

## Enhanced PET Processing with Organophosphorus Additive: Flame Retardant Products with Added-Value for Recycling

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**Abstract.** At elevated temperatures, polyethylene terephthalate (PET) is known to undergo a cascade of interconnected chemical reactions, in particular oxidative crosslinking, which can lead to severe limitations in processability, product properties, and recyclability. To control such undesired reactions, a newly synthesized phosphorus-based additive with promising flame retardant properties (T. Stelzig et al. *Dopo-Based Hybrid Flame Retardants*. EP2921498 (A1), 2015), by the chemical name 6-((1-oxido-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octan-4-yl)methoxy)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DOPO-PEPA, or simply DP), was added to PET in different concentrations. To assess the miscibility of DP and PET at the nanoscale, a multiscale simulation scheme was developed by combining molecular dynamics and dissipative particle dynamics. DP showed a prominent inter-chain lubrication effect in PET in extrusion experiments. To replicate the heating cycles during repeated recycling, the thermal stability of PET melts was assessed on extended timescales using rheological measurements. Time-resolved frequency sweep experiments were conducted with or without the novel DP additive, under air and nitrogen atmospheres. By combining various chemical analysis techniques, a chemical stabilizing mechanism could be proposed that describes how the DP molecule intervenes with the

degenerative chemical reactions of PET chains in the melt processing phase. The proposed mechanism outlines trace-release from DP involving the formation of phosphorus radicals including DOPO $\cdot$ , PEPA $\cdot$ , and PO $\cdot$ . Such radicals scavenge the oxygen radicals from air and can thus protect the linearity of PET chains. The results underline the synergistic effects of DP on the processing of high performance PET. Together with flame retardancy of the original product, the environmental-friendly DP chemically-protects and lubricates PET during subsequent recycling of the waste.

**Keywords:** Polyethylene terephthalate, Degradation, Flame retardants, Recycling, Thermo-oxidative crosslinking

## 1. Introduction

Polyethylene terephthalate (PET) offers some highly desirable properties including good mechanical performance, low permeability, and high-temperature resistance. In high-temperature applications and during the melt-processing of polymers, proper control of the molecular integrity is challenging since there is a direct relationship between the properties of a polymer and its molecular structure. In case of PET, the chemical structure of its molecules can undergo various changes that are largely interconnected [1–3]. This complexity makes it extremely difficult to protect PET against undesired changes. At high processing temperatures, one can expect to observe thermal, oxidative-thermal, and mechanical-thermal degradation mechanisms. At a molecular level, radical decomposition or crosslinking in the presence of oxygen [1,2,4], as well as esterification and transesterification [1,3,5,6], or hydrolysis due to residual humidity [3,6–9] are the main reactions which affect the structure of PET. Among these reactions, the crosslinking of chains is of practical significance as it can lead to complete blockage of the extruder during repeated extrusion cycles (i.e. recycling) [2,4]. Other reactions have a more reversible nature and

can thus be better controlled by an accurate process design. Considering that a large number of disposable products are made of PET with a high potential for recycling, controlling crosslinking and degradation in repeatedly processed PET melts is of high significance. In this regard, a multifunctional additive would be ideal, which can add to the value of PET products during their first production cycle (e.g. flame retardancy), and, even at lower concentration, improve their sustainability by enabling recycling (e.g. lubrication and chemical protection). Considering the environmental-friendly and non-toxic nature of organophosphorus flame retardants [10,11], a simplified additive-strategy can be established for PET recycling since the flame retardant material does no longer have to be removed during recycling. This paper focuses on the promoting effects of one such flame retardant on the oxidative-thermal degradation of PET at high temperatures.

A common approach in PET recycling is the blending of already processed PET with pristine PET at melt temperatures [3,12,13]. This operation allows the former waste material to be upgraded to a compound with overall properties that are industrially satisfactory [14]; the method is popular due to its simplicity and low cost [15]. Another major trend in PET recycling was developed over the past 25 years, namely to chemically depolymerize PET into its constituent oligomers, or even monomers, and subsequently re-polymerize them to a pristine PET quality [3,6,9,16–19]. In this technique, intelligent use of water with or without solvents (such as xylene) promotes severe hydrolysis of PET macromolecules, which is particularly attractive [9]. Overall, the mechanical recycling has the advantage of producing no extra solvent waste as opposed to the chemical method, albeit the chemical method has received a lot of attention recently to improve its sustainability and economics [19–21].

The complex and diverse chemical reactions that occur during high-temperature processing of PET were subject to detailed investigations. Documented chemical reactions include hydrolysis of ester groups [22,23], esterification of carboxyl and hydroxyl ethyl ester chain ends [22,23], transesterification of hydroxyl ethyl ester chain end pairs and hydroxyl ethyl ester and vinyl ester chain ends [24–26], thermal decomposition of ester groups [27–30], thermal oxidation of methylene groups [22,24,31], thermal oxidation of aromatic cycles [28], hydroxylation of aromatic cycles [28,30,32–34], and polyaddition of vinyl ester chain ends [22,24,25] and aromatic cycles [27]. The resultant molecular alterations occurring in the PET melt influence its rheological behavior (i.e. processability) [35–38] as well as its mechanical properties in solid state (i.e. tensile strength) [13,39,40]. It is well-established that the thermal oxidation of PET during its extrusion is the main source of its molecular reformations [1,2,4,12,34].

To overcome the oxidation problem, different thermal stabilizers have been used with the majority being metal based, such as butyl tin mercaptide, antimony mercaptide, and lead phthalate [3,41,42]. Also, various radical scavengers and chain end capping compounds were used in PET at elevated temperatures. *p*-aminobenzoic, 3,5-dihydroxybenzoic, and 4-hydroxybenzoic acids are some examples of these stabilizers [43]. Organophosphorus compounds such as triphenyl phosphate [44–46], triphenyl phosphite [46], phosphoric acid [44,47], bis(2,4-dicumylphenyl) pentaerythritol diphosphate [48,49], and bis(2,4,di-*tert*-butylphenyl) pentaerythritol diphosphate [50], are also used to control thermal degradation of PET. Nevertheless, there is no evidence for their positive influence against crosslinking of PET chains, which can be particularly detrimental to PET recycling. In addition, the use of antioxidants and stabilizers has been suggested by researchers as a possible solution for the degradation of polymers under successive recycling processes [46,51,52].

Recently, we synthesized a new organophosphorus compound from the reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (PEPA), namely the DOPO-PEPA or simply DP, which is also an excellent flame retardant [11,53]. Our preliminary tests on DP using well-established in-vitro platforms showed its non-toxic nature [11]. DOPO was originally developed as an antioxidant for polycarbonates [54], polyesters [55], and as a heat stabilizer for textiles [56,57]. However, the mechanism of its antioxidant and thermal stabilizing effects has not been studied. A novel application of DOPO is in DOPO-immobilized silica nanoparticles which is used to improve the thermal stability of polypropylene by increasing its activation energy of thermal decomposition [58]. During processing of PET, we realized that the additive has a profound lubrication effect which could be beneficial for processing of high molecular weight PET. Further investigations in this direction gave us clues regarding the stabilizing nature of DP particularly interesting for repeated mechanical recycling. In this study, we aim to explore the multifunctional characteristics of DP when used to modify PET melts. Namely, we show that the addition of a small amount of DP to PET is sufficient to lower the melt viscosity, and provide a better control of molecular crosslinking. This should provide a very attractive framework for PET industries towards a more sustainable added-value chain. For instance, PET foams used in applications such as wind energy, transportation, marine, packaging, as well as building and construction can greatly benefit from a combination of recyclability and flame retardancy.

