones.

1. Introduction

The ever-growing concern about the depletion of fossil fuels, the accumulation of fossil-based plastics in the environment and the continuous increase of greenhouse gas emissions in the atmosphere has led to vigorous research as well as commercial investments on biobased and biodegradable polymers. The European Commission has recently devoted much attention on the evolution of one-use plastics towards reusable, recyclable and renewable materials [1]. This focus on minimizing plastic waste is reflected on the large amount of funding for research and investments in the field of biobased plastics [2].

One of the biobased polymers that stands out, especially for food packaging applications, is poly(ethylene 2,5-furan dicarboxylate) (PEF) [3–7]. PEF is synthesized by the polycondensation of the biobased monomers 2,5-furandicarboxylic acid (FDCA) or its dimethyl ester, and ethylene glycol [7,8,9]. Due to its structural similarity with poly(ethylene terephthalate) (PET), it is considered to be its biobased homologue that will gradually replace it [10]. Besides its green character, PEF exhibits improved gas barrier [11], mechanical and thermal properties in comparison with PET, and can be recycled in the same infrastructures as PET. It suffers, however, from a few problems, with the most notable ones being the cost of high-purity monomer FDCA as well as discoloration after thermal treatment [12,13]. Monomer purity and selection of the proper catalyst seems to be the key for the successful preparation of PEF films and bottles of acceptable color, and companies like Avantium and DuPont are optimistic about the wide-scale production of FDCA-based products and their commercialization, which implies they are close in overcoming the aforementioned problems [14,15].

Like all thermoplastics, the thermal properties of PEF are crucial for its thermal processing. Recently we reported the effect of remelting cycles on the properties of PEF, which is relevant to its post-consumer processing for reuse and recycling purposes [12]. Significant changes in the chemical structure of PEF that arise from its thermo-oxidative degradation were noticed and were affected by the catalyst type used. In order to reduce the extend of degradation and aging of polymers, manufacturers resort to the use of stabilizers including antioxidants, heat and UV stabilizers as additives, particularly during recycling, to minimize depolymerization reactions and discoloration [16]. Therefore, in this work the effect of different stabilizers on the properties of PEF polyester were investigated with the aim of providing valuable insight into its thermal stability during its synthesis and thermal/
physical aging. PEF was synthesized by the transesterification and polycondensation of FDCA and ethylene glycol in the presence of Antimony(III) acetate catalyst, and different stabilizers (phosphoric acid, triphenyl phosphate, Irganox 1098) in concentration 0.5 wt% were added before the polycondensation step. The polyesters were characterized in terms of their viscosity, structural and thermal properties. Finally, the thermo-oxidative stability during aging was studied during incubation in an air circulation oven at 70 ± 1°C for 20 days followed by spectroscopic characterization and evaluation of the thermal characteristics of the samples.

2. Experimental

2.1. Materials

2,5-furan dicarboxylic acid (2,5-FDCA, 99%) was supplied from Sunshine Chemical Co, Ltd (Mianzhu, Sichuan, China), ethylene glycol (99.8%), and Antimony(III) acetate (Sb(CH₃COO)₃, 99.99%) catalyst were purchased from Aldrich Co. Phosphoric acid (PA), triphenyl phosphate (TPP), trifluoroacetic acid (99%), chloroform (99.5%) were of analytical grade and also purchased from Aldrich Co. Irganox 1098 (N,N’-hexane-1,6-diylbis(3-(3,5-di-tert.-butyl-4-hydroxyphenylpropionamide)), Irg) with a melting point of 156−161°C was supplied from BASF (Ludwigshafen Germany). The chemical structures of the additives are presented in Fig. 1.

2.2. Polyester synthesis

The polyesters were prepared by the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor [5, 17]. FDCA and EG in a molar ratio of diacid/EG = 1/4 were charged into the reaction tube of the polyesterification apparatus. The catalyst (Sb(CH₃COO)₃, 400 ppm metal trace) was added and the apparatus containing the reagents was evacuated several times and filled with argon in order to remove all the oxygen. The reaction mixture was heated at 150°C under argon atmosphere for 2 h, at 160°C for additional 1 h, and finally at 170−180°C for 1 h. This first step (esterification) is considered completed after the collection of almost all the theoretical amount of H₂O, which was removed from the reaction mixture by distillation and collected in a graduated cylinder.