## 2. Experimental Details

### 2.1. Materials and Processing

PET was prepared and provided by Serge Ferrari Tersuisse AG (Emmenbrücke, Switzerland) with a  $M_w \approx 124 \text{ kg} \cdot \text{mol}^{-1}$  as measured by gel permeation chromatography (GPC). DP was synthesized according to a novel and sustainable protocol described in details elsewhere [59]. Compounds of PET and DP were mixed with a gravimetric feeding system in a twin screw extruder (Collin, Germany) to produce a master batch of PET/DP with ~15 wt% of the DP. Also, pristine PET was extruded with the same processing conditions in order to provide a reference material representing already processed PET. The master batch pellets were physically mixed with pristine PET or reference processed PET and fed into the extruder, all from the hopper in certain fixed weight ratios to produce the final compounds, see Table 1. In the formulations, the fraction of pre-processed PET was kept constant and equal to 29 wt%. This mixing ratio resembles the amount of recycled PET mixed with the pristine PET in a typical mechanical recycling process. The extruded strand was cooled down to room temperature and pelletized. The pellets were then used in a hot press at 300 °C to produce films with 1 mm thickness for further experimentation. Note that prior to each step of the materials preparation, the PET and its compounds and their physical mixtures were vacuum dried in two steps, for 12 h at 100 °C, followed by 4 h at 140 °C, to drive out any residual water and thus prevent hydrolysis during processing.

Table 1. The nomenclature and formulations of different samples are listed here. During the extrusion, a variable amount of master batch was added to the pristine PET, plus a complementary amount of reference processed PET. In this way, the total amount of the processed PET in the final compound was kept constant. For each sample, both blended formulations are given in the table; first, the fractions which were added during the extrusion, and second, the actual content of each material in the final product. The final phosphorus contents in the samples were measured by phosphorus ICP. Finally, the total amounts of the DP in the samples were calculated based on the measured phosphorus content. \*The PET/DP-3 sample was processed by directly adding 3 wt% of pure DP powder to the pPET during extrusion by using the gravimetric side feeder.

Sample	Pristine PET (wt%)	Amounts added during extrusion		Intended amounts in the final mixture		Calculated DP content (wt%)	Measured phosphorus content (wt%)
		Reference Processed PET (wt%)	Master Batch (wt%)	Processed PET (wt%)	DP (wt%)		
pPET	100	-	-	-	-	-	0.00 ± 0.00
rPET	-	100	-	100	-	0.00	0.00 ± 0.00
PET/DP-0	71	29	-	29	-	0.00	0.00 ± 0.00
PET/DP-1	70	23.25	6.75	29	1	1.23	0.19 ± 0.00
PET/DP-2	69	17.5	13.5	29	2	2.27	0.35 ± 0.01
PET/DP-3*	97	-	-	-	3	2.98	0.46 ± 0.01
PET/DP-5	66	-	34	29	5	5.26	0.81 ± 0.02

## 2.2. Extrusion Trials

In order to assess the lubrication effect of DP in the melt processing of PET, additional extrusion trials were performed using a single screw extruder connected to a capillary die. In these experiments, small amounts of DP master batch were directly extruded with pristine PET and the pressure drop across the die was used to measure the viscosity. These extrusion trials resemble the actual processing conditions in some industries, such as fiber melt spinning.

Pristine PET samples were physically mixed with the master batch material containing ~15 wt% DP to achieve the final DP concentrations as defined in Table 2. Mixing was carried out in an extrusion line (Thermo Fisher Scientific, Karlsruhe, Germany). Here, a Rheomex OS single screw extruder with diameter  $D = 19$  mm and a length to diameter ratio of  $L/D = 25$  feeds the molten polymer to a Haake OS melt pump, which supplies the polymer melt at a defined flow rate to a custom-made capillary die with diameter  $D = 1$  mm and  $L/D = 35$ . This high  $L/D$  ratio was chosen to achieve sufficient pressure drops (see Table 2). A static mixer was installed between extruder and melt pump to improve the mixing and temperature uniformity in the melt. The extruder pressure was typically set between 25 and 120 bar. Prior to extrusion, the polymers were dried for 8 h at 140 °C.

Table 2. The processing parameters for the single screw extrusion trials.

Intended Amount of added DP (wt%)	Calculated DP content (wt%)	Measured phosphorus content (wt%)	Melt pressure drop in the capillary (bar)	Average mass flowrate (g/s)	Shear rate at capillary wall $\dot{\gamma}_w$ (1/s)	Measured viscosity (Pa·s)
0	0.00	$0.00 \pm 0.00$	$268.9 \pm 1.1$	0.080	580	331.2
1	1.10	$0.17 \pm 0.002$	$152.0 \pm 1.0$	0.080	600	180.8
2	1.94	$0.30 \pm 0.007$	$86.4 \pm 0.3$	0.084	610	101.1
3	2.84	$0.44 \pm 0.023$	$50.1 \pm 0.3$	0.085	620	57.7
5	5.10	$0.79 \pm 0.008$	$23.2 \pm 0.1$	0.088	643	25.8

For all extrusion trials, the volumetric flow rate was set to  $0.075 \text{ cm}^3 \cdot \text{s}^{-1}$ . The actual flow rate may be subject to variations since it slightly depends on the pressure difference over the pump, and the melt compressibility at the actual processing temperature and pressure. To obtain an independent measure of the integrated mass flowrate, the material was collected and weighed (Table 2), after an initial run-in for 30 min. The controlled extrusion temperatures were set to 290 °C in all zones. The measured melt temperature in the die was ~296 °C in all studied cases and the pressure drops of the polymer melt in the capillary are given in Table 2.



## 2.3. Characterization Techniques

### 2.3.1. Rheological Measurements

Rheological measurements were conducted on the hot-pressed films of PET containing different amounts of DP. Prior to experiments, the samples were dried in a vacuum oven for 12 h at 100 °C and for 4 h at 140 °C to completely remove any moisture in the films before the tests. The tests were carried out utilizing an Anton Paar Physica 301 MCR rotational rheometer (Austria) equipped with a parallel plate fixture with a diameter of 25 mm and a constant gap of 1 mm. First, oscillatory amplitude sweep tests were performed under a nitrogen environment at a constant oscillation frequency of 10 rad/s to determine the limit of the linear viscoelastic deformations, which was found to be below 5%. Afterwards, the thermal and thermal-oxidative stability of the melts were studied in the repeating time-resolved frequency sweep (TRFS) runs at a range of oscillation frequencies between 0.126 and 500 rad/s, and a constant strain of 1%. In total, 19 frequency sweep runs were conducted on each sample with a 60 s resting time between the consecutive runs. The tests were performed under both oxygen and nitrogen environments. After loading the samples, they were allowed to equilibrate in the rheometer chamber for 30 s at the test temperature before starting the measurements, in order to minimize history effects. All rheological tests were carried out at a constant temperature of 290 °C. The TRFS experiments replicate the repeated heating cycles that PET melt experiences during multiple recycling processes [1,2]. Thus, they help to assess the long term recyclability of PET with or without DP.

### 2.3.2. Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) analyses were performed by dissolving pieces of hot-pressed films and passing the solution through a Viscotek GPC max VE 2001 solvent/sample

module equipped with Viscotek TriSEC Model 302 detector unit. Measurements were made on Waters Styragel HT (4/10  $\mu\text{m}$  particle size) column and the measurement conditions were: column temperature of 35 °C, hexafluoro isopropanol (HFIP) 1  $\text{ml}\cdot\text{min}^{-1}$  as the solvent, injection volume of 300  $\mu\text{l}$ , and a sample loop of 100  $\mu\text{l}$ . 2-4 mg of polymer sample was dissolved in 10 ml of HFIP and stirred for a week before injection in GPC.

### 2.3.3. Elemental Analysis

The phosphorus content of the samples was measured after extrusion in order to evaluate the actual DP content in each sample. Phosphorus analysis was carried out using the inductively coupled plasma optical emission spectrometry method (ICP-OES), on an Optima 3000 (PerkinElmer AG, Rotkreuz, Switzerland) apparatus. Sample preparation for ICP-OES consisted of mixing 300 mg of samples with 1 ml of  $\text{H}_2\text{O}_2$  and 3 ml of  $\text{HNO}_3$ , followed by digestion under microwave.

### 2.3.4. Direct Inlet Probe Mass Spectroscopy

Direct inlet probe mass spectroscopy (DIP-MS) was used to detect possible volatile products developed by exposing DP to PET melt temperatures. The technique is based on the direct insertion of the sample in the ionization chamber, where the sample is exposed to heating and ionized by electronic impact. The measurement was performed on a Finnigan/Thermoquest GCQ ion trap mass spectrometer equipped with a DIP module. The sample (about 1 mg) is introduced in a quartz cup situated on the tip of the probe, which is inserted into the ionization chamber through an inlet. The measurement was performed with an ionization voltage of 70 eV, temperature of the ionic source of 200 °C and pressure below  $10^{-6}$  mbar. A probe temperature ramp was run from 30 °C to 450 °C at a rate of 50 °C/min.

### 2.3.5. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy was performed to investigate possible changes in the chemical structure of the DP due to the thermal and mechanical processes during extrusion and rheological measurements. In order to extract the additive, PET/DP-5 was steeped in deuterated chloroform at 100 °C under 30 bar of N<sub>2</sub> pressure for 12 h using high pressure microwave reactor (Synthwave Microwave Single Reaction Chamber, MWS Mikrowellen Systeme GmbH, Switzerland). The solvent was collected and used for the NMR measurements after filtration with a micro syringe filter with a pore size of 0.45 μm. The same procedure was carried out for PET/DP-5 before and after rheology measurement (in air and nitrogen). NMR spectroscopy was also performed to investigate the thermal stability of DP. A sample of about 15 mg was heated in two cycles up to the typical PET extrusion temperature of 290 °C, and then cooled down to 25 °C at a heating/cooling rate of 10 °C/min using a differential scanning calorimeter DSC 214 Polyma (Netzsch). The residual was dissolved in deuterated DMSO (dimethyl sulfoxide) and analyzed. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were collected at ambient temperature using Bruker AV-III 400 spectrometer (Bruker Biospin AG, Fällanden, Switzerland). <sup>1</sup>H chemical shifts (δ) in ppm are calibrated to residual solvent peaks. The <sup>31</sup>P chemical shifts were referenced to an external sample with neat H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm.

## 3. Simulation Details

From various studies with supercritical fluids, it is known that an internal lubrication effect depends on molecular scale miscibility of the additive with the PET melt [60–63]. Therefore, the thermodynamic miscibility of DP molecules in PET melt was assessed at nanoscale utilizing dissipative particle dynamics (DPD). DPD simulates a coarse-grained representation of the molecules interacting through softer potentials than the classic full-atomistic molecular dynamics

(MD) [64,65]. Therefore, DPD is preferred for unraveling the molecular interactions on longer time scales and has been successfully used in various polymeric systems before [66–69]. In this study, we combine MD and DPD to simulate the molecular characteristics of DP and PET in both full-atomistic and coarse-grained representations. At first, the DP molecules and PET chains were coarse-grained into DPD beads as shown in Figure 1. Afterwards, the atomistic representations of these beads were simulated by MD to calculate their pure thermodynamic properties, more importantly their densities and cohesive energy densities (CED) at 290 °C and 1 atm (Table S1 of the Supporting Information). Afterwards, the MD results are used to map DPD potentials. The DPD simulation box is constructed as a cube of real spatial dimensions of ~50 nm on each side. The simulated systems contained different volume fractions of DP, equivalent to 1, 2 and 5 wt% of DP in the final blends, the same as the experimental samples. The DPD simulation runs correspond to a real time of 0.762  $\mu$ s. Further details of the simulations are provided in the Supporting Information.

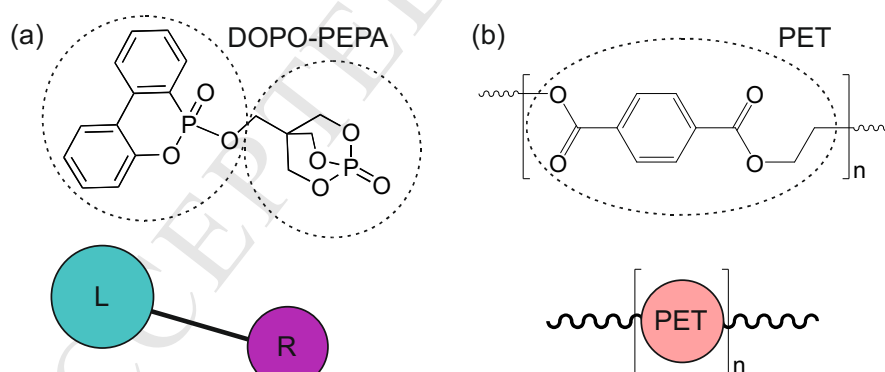


Figure 1. Chemical structures of (a) DP molecule and (b) PET chains, and their coarse-grained representations in DPD simulations.

## 4. Results and Discussion

### 4.1. Molecular Compatibility and Lubrication Effect of DP in PET

It is critical for any additive to be thermodynamically compatible with its host polymer matrix. The compatibility not only ensures that the full advantage is taken from the amount of additive, but is also crucial for their homogeneity, and for further processing of their blends. It should be noted that in this work lubrication refers to an internal effect of DP molecules (lubricating macromolecules) and does not mean the lubrication of a polymer-surface contact. Thus, the desired effect of lubrication depends on a perfect mixing of additive and polymer on the length scale of their molecules [60–63]. As the mixing quality is improved on such fine length scales, the internal lubrication (of polymer molecular motions) becomes more efficient. To assess the thermodynamic miscibility of DP and PET on the nanoscopic level, DPD simulations were used, which were parameterized based on the thermodynamic data from full-atomistic MD simulations. The time-dependent inter-diffusion and dispersion of DP molecules in the PET bulk is shown in Figure 2, starting from a slab configuration. The DP molecules start to diffuse into the PET bulk during the early stages of the simulation, and form a well-dispersed mixture within PET at the end of the equilibrium runs. The homogeneity of such dispersions is further investigated by plotting the running average of the bead number density profiles of DP in all orthogonal x, y and z directions parallel to the box axes, see Figure 3. It is obvious from the results that a homogenous dispersion of DP is achieved in PET at all concentrations and in all directions. Considering that these simulations are purely driven by thermodynamic arguments and no external deformation is applied on the simulation box (as opposed to typical non-equilibrium simulations) [70,71], one can conclude that these molecules are miscible on the nanoscopic scale. Since the simulations were carried out at the typical processing temperature of such blends

(290 °C), DP can be easily mixed with PET, and form stable homogeneous blends during the melt processing.