In the second step of polycondensation, vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min to remove the excess of diol and to avoid excessive foaming, and furthermore to minimize oligomer sublimation. During this time interval, the temperature was gradually increased to 220°C while stirring speed was increased to 720 rpm. The reaction continued at this temperature for 2 h, at 230°C for 1 and at 240°C for additional 1 h. After the end of the polycondensation reaction, the polyesters were removed from the reactor, milled and washed with methanol. In a similar way, polyesters containing 0.5 wt% PA, Irg or TPP were prepared, using the same conditions. All additives were added in the reaction mixture after the completion of the first stage of esterification.

2.3. Polyester characterization

2.3.1. Intrinsic viscosity measurement

Intrinsic viscosity $[\eta]$ measurements were performed with an Ubbelohde viscometer at 25°C in a mixture of phenol and tetra-chloroethane (60/40, w/w). The samples were maintained in the above mixture of solvents at 90°C for 20 min to achieve complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter (Teflon) to remove any non-soluble materials. The intrinsic viscosity of each sample was calculated using the Solomon–Ciuta equation of a single point measurement:

$$[\eta] = \frac{2(t/t_0 - \ln(t/t_0) - 1))^{1/2}}{c}$$  \hspace{1cm} (1)

where $c$ is the concentration of the solution; $t$, the flow time of solution, and $t_0$ the flow time of pure solvent. For each sample, three different measurements were performed, and the average value was calculated.

The number average molecular weight $M_n$ was then calculated using the $[\eta]$ values through the modified Berkowitz equation [18, 19]:

$$M_n = 3.29 \times 10^4 [\eta]^{1.54}$$  \hspace{1cm} (2)

2.3.2. Wide angle X-Ray diffraction patterns (WAXD)

X-ray diffraction measurements of the samples after SSP were performed using a MiniFlex II XRD system from Rigaku Co, with CuKα radiation ($\lambda = 0.154$ nm) in the angle (2θ) range from 5 to 65°.

2.3.3. Differential scanning calorimetry (DSC)

Differential scanning calorimeter (DSC) measurements of the polyesters after SSP performed on a Perkin-Elmer, Pyris Diamond DSC differential scanning calorimeter, calibrated with high purity standards. Samples of 7 ± 0.1 mg were sealed in aluminium pans and heated from 30 to 250°C with a heating rate 20°C/min under nitrogen flow (50 mL/min). Crystallinity degree ($X_c$) was calculated with Eq. (3):

$$X_c (%) = \frac{\Delta H_{m} - \Delta H_{c}}{\Delta H_{m}^{0} \times (1 - \alpha) \times 100}$$  \hspace{1cm} (3)

Where $\Delta H_{m}$, $\Delta H_{c}$ and $\Delta H_{m}^{0}$ are the experimental melting enthalpy, the experimental cold crystallization enthalpy and the theoretical melting enthalpy of 100 % crystalline PEF (137 J/g) [5], respectively.

2.3.4. Thermogravimetric analysis (TGA)

Thermogravimetric analysis of the polyesters after SSP was carried out with a SETARAM SETSYS TG-DTA 16/18 instrument. Samples (5.0 ± 0.3 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. Samples were heated from ambient temperature to 800°C in a 50 mL/min flow of N₂ or air at heating rate of 10°C/min. Continuous recordings of sample temperature, sample weight and heat flow were obtained.

2.3.5. Oxidation induction time (OIT) and temperature (OIT*)

OIT* was calculated after heating the polyesters under O₂ flow (50 mL/min) with a rate of 10°C/min. OIT* was determined as the point in the thermogram where the onset of the decomposition signal appeared. For the determination of the OIT of the polyesters, about 15 mg of each sample was added in open aluminium caps and heated

![Fig. 1. Chemical structures of (a) Irganox 1098 (b) PA and (c) TPP.](image-url)
(20 °C/min) in DSC from 30 °C up to the desired temperature of 270 °C under nitrogen flow. After 3 min isothermally heating, the gas flow was changed to O₂ (50 mL/min) until an exothermic signal appeared. The OIT value is defined as the time between the switching of the gas to O₂ and the appearance of the exothermic signal. The procedure of OIT determination was according to European standard EN 728:1997:E [20,21].