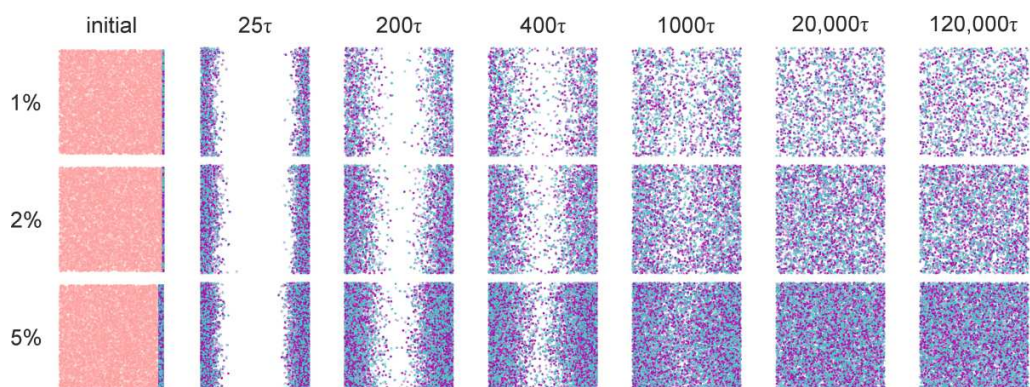


Figure 2. The inter-diffusion and dispersion of different concentrations of DP molecules in the PET bulk with simulation time. The DPD beads are colored as shown in Figure 1a. The PET chains are only shown in the initial system configuration and are removed from consequent frames to preserve clarity.

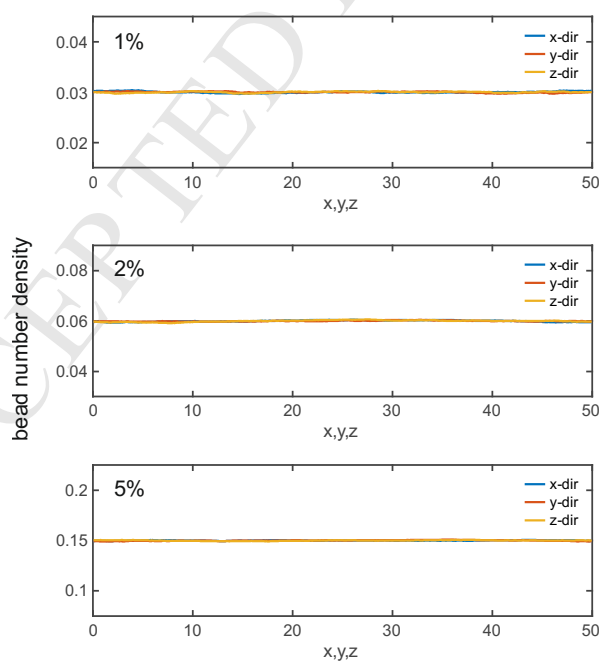


Figure 3. The average bead number densities of DP in different directions for systems containing varied DP contents.

The simulations suggest that the DP miscibility in the PET melt is homogeneous down to the nanoscale. Therefore, DP is a promising additive to lubricate the melt and lower the melt viscosity during processing. Such lubrication effect would enable the melt processing of high molecular weight PET at lower pressures and/or temperatures for delicate performance-oriented applications such as high tenacity fibers and durable, flexible printed electronics. In order to quantify the lubrication effect of DP, single screw extrusion trials were carried out and the pressure drop across the capillary die was recorded, see Table 2. The results clearly show the influence of the addition of DP, i.e. a reduced buildup of spin pressure. With each additional 1 wt% of DP, the spin pressure is roughly divided in half. In other words, the addition of DP can significantly facilitate the processing of high molecular weight PET at remarkably low concentrations. This is beneficial for the processing of high molecular weight PET used in thin films for flexible electronics, or, the melt-spinning of high-performance fibers. These applications are particularly prone to the build-up of excessive pressures at the extrusion die. From the measured pressure drops and flowrates, the apparent shear viscosities were calculated (Table 2, Figure 4). Viscosity drops by one order of magnitude after the addition of 5 wt% of DP in PET. Alternatively, this lubrication effect can also be utilized to process PET melts at effectively lower temperatures. This would further restrict thermal damage, as well as the undesired chemical reactions and molecular transformations, otherwise taking place at higher temperatures. In the experiments reported in Figure 4, shear rates at capillary wall  $\dot{\gamma}_w$  are in the range 580-643 1/s (see Table 2). If the evaluated viscosities are mapped to a shear rate of 580 1/s (for neat PET as reference, using a power-law equation with an exaggerated power-law index of 0.01), viscosity deviations of ~3, 5, 6, and 10% are calculated for samples with 1, 2, 3, and 5 wt% DP, respectively (shown by error bars in Figure 4). Therefore, one can see that even with such an exaggerated shear rate-dependent viscosity the comparisons of the viscosities remain the same.

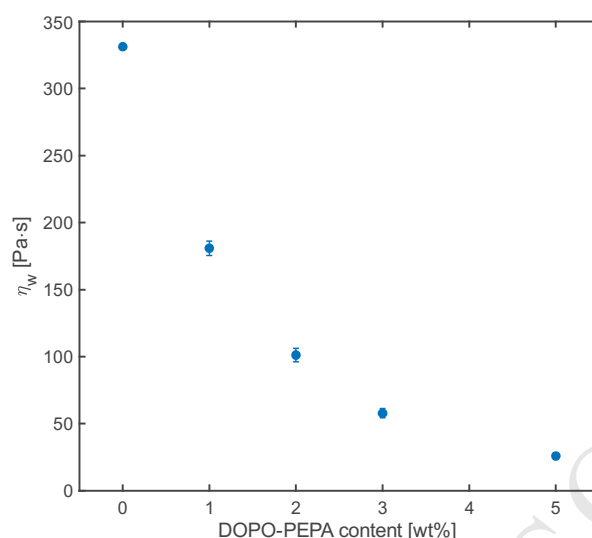


Figure 4. Apparent shear viscosity  $\eta$  as a function of DP content. The processing data of the extrusion trials are given in Table 2. The error bars show the viscosity deviations mapped to a reference shear rate of 580 1/s (see text for details).

The molecular lubricating effect of DP is only useful provided that it does not lead to excessive loss of molecular weight, particularly since the mechanical performance of a polymer critically relies on its molecular weight. Furthermore, a small polydispersity index (PDI) ensures a more uniform melt rheology with a narrower chain relaxation time spectrum. To monitor changes in molecular weight, the samples were analyzed using GPC, see Table 3. By comparing pPET and rPET, with the latter being extruded once, one can see that both  $M_n$  and  $M_w$  are roughly divided in half while the PDI is virtually unchanged. To investigate the effect of DP, pure DP powder was added directly to the pPET, using the gravimetric feeding system during compounding in the twin screw extruder (sample PET/DP-3, Table 1). The molecular weights of the resulting sample are provided in Table 3. We note that the molecular weights in this sample are slightly larger than that of rPET which can be related to the way DP is added to PET. Therefore, DP does not significantly influence the mechanical-thermal degradation of PET. However, it is shown later that oxidative-thermal degradation of PET can be controlled effectively by DP.