2.3.6. Pyrolysis-gas chromatography–mass spectroscopy (Py-GC/MS)

For Py-GC/MS analysis of the polyesters, a very small amount of each material is “dropped” initially into the “Double-Shot” EGA/ PY-3030D Pyrolyzer (Frontier Laboratories Ltd, Fukushima Japan) using a CGS-1050Ex (Japan) carrier gas selector. For EGA analysis the furnace temperature is programmed from 100 to 600 °C with a heating rate 20 °C/min using He as purge gas and air as cooling gas. For pyrolysis analysis (flash pyrolysis), each sample was placed into the sample cup which afterwards fell free into the Pyrolyzer furnace. The pre-selected pyrolysis temperatures were 375 °C and 410 °C the GC oven temperature was heated from 50 to 300 °C at 20 °C/min. Those two temperatures were selected based on the EGA pyrogram and represent the sample prior and after thermal decomposition. Sample vapours generated in the furnace were split (at a ratio of 1/50), a portion moved to the column at a flow rate of 1 mL/min, pressure 53.6 kPa and the remaining portion exited the system via the vent. The pyrolyzates were separated using temperature programmed capillary column of a Shimadzu QP-2010 Ultra Plus (Japan) gas chromatograph and analysed by the mass spectrometer MS-QP2010 SE of Shimadzu (Japan) use 70 eV. Ultra-AlLOY® metal capillary column from Frontier Laboratories LTD (Fukushima, Japan) was used containing 5 % diphenyl and 95 % dimethylpolysiloxane stationary phase, column length 30 m and column ID 0.25 mm. For the mass spectrometer the following conditions were used: Ion source heater 200 °C, interface temperature 300 °C, vacuum 10⁻⁴-10⁻⁵ Pa, m/z range 10–50 amu and scan speed 10.000. The chromatogram and spectra retrieved by each experiment were subject to further interpretation through Shimadzu and Frontier post-run software.

2.3.7. Thermo-oxidative stability study during aging

Aging of the polyesters was performed in an air circulation oven at 70 ± 1 °C. Films with dimensions of 10 × 10 cm and a thickness of 110 ± 5 μm were prepared in a hydraulic thermopress by melting them and afterwards quenching. The samples were removed from the oven at different incubation times. Changes in the chemical structure during sample incubation were examined using FTIR spectroscopy and DSC [22].

FTIR spectra were obtained using a Perkin-Elmer FTIR spectrometer, model Spectrum One, in absorbance mode and in the spectral region of 400 – 4000 cm⁻¹ using a resolution of 4 cm⁻¹ and 64 co-added scans. The peak height ratios of the hydroxyl peaks (3465, 3555 and 3450 cm⁻¹) to the C–H stretching of the furan ring at 3120 cm⁻¹ that should remain constant [23] were calculated after subtracting the absorbance of the baseline.

DSC thermograms were obtained as described in 2.4.3.

3. Results and discussion

3.1. Synthesis and characterization of polyesters

PEF polyesters were synthesized with the two-step esterification and polycondensation method, with antimony acetate as catalyst. This catalyst was selected because previous studies reported that it is one of the most effective in the synthesis of PEF in terms of final molecular weight and yield [9,24]. All produced polyesters were of light yellow color.

Phosphorus containing compounds in the form of phosphates or phosphites are commonly used as stabilizers to prevent degradation and discoloration and when added during melt processing they can also act as chain extenders through the reaction of the polyester’s end groups with the non-participating electrons of phosphorus [25–29]. They are also widely used as flame retardants in oxygen-containing polymers [30–32]. However, addition of such stabilizers during the first stage of the polymerization results in slower reaction rates and products with reduced molecular weight [33]. TPP is effective in reducing its carboxyl content and inhibit its degradation in low contents [34,35]. This stabilizing effect is especially useful during post-consumer melt processing of PET. Phosphoric acids, polyphosphoric acids along with their esters and anhydrides are used as stabilizers in several polymers such as polycarbonates [36], PET [33,37], polyurethanes [38]. PA when added in small quantities (< 15 ppm) immediately after the esterification stage during the synthesis of PET with antimony catalysts accelerates the reaction and reduces hazing [39], and can limit the thermal degradation of PET that is catalyzed by titanium catalysts and causes discoloration.