Table 3. Average molecular weights of the PET samples from GPC measurements of the hot pressed films; also shown is the polydispersity index,  $M_w/M_n$  (PDI).

Sample	$M_n$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	$M_w$ ( $\text{kg}\cdot\text{mol}^{-1}$ )	PDI
pPET	52.3	124.3	2.38
rPET	30.4	76.3	2.51
PET/DP-3	35.5	81.8	2.30

#### 4.2. Stability of Molten PET/DP Compounds

Changes in molecular weight can be investigated in-situ by analyzing the temporal evolution of the rheological properties of melts with different amounts of additive, and in different atmospheres [1,2,4,36,72,73]. The complex viscosity describes the viscoelasticity of the blends and thus also provides a practical description of their processability. TRFS tests were performed in a heated plate rheometer to assess the long term melt stability in repeated processing cycles (i.e. recycling). In the first set of TRFS cycles, the samples were tested under ambient atmosphere (Figure 5). The results show a systematic increase in the complex viscosity of the pPET and rPET samples, following an initial decrease in the first 50 minutes. It has been previously reported that the oxygen in ambient air is sufficient to initiate radical attack on the PET backbone, which can result both in chain scission as well as in random bonding events [1,2,4,74]. It has also been suggested that a viscosity increase is a clear sign for such branching and crosslinking reactions [2,4]. Oxygen-induced crosslinking at high processing temperatures is a problem of practical relevance, since it can ultimately bring the extrusion process to a halt by excessive torque [2]. The mechanical recycling of PET involves repeated extrusion; therefore, excessive crosslinking should be avoided. As it can be observed in Figure 5, the PET/DP-0 sample, which is a model for a mixture of recycled and pristine PET, indeed exhibits such molecular changes. The presence of this crosslinked fraction was also confirmed by testing the solubility of the residues after the rheological tests in different solvents. While the crosslinking issue has been described before, the

only practical solution offered so far is a reduction of processing time. This solution is less effective for recycling. High molecular weight PET is expected to be more susceptible to changes in molecular structure than low molecular weight PET. We found that the incorporation of DP in such PET samples could offer a chemical solution to this issue. As observed in Figure 5d,e,f, the time elapsed before crosslinking occurs is delayed three to four fold by addition of DP, as compared to the reference PET/DP-0. This prolonged stability in complex viscosity (and hence in the molecular structures) is further extended to longer times as the DP content is increased. This result is particularly encouraging considering that ~1 wt% of the additive already has a significant effect. The viscosity of PET/DP-1 is lower than that of PET/DP-0, and it further decreases in PET/DP-2 and PET/DP-5 samples providing an easier flow of their blends. This observation is in accordance with the single screw extrusion trials, and with the apparent shear viscosity values derived using the capillary die. The overall reduction of viscosity (i.e. lubrication) acts synergistically to the chemical prevention of crosslinking since it allows lowering the processing temperature [1,72,75].

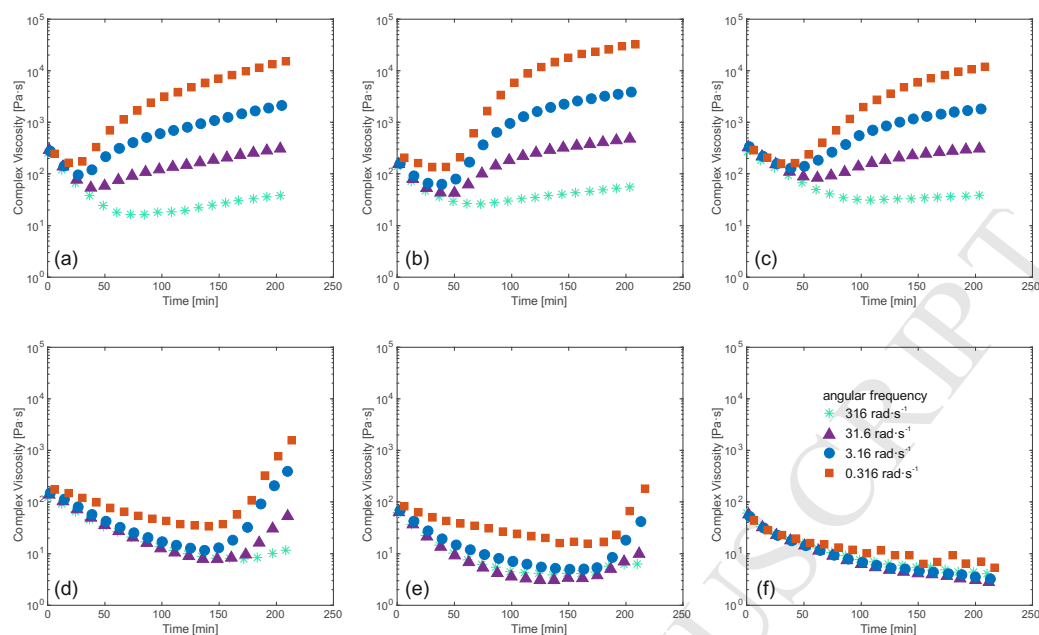


Figure 5. Time-dependent behavior of the melt complex viscosity for (a) pPET, (b) rPET, (c) PET/DP-0, (d) PET/DP-1, (e) PET/DP-2, and (f) PET/DP-5 at 290 °C under ambient atmosphere. The legends in all plots are similar to that shown in part f.

The reactions triggered by oxygen in PET are excluded from the rheological behavior of the material if the test is performed under nitrogen atmosphere (Figure 6). The pPET and rPET samples show a typical thermal degradation behavior during the entire experiment [1,2,4]. The same trend is also witnessed in the PET/DP-0 sample, which previously showed crosslinking. At low concentrations of ~2 wt%, DP shows a lubrication effect, yet does not apparently reduce the crosslinking issue. Interestingly, the PET/DP-5 sample containing ~5 wt% DP shows a gradual viscosity increase at longer experimental times. Clearly, the molecular architecture is somewhat altered when there are more amounts of DP in the polymer bulk. Regardless of this intriguing case, it can be stated that the addition of less than ~2 wt% of DP to the PET suppresses the unwanted oxygen-induced molecular changes, without significantly altering its degradation behavior under inert conditions. Moreover, it adds a lubrication effect to the blends, and facilitates their processability to some extent.