Irg is a sterically hindered phenolic primary antioxidant recommended for the stabilization of polyesters, polycetals, polyurethanes, adhesives etc. [40–42]. According to the guidelines of the manufacturer, the recommended concentration of Irg when added during the polymerization is 0.05 %-0.5 wt%. It acts by disrupting the degradation of the polymer by inactivating free radicals. As a hydrogen donor, it can transform a macroradical back to a macromolecule and a hydroperoxide radical into hydroperoxide.

The stabilizers were added in the polymer during the polycondensation step, because several problems arise when they’re added either during transesterification or after the end of the polymerization, in the polymer melt during processing. These include reduction of the reaction rate and molecular weight in the first case, and incomplete blending of the additive in the latter [33].

3.1.1. Intrinsic viscosity – molecular weight

The [η] values of intrinsic viscosity of the polyesters after SSP at 195 °C for 5 h and the corresponding M_n are presented in Error! Reference source not found.. The [η] of neat PEF is 0.36 dL/g, which remains practically unaffected in the presence of TPP and is reduced to 0.22 dL/g for PEF PA and increased to 0.53 dL/g for PEF Irg, respectively. This suggests that both PA and Irg affected the final molecular weight of PEF, albeit in different ways. While PA could have hydrolyzed PEF and reduced its M_n, Irg increased it which is an indication that it might be a good inhibitor of the degradation of PEF by neutralizing oxygen radicals [34].

The use of PA as a stabilizer in PET has been reported in several patents [39,43], as well as in research papers. Van Hoof found that PA, when added in PET during its synthesis with titanium catalyst in concentrations up to 75 ppm reduced its molecular weight by retaining ethylene glycol in the reaction, displacing the equilibrium of the polycondensation and finally resulting in blocking the progress of the reaction [44]. This phenomenon, in addition to possible hydrolysis or acidolysis caused by the acid, could explain the reduced [η] value of PEF PA. In larger concentrations and with antimony catalyst, Kamatani et al. suggested that PA reacts with bis-hydroxyethyl terephthalate or with ethylene glycol to give the phosphate compound O=P(OCH₂CH₂OR)₃, and forms a complex with the catalyst, accelerating the reaction [45]. In contrast with PA, TPP didn’t affect the final [η] and therefore molecular weight of the polyester.

The addition of Irg increased the [η] of PEF significantly, which could be a result of its antioxidant activity during the synthesis that can protect the polyester from decomposition. Other types of additives, namely Irgafos 126, a secondary, organo-phosphite stabilizer could increase the molecular weight of PET, acting as a chain extender [28].

3.1.2. WAXD

The WAXD patterns of the polyesters after SSP are presented in Fig. 2, witnessing their semicrystalline character. Its main diffraction peaks appear at 15.8°, 17.7°, 23° and 26.4°, with a pattern typical for
cold crystallized PEF (α-crystal form) [17,46]. PEF is received amor-
phous after polycondensation [5], as it is a slow-crystallizing polymer,
but crystallizes during SSP, as it cold-crystallizes in the temperature
range 150–200°C [17]. The stabilizers didn’t affect the crystalline
form of PEF, as all samples presented with the same diffraction peaks.

3.1.3. Differential scanning calorimetry and thermogravimetry

The thermograms obtained after heating the PEF polyesters under
N₂ flow with a heating rate of 20°C/min are presented in Fig. 3 and the
corresponding thermal transition temperatures as well as the crystal-
linity in Table 1. Neat PEF has a T_g of 84.6°C, a T_m of 211.8°C and
crystallinity 49 %. All stabilizers decreased the T_g and the crystallinity,
and didn’t affect the T_m, except for Irg which increased it significantly,
due to the higher molecular weight of that sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[η] (dL/g)</th>
<th>M¯n (g/mol)</th>
<th>T_g (°C)</th>
<th>T_m (°C)</th>
<th>ΔH_m (J/g)</th>
<th>X_c (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEF</td>
<td>0.36</td>
<td>6800</td>
<td>84.6</td>
<td>211.8</td>
<td>66.9</td>
<td>48.8</td>
</tr>
<tr>
<td>PEF PA</td>
<td>0.22</td>
<td>3200</td>
<td>78.2</td>
<td>212.0</td>
<td>58.5</td>
<td>42.9</td>
</tr>
<tr>
<td>PEF Irg</td>
<td>0.53</td>
<td>12400</td>
<td>83.3</td>
<td>216.6</td>
<td>56.9</td>
<td>41.7</td>
</tr>
<tr>
<td>PEF TPP</td>
<td>0.37</td>
<td>7100</td>
<td>82.8</td>
<td>212.8</td>
<td>56.9</td>
<td>41.7</td>
</tr>
</tbody>
</table>

The oxidation induction temperature (OIT*) and oxidation induc-
tion time (OIT) of the polyesters was also evaluated by DSC, and the
corresponding thermograms are presented in Fig. 4.