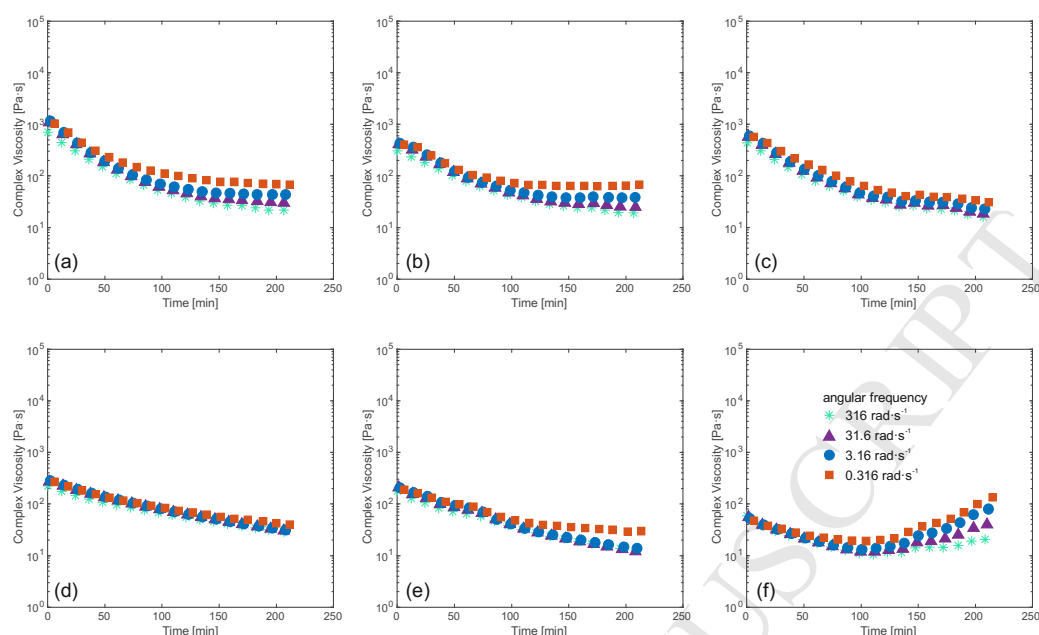


Figure 6. Time-dependent behavior of the melt complex viscosity for (a) pPET, (b) rPET, (c) PET/DP-0, (d) PET/DP-1, (e) PET/DP-2, and (f) PET/DP-5 at 290 °C under nitrogen atmosphere. The legends in all plots are similar to that shown in part f.

### 4.3. Proposed Mechanism for Chemical Melt Stabilization by DP

We have investigated the stabilization mechanism by which DP delays the chain crosslinking reactions in the presence of oxygen, as well as the crosslinking leading to a viscosity increase at higher additive loadings in the absence of oxygen. Previous studies revealed that at high temperatures, the degradation of PET chains begins with oxygen attack by abstraction of hydrogen from the methylene carbon of an ethylene glycol unit [2]. Subsequently, carbon radicals are formed on the polymer backbone, which combine with other active radicals resulting in crosslinking between individual polymer chains.

We hypothesize that a small fraction of DP molecules can decompose via bond cleavage during processing. In case of a homolytic bond cleavage, the phosphorus radicals can neutralize oxygen radicals and protect PET chains. In the absence of oxygen, however, such radicals remain unquenched and can thus initiate the crosslinking of PET chains. Volatile decomposition products

of DP can be detected with the help of DIP-MS. Analysis of DIP-MS data shown in Figure 7 indeed suggest the formation of four major decomposition products of DP, namely DOPO, PEPA, DOPO-OH, and dibenzofuran. It should be noted that DIP-MS also reveals the formation of an unspecified species (marked with asterisk in Figure 7), which was not found in the reference chemical database [76]. Regardless of the nature of this unknown compound, the results confirm the formation of various decomposition products which are derived from DP. According to the DIP-MS results, the covalent bond between DOPO and PEPA in the additive molecule breaks, and a release of phosphorus decomposition products occurs. These products start to appear at temperatures  $\sim 240$  °C, as illustrated in the inset of Figure 7. The presence of dibenzofuran, a decomposition product of DOPO, is direct proof of the formation of  $\text{PO}^\bullet$  radicals (also experimentally shown before by us [11]) that are responsible for the additive's flame retardant action, see Scheme 1.[77,78] The  $\text{PO}^\bullet$  radicals are well known to act in the gas phase by recombining the active  $\text{H}^\bullet$  and  $\text{OH}^\bullet$  in a flame [77]. It is likely that such phosphorus radicals can also be active in a condensed phase and interfere with the oxidative degradation of PET chains at the melt temperature, already below typical flame temperatures. Furthermore, such radicals may also attack polymer chains via hydrogen abstraction in the absence of oxygen. Hence, they have the potential to initiate chain crosslinking, as it was observed in the rheological tests (particularly for the PET/DP-5 sample) under  $\text{N}_2$  atmosphere. In order to confirm that volatile phosphorus radicals (e.g.  $\text{PO}^\bullet$ ) are formed and transferred to the gas phase during the rheological tests, the phosphorus content of the PET/DP-5 sample after extended rheological tests under air or  $\text{N}_2$  was measured (Table 4). Considering that the PET/DP-5 sample initially contains  $\sim 0.81$  wt% of phosphorus, the phosphorus content was reduced to  $\sim 0.39$  and  $\sim 0.64$  wt% (with a corresponding  $\sim 52$  % and  $\sim 21$  % loss) after rheological tests under air and  $\text{N}_2$ , respectively. This confirms that at high temperatures phosphorus is indeed lost to the gas phase at small rates. Therefore, the

decomposition of DP produces phosphorus radical species, which can capture and quench oxygen radicals at processing melt temperatures and, thus, control the otherwise detrimental crosslinking and branching of PET chains.

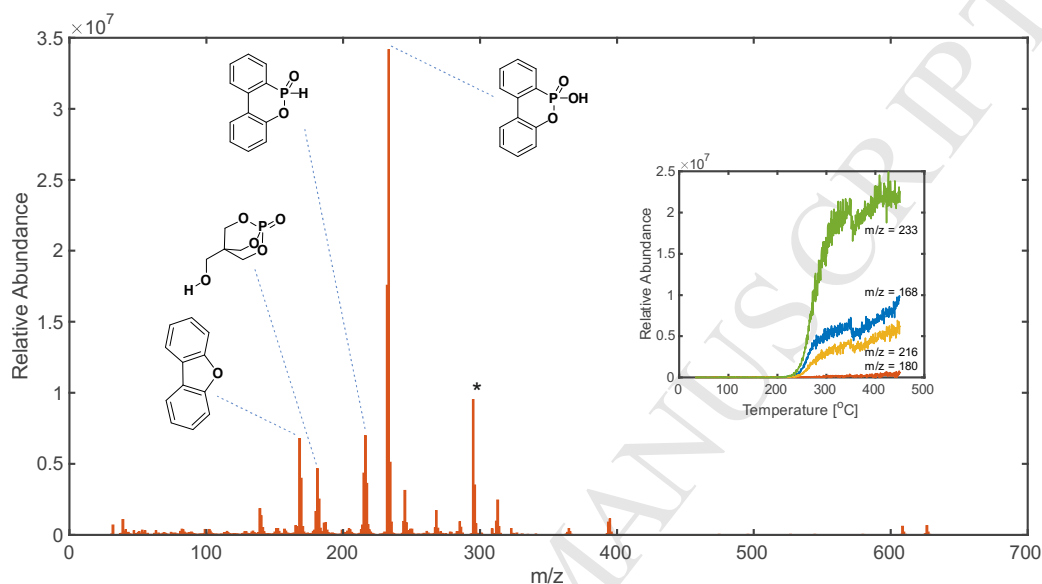
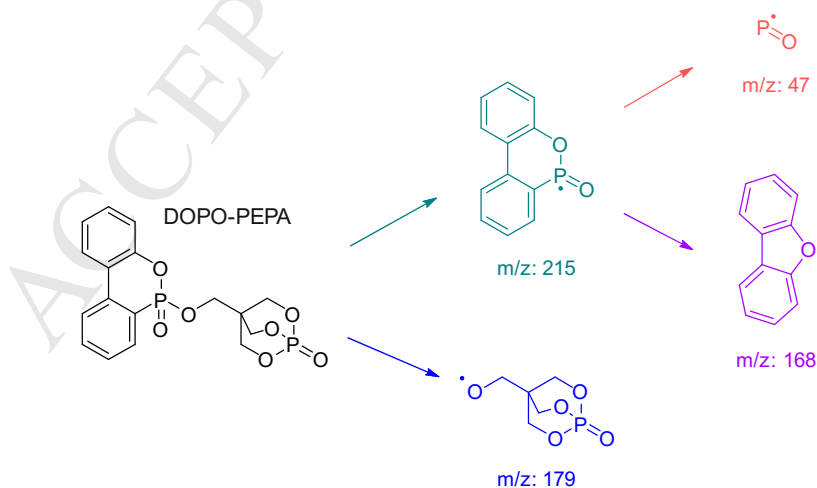


Figure 7. Full mass spectrum of pure DP during a temperature ramp from 30 to 450 °C with the corresponding chemical structures. The inset shows the DIP-MS thermograms for specified species. \*Unspecified compound.