OIT* was determined by heating the polyesters under O₂ gas flow.
The resulting thermograms are presented in Fig. 4a. After 250°C, PEF
exhibits an exothermic shift of the baseline that indicates oxidation. In
the presence of PA and TPP such a transition isn’t noticeable, suggesting
these stabilizers inhibit the oxidation of PEF under dynamic heating
conditions until 300°C. PEF PA also presents a small and sharp endo-
thermic peak which can mean sudden volatilization due to the ini-
tiation of the oxidation. Irg increased the oxidation initiation tem-
perature by approximately 25°C. Based on this observation, the
temperature chosen for OIT study was 270°C in order to attempt to
induce oxidation to all the samples. The thermograms of the polyesters
during the OIT study are presented in Fig. 4b.

Sometimes the resulting thermograms of OIT determination DSC
measurements lack a clearly defined oxidation onset, and a slow decline
of the baseline is observed instead. In these cases, it is generally ac-
cepted that the time of the onset of the oxidation can be considered
the start of the deviation of the predetermined baseline [47]. Since two of
the samples exhibited a better-defined oxidation initiation (PEF and
PEF Irg) and two didn’t (PEF PA and PEF TPP), for the OIT values to be
comparable, they were determined through the baseline decline ap-
proach. PEF showed OIT = 1.45 min, and PEF Irg OIT = 1.47 min
which can be considered unaffected. Both P-containing stabilizers de-
layed the oxidation initiation temperature showing an OIT of 1.74 min
and 2.66 min for PEF PA and PEF TPP, respectively.

The effect of the stabilizers in the thermal stability of PEF was
studied with TGA, both under N₂ and air flow, and the results are
presented in Fig. 5 and Table 2. The thermal stability of PEF is im-
proved in the presence of all stabilizers, both in inert and oxidative
conditions. PEF degrades in one step under N₂ that starts at T_{0.5} = 372°C
and maximum rate of decomposition at T_{p,1} = 402°C. Both these
temperatures are shifted to greater values after the addition of all sta-
bilizers. Under oxidative atmosphere, PEF degrades in two steps, with
both the second one corresponding to carbonization. The T_g and the T_{p,1}
of PEF increased after the incorporation of the additives from 355°C up to
364°C and from 381°C up to 389°C, respectively. An even greater
shifting was observed in the second T_{p,2}, that of the carbonization.
The presence of all fillers also led to formation of a small amount of ther-
mally stable char, in contrast with neat PEF which lost all its mass at
around 550°C. Thermal stability in both atmospheres (N₂ and air) of
the polyesters follows the trend PEF < PEF Irg < PEF PA < PEF TPP
taking into account the onset of degradation. The two P-containing
compounds have the biggest influence on thermal stability in both at-
mospheres studied, suggesting they could potentially be efficient
thermal stabilizing agents for PEF. This observation is in agreement
with the OIT measurements. Very small amounts of TPP have been
reported to increase the thermal stability of PET as well [34]. TPP and
PA yield PA when heated, which in turn generates pyrophosphoric acid,
a heat transfer barrier in the condensed phase [48].

3.1.4. Py/GC–MS

To determine whether the used additives affect the mechanism of
thermal degradation of PEF, Py-GC/MS measurements were performed.
Initially, the samples were heated in dynamic conditions, under He atmosphere, and the temperature range in which pyrolysis products are released was evaluated. This method is called EGA and takes place with the use of an inert column. The resulting pyrograms are presented in Fig. 6a. Neat PEF releases degradation products in the temperature range 350–450 °C, with a peak at 402 °C. This peak that corresponds to the temperature where the majority of the pyrolyzates are produced is slightly shifted to higher temperatures for all the polyesters containing the stabilizers, in agreement with the TGA measurements. Based on these data, the flash pyrolysis temperatures chosen for the single shot method were 375°C and 410°C, i.e. the temperature where pyrolysis starts and the temperature with the maximum production of pyrolysis products.

The resulting total ion chromatographs (TICs) after pyrolysis of PEF polyesters in 375°C and 410°C are presented in Fig. 6b and c, respectively. There are no major differences between the overall patterns of the TICs of PEF and PEF containing either of the stabilizers, suggesting their degradation mechanism is identical.

The major compounds released were identified via their MS spectra (not presented for brevity) and their retention times (Rt), molecular weight (MW) and possible chemical structure are shown in Error! Reference source not found.. The mechanism of thermal degradation of PEF has been reported in detail in previous studies [12,13,49,50], and consists of mainly β-heterolytic scission to the ester bond, and on a smaller extend radical homolysis including acyl-oxygen and alkyl oxygen scission. The main products that are derived from heterolysis are vinyl- and carboxyl- terminated molecules, that are detected in the present study as well, and alkyl-, hydroxyl- and sometimes aldehyde-terminated molecules from the radical, homolytic scission reactions. Decarboxylation reactions yield furan- terminated molecules. These types of pyrolysis products are also detected in the present work; therefore, the mechanism will not be explained in detail. It has been suggested that since in lower pyrolysis temperatures only heterolysis products are identified, while in higher ones a mixture of heterolytic and homolytic products are released, homolysis requires more thermal energy to take place.

As no important differences can be noticed in the TICs of PEF and stabilizer-containing PEF, it can be assumed that they didn’t affect the mechanism of thermal degradation. Their thermal-stabilizing effect can therefore be attributed mainly to their action as heat and volatile compound transfer barriers. Irg acts by consuming free radicals that propagate degradation reaction, but since degradation of PEF occurs mainly via heterolysis, no significant effects on the mechanism or the progress of degradation are expected to be noticed. Finally, no peaks that correspond to the stabilizers could be detected, possibly because of their very small amount in the samples.

3.2. Thermo-oxidative stability during aging

The PEF polyesters prepared were thermally aged in an air-circulating oven at 70 °C to accelerate thermo-oxidative degradation and compare the effect of the different stabilizers on the physicochemical
properties. After 5, 7, 10, 12, 15 and 20 days of incubation, samples were removed and their FTIR spectra (Error! Reference source not found.) as well as their DSC thermograms (Error! Reference source not found.) were recorded. Annealing of polymers in temperatures below their $T_g$ is known as physical aging and can be used to simulate storage conditions [51]. It usually involves amorphous polymers, but has also been applied to semi-crystalline polymers [52,53].

All FTIR spectra showed the same, typical pattern of PEF. The main bands appear in the regions 3650−3450 cm$^{-1}$ that are associated with O−H stretching of the hydroxyl end groups, at 3128 cm$^{-1}$ with C–H stretching of the furan ring, at 2964 cm$^{-1}$ and 2890 cm$^{-1}$ with asymmetric and symmetric C–H stretching of the methylene groups, at 1725 cm$^{-1}$ with C=O stretching of the ester group [9,12,23]. Thermo-oxidative degradation of PET is believed to occur via the formation of hydroperoxides at the methylene group and yield carboxyl-, vinyl- and hydroxyl- ended compounds [29]. Assuming PEF follows a similar mechanism, the FTIR analysis was focused on the hydroxyl absorbance region. In order to compare the spectra obtained at different aging times, the peak height ratios of the hydroxyl peaks to the furan’s C–H peak were calculated and the results are presented in Fig. 7. The peak height ratios for all three peaks increase with aging time for neat PEF, as well as for PEF Irg, although in a smaller extend. Both P-containing additives decelerated the rate of the hydroxyl’s peak height ratio increase, which is noticeable after the 12th day, indicating their capability to stall the process of degradation. These results are in agreement with the OIT and TGA measurements of Figs. 4 and 5, respectively.

Thermal treatment and degradation of polyesters can impart changes in their characteristic thermal transition temperatures. DSC heating scans were performed during aging of the PEF polyesters (Error! Reference source not found.). The effect of the presence of the stabilizers on the $T_m$ and $T_g$, as well as the peak temperature ($T_p$) of the relaxation of the polyesters during aging at 70°C is presented in Fig. 8.