Scheme 1. The decomposition pathways of the additive DP.

Table 4. Measured phosphorus contents in PET/DP-5 sample before and after rheological tests under air or N<sub>2</sub> atmospheres.

PET/DP-5 Sample	Measured phosphorus content (wt%)
before testing	0.81 ± 0.02
after testing under air	0.39 ± 0.01
after testing under N <sub>2</sub>	0.64 ± 0.05

Investigation of the decomposition products of DP dispersed in the condensed phase (i.e. polymer) yield information about the underlying thermal decomposition chemistries occurring during the rheological experiments. Consequently, phosphorus-containing extracts, soluble in chloroform, were characterized utilizing  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy (Figure 8). DP of PET/DP-5 sample, taken from the twin screw extruder, was extracted in chloroform at 100 °C under 30 bar of N<sub>2</sub> pressure using the high pressure microwave reactor. The  $^{31}\text{P}\{^1\text{H}\}$  NMR analysis of chloroform extract only shows the appearance of two phosphorus peaks at 11.5 and -8.3 ppm, which is characteristic to the original DP molecule, see Figure 8a [53]. This observation (in addition to the phosphorus content measurements, Table 4) indicates that the DP molecules are mostly intact in the polymer matrix and are rather stable under typical PET processing conditions. Thus, it can be stated that a typical extrusion process has no severe thermochemical side effects on the DP. Similar extraction experiments were carried out on the PET/DP-5 sample after extended rheological measurements under N<sub>2</sub> and air atmospheres, (Figure 8b and c). In case of the N<sub>2</sub> atmosphere, the extracted solution shows the decomposition products of DP (mainly PEPA at -8.5 ppm) in addition to the DP peaks. In case of samples obtained from the rheological measurement in air, DOPO-OH at 14.4 ppm and PEPA at -8.5 ppm, are detected as the decomposition products. The NMR results confirm that DP molecules can undergo

decomposition in the molten state, producing radical species that can either defuse or activate chain crosslinking in PET melts.

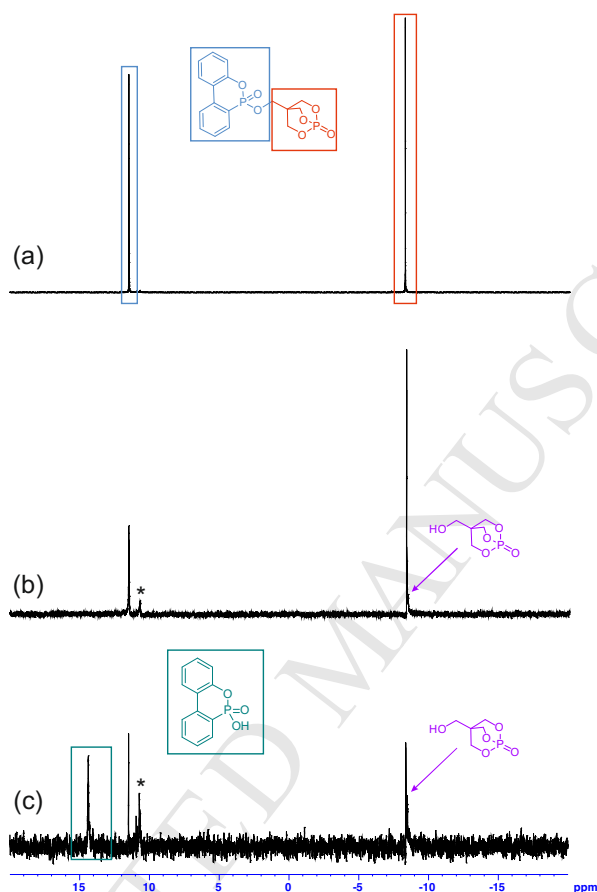
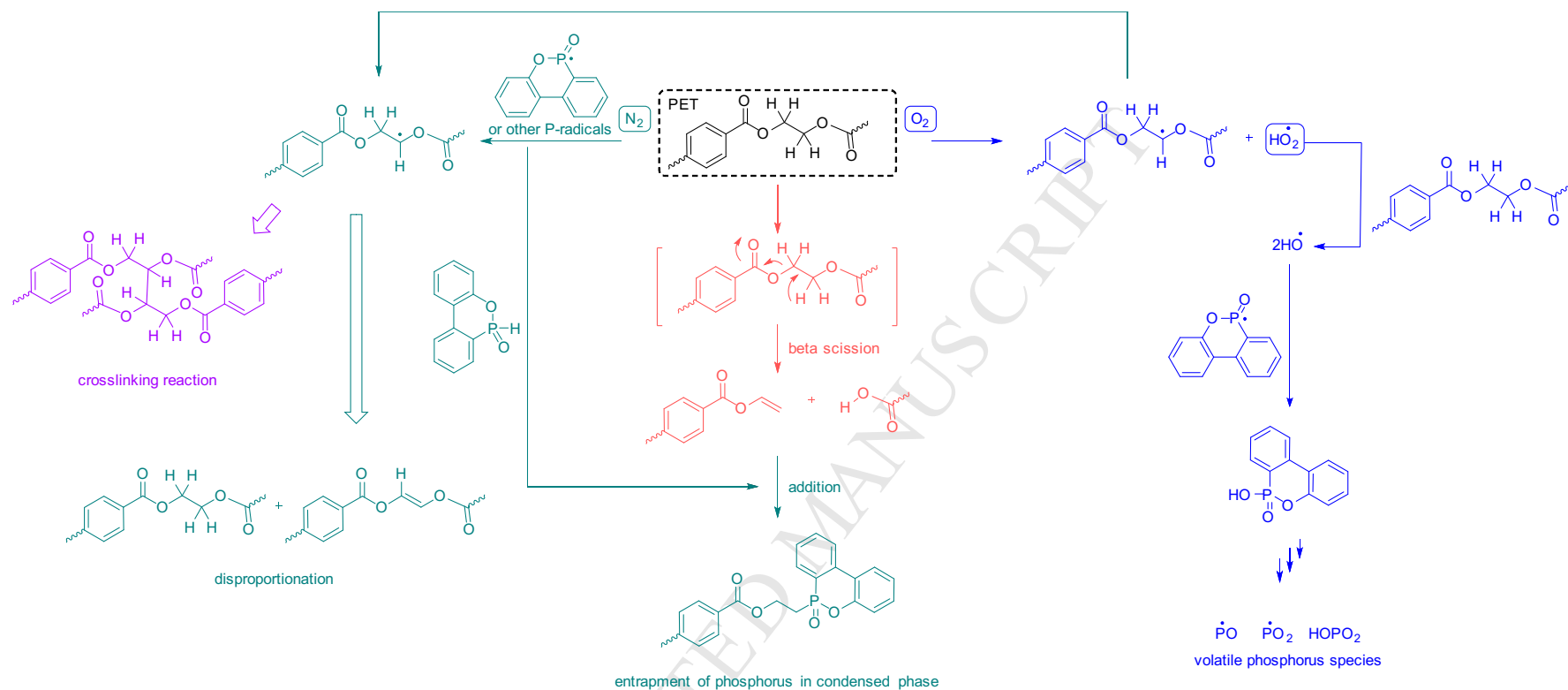


Figure 8.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra (161 MHz) of the extracted organics in  $\text{CHCl}_3$ . (a) after extrusion (PET/DP-5), (b) PET/DP-5 sample after rheological measurement under  $\text{N}_2$ , and (c) PET/DP-5 sample after rheological measurement under air. \*Uncharacterized impurity residues are observed at 11.0 ppm.

Based on the results discussed so far, a general mechanism is proposed (Scheme 2), which can underline the role of DP in the molecular reactions of PET under air and/or nitrogen at elevated temperatures. Considering that  $\text{DOPO}^\bullet$  is the main decomposition product of DP, the chemical reactions of PET must be influenced in its presence. In a nitrogen atmosphere, where only thermal degradation takes place, PET chains can undergo beta chain scissions [79]. This leads to a gradual decrease in the viscosity over time, as was observed in the rheological measurements.



In parallel,  $\text{DOPO}^\bullet$  (or other similar phosphorus radicals) can attack the PET chains and abstract a hydrogen radical, thus forming both DOPO and an active carbon radical on the PET backbone. The radical polymer chains can either undergo a radical disproportionation, or attach to other radicals on the PET chain and crosslink over time [2,3]. DOPO, on the other hand, can react with the beta scission products of PET and attach to the backbone. This leads to the entrapment of DOPO in the condensed phase and can explain the higher phosphorus content observed after rheological tests under nitrogen. The effect of the phosphorus radicals depends on the initial amount of DP and can be increased by an increased concentration within the samples. In the case of air atmosphere, the oxygen abstracts a hydrogen radical from the PET chain, and forms  $\text{HO}_2^\bullet$  radicals which are later transformed into  $\text{HO}^\bullet$  radicals [2]. The PET chain radicals follow the same pathways of disproportionation or chain crosslinking. According to the rheological data, the crosslinking reactions dominate over time, and lead to severe networking and branching of PET chains. However, in the presence of  $\text{DOPO}^\bullet$  radicals the active oxygen radicals are neutralized and turned into volatile phosphorus species such as  $\text{PO}^\bullet$ ,  $\text{PO}_2^\bullet$ , and  $\text{HOPO}_2$  [80]. Consequently, more phosphorus is consumed (transferred to the gas phase) in air, which is in agreement with the phosphorus content measurements. As a result of this consumption, the crosslinking reactions triggered by oxygen are delayed to longer times. Indeed, the proposed mechanism is a simplified scheme for the complex picture of chemical reactions in PET/DP. Still, it is in agreement with the available experimental evidence, and enables the impact of DP in controlling thermal oxidation of PET to be comprehended.



Scheme 2. The proposed mechanism of PET/DP reactions under oxygen ( $O_2$ ) or nitrogen ( $N_2$ ) atmospheres.

DP acts as a flame retardant additive for PET at concentrations around 5 wt% [11,53]. Moreover, its stabilizing role on the molecular structure at five times lower concentrations, and its lubrication effect on PET melts, demonstrates its multifunctional character. These properties taken together make DP particularly attractive for sustainable manufacturing of consumable/disposable products such as high-performance fibers and flexible electronics produced from high molecular weight PETs. During the recycling of flame retardant PET products, the overall concentration of DP would be diluted with the addition of pristine PET. At this point, the mixture of pristine and waste PET/DP with say effectively ~1 wt% DP is sufficient to benefit from the enhanced processing conditions. Considering the environmental-friendly and non-toxic nature of DP [10,11], it offers a novel additive-strategy for added-value recycling of PET, since it does not need to be selectively removed from PET waste, like other more conventional flame-retardant additives.

## 5. Concluding Remarks

DOPO-PEPA (or DP), a novel multifunctional additive with previously established flame retardant properties, was used in this research to enhance both the chemical structure stability and the viscosity of PET during melt processing and (repeated) recycling. Having successfully incorporated DP in PET as an additive, a significant inter-chain lubrication effect was observed, enabling the processing of PET at much lower spin pressures and/or temperatures. A multiscale simulation scheme was developed by combining MD and DPD, which showed the perfect mixing of DP molecules in PET as it is required for a lubricant. The extrusion trials further confirmed the anticipated lubrication effect. Rheological measurements were performed under air or nitrogen atmospheres to address the long term melt stability of PET/DP blends. In air, significant thermo-oxidative crosslinking was observed in pristine PET while the initiation of such crosslinking was

significantly delayed by adding DP. Using NMR spectroscopy, DIP-MS, and phosphorus content measurements, a chemical mechanism could be proposed of how DP intervenes with the radical oxygen attacks on PET chains. DP molecules can, as prelude to their flame retardant function, trace-release a number of radicals including  $\text{PO}^\bullet$ ,  $\text{DOPO}^\bullet$ , and  $\text{DOPO-O}^\bullet$ . Such radicals scavenge the oxygen radicals and hence protect the PET chains. The downside is that a release of such radicals, in absence of oxygen, can also create unwanted reactions with PET. Considering the non-toxic nature of DP, the present results emphasize its multifunctionality also at low concentrations as a molecular lubricant and as a thermal oxidative stabilizer. Therefore, it provides a very attractive framework for PET industries to reach a truly sustainable production of flame retardant high-performance PET materials with sustainable enhanced processability and chemical stability in recycling.

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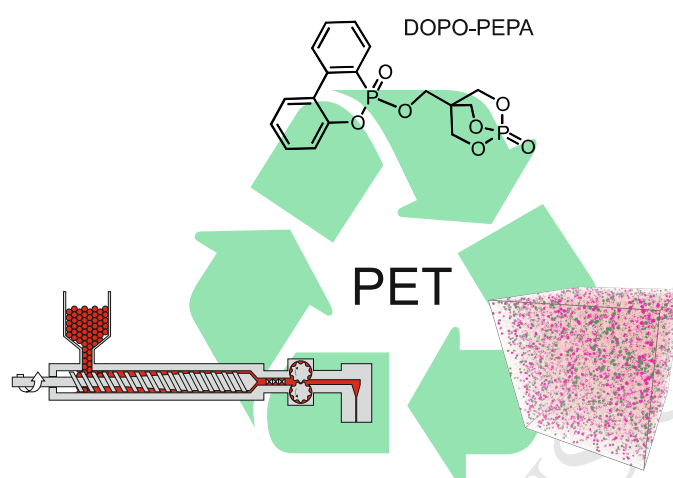
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## Graphical Abstract



## Highlights:

- DOPO-PEPA is a multifunctional, non-toxic, and eco-friendly additive
- DOPO-PEPA acts as a molecular lubricant in PET melt
- PET melt stability at elevated temperatures is improved by the addition of DOPO-PEPA
- Thermo-oxidative crosslinking is controlled in PET melt at elevated temperatures
- The recyclability of PET is improved due to synergistic behavior of DOPO-PEPA