As seen in Fig. 8a, the $T_p$ of the relaxation of all PEF polyesters increases during aging. When a polymer is aged in temperatures lower, but close to the $T_g$, it becomes a thermodynamically unstable glass that will try to reach an equilibrium state through rearrangements. The PEF films used were prepared by melting of PEF powder and subsequent quenching, in order to “freeze” the polymer chains and reduce their segmental mobility. Aging is expected to increase segmental mobility, cause volume relaxation that will result in less free volume which means the aged sample will require more energy to transit from the glassy to the rubbery state. This process is reflected as an increase in the $T_p$ and the relaxation enthalpy of PEF when the aging time is increased. Additionally, the values of $T_g$ have an increasing trend (Fig. 8b). Aging

Table 2
Characteristic thermal degradation temperatures of PEF polyesters obtained by TGA analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$N_2$</th>
<th>Air</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_p$ (°C)</td>
<td>$T_a$ (°C)</td>
</tr>
<tr>
<td>PEF</td>
<td>401.8</td>
<td>372.2</td>
</tr>
<tr>
<td>PEF PA</td>
<td>409.1</td>
<td>382.4</td>
</tr>
<tr>
<td>PEF Irg</td>
<td>403.8</td>
<td>381.2</td>
</tr>
<tr>
<td>PEF TPP</td>
<td>409.2</td>
<td>385.7</td>
</tr>
</tbody>
</table>

*$T_p$: DTG peak temperature; $T_a$: onset of degradation (determined using the intersection of tangents to the TGA curve of the pre-degradation region and region of steep decline); $T_{d,10\%}$: temperature corresponding to 10 % mass loss.
of both amorphous and semicrystalline PET at 68 °C also resulted in increase of its T_g while increasing time [54]. The same phenomenon has been observed for poly-L-lactide [55]. Two of the stabilizers, namely Irg and TPP seem to have imparted a greater increase on the T_g and T_p values of PEF. This could be attributed to their bulkier structure in comparison with PA, that can hinder the mobility of the polymer chains, requiring more energy to transit. Concerning the T_m, aging of neat PEF resulted in a decreasing trend on the melting point values, which could be caused by reduction of its molecular weight due to degradation. In contrast, the presence of all stabilizers caused the opposite result; T_m showed the tendency to increase. Therefore, the three stabilizers are able to decelerate the process of physical aging of PEF.

4. Conclusions

The effect of three different stabilizers on the physicochemical properties of the biobased polyester PEF were evaluated. All the stabilizers slightly improved the thermal stability of PEF in inert and oxidative atmosphere, increased the oxidation induction time and slightly reduced the % crystallinity. The two P-containing stabilizers had the biggest influence on thermal stability. Py/GC–MS studies showed that improvement wasn’t caused by changes in the thermal degradation mechanism, but most likely by inhibition of heat transfer. All polyesters were thermally aged at 70 °C for 20 days, during which the amount of hydroxyl end groups increased significantly for neat PEF.

Fig. 6. (a) EGA pyrogram, (b) TICs after pyrolysis at 375 °C and (c) TICs after pyrolysis at 410 °C of PEF polyesters.

Fig. 7. Peak height ratios of the hydroxyl FTIR peaks of PEF during aging.
Presence of the P-containing stabilizers reduced the rate of hydroxyl amount increase significantly. DSC measurements revealed increase in the Tg and excess enthalpy of relaxation values during aging for all samples. Finally, while the Tm of neat PEF decreased during incubation, the Tm of PEF with stabilizers showed a decreasing trend. In conclusion, the stabilizers can successfully decelerate the thermal degradation and physical aging of PEF in very small quantities, with the P-containing ones PA and mainly TPP being the most effective.

CRediT authorship contribution statement

Zoi Terzopoulou: Conceptualization, Methodology, Investigation, Writing - original draft. Mohamed Wahbi: Conceptualization, Methodology, Investigation. Nejib Kasmi: Methodology, Investigation, Writing - original draft. George Z. Papageorgiou: Supervision, Writing - review & editing. Dimitrios N. Bikiaris: Conceptualization, Supervision, 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.

Acknowledgements

The authors would like to thank Dr. Alexandra Zamboulis (Department of Chemistry, Aristotle University of Thessaloniki) for her helpful advice on the interpretation of the results of this work. This publication is based upon work from COST Action FUR4Sustain, CA18220, supported by COST (European Cooperation in Science and Technology).

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.tca.2020.178549.

References


Fig. 8. Effect of the presence of the stabilizers on the (a) Tp, (b) Tg, (c) excess enthalpy of relaxation and (d) Tm of PEF during aging. The full lines represent the linear least-square fit.