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Enhanced thermo-oxidative stability of polydicyclopentadiene containing covalently bound nitroxide groups

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Abstract :

The antioxidant 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) group was covalently introduced into polydicyclopentadiene (PDCPD) through ring-opening metathesis polymerization (ROMP) copolymerization of dicyclopentadiene (DCPD) with a TEMPO-derived norbornene comonomer. The thermal oxidation of the resulting thin films was monitored by ThermoGravimetric Analyses (TGA) and Fourier-Transform Infra-Red spectroscopy (FT-IR). This new PDCPD stabilized by immobilization of the TEMPO antioxidant shows a better thermo-oxidative stability at 60°C under air than an industrial formulation of PDCPD stabilized with 2,6-di-tert-butyl-4-methylphenol (BHT). Impact of thermal oxidation on mechanical behavior of both formulations have been studied by tensile tests and fracture tests, based on the essential work of fracture (EWF) concept. The TEMPO-functionalized PDCPD offers a promising alternative to BHT-stabilized PDCPD with comparable ductility but slower decay and better cracking resistance, confirming the benefit of the TEMPO antioxidant in PDCPD formulation when chemically bound to the matrix.

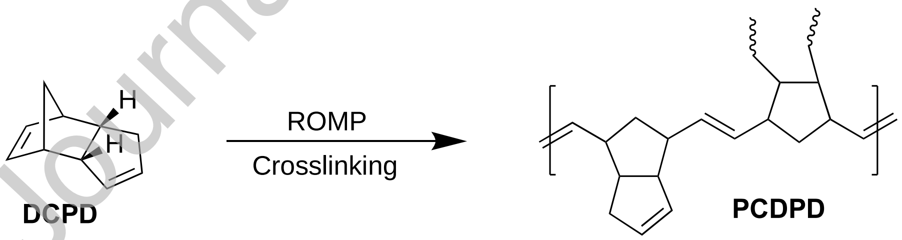
Highlights

► Copolymerization of a TEMPO-derived norbornene and a dicylopentadiene industrial formulation ► Thermal ageing of thin films of this stabilized bulk PDCPD material ► Impact of thermal oxidation on mechanical behavior of this formulation ► Comparison with an industrial BHT-stabilized PDCPD formulation

Keywords : polydicyclopentadiene, nitroxide radical-containing norbornene, ring-opening metathesis polymerization (ROMP), thermo-oxidative ageing, mechanical properties

Introduction

Polydicyclopentadiene (**PDCPD**) is one of the most industrially manufactured polymers by ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (**DCPD**) [1], which is produced in large quantities as a byproduct of petroleum cracking [2-4] (Scheme 1). This thermoset polymer processed by reaction injection molding (RIM) is extensively crosslinked [5] and displays particularly interesting physical and chemical properties, *i.e.*, a very high impact resistance coupled with a good resistance to chemical corrosion and a high heat deflection temperature [6,7]. These properties have been exploited for manufacturing of impact-resistant and tough molded parts used in automotive industry to produce body panels, bumpers, and other components for trucks, buses and tractors [8-10]. However, compared with other hydrocarbon polymers, the high concentration in remaining double bonds in **PDCPD** and a high catalyst residues concentration used for the ROMP of **DCPD** enhances the sensitivity to oxidation compared to other hydrocarbon polymers [11], limiting its use in severe environments such as the marine environment for deep-sea oil extraction [12].



Scheme 1. PDCPD structure.

PDCPD is usually stabilized by adding 2,6-di-*tert*-butyl-4-methylphenol (**BHT**) to the **DCPD** formulation, which offers high inhibition efficiency and low cost [13-15]. However, the effectiveness of such low-molar mass additive is limited by incompatibility [16] and migration out polymer matrix [17-18]. Despite the presence of **BHT**, **PDCPD** undergoes oxidation that favors crosslinking leading to a large increase in glass transition temperature

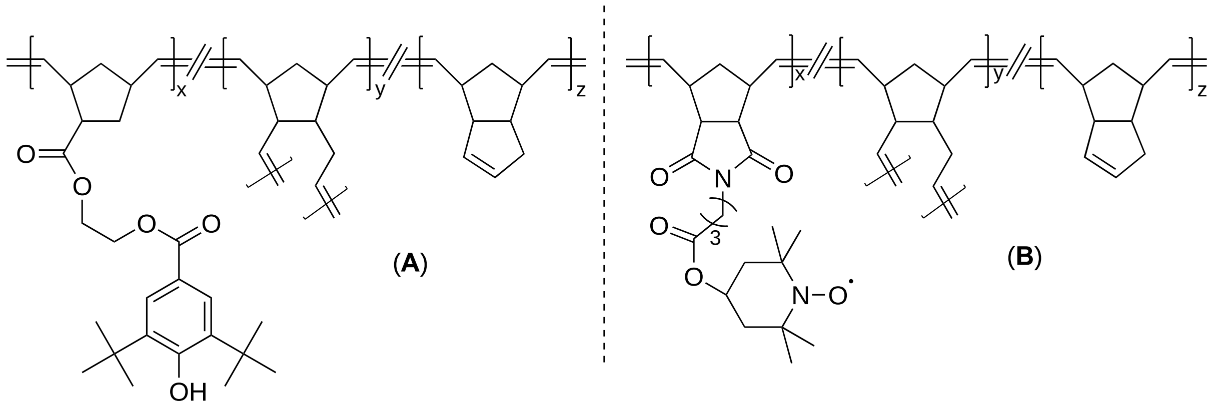
(T_g) together with an increase in rubbery modulus and maximal stress [19] and, as a consequence, an embrittlement of the polymer. Use of the hindered amine light stabilizer (HALS) stabilizer Tinuvin 123 or Chimassorb 2020 instead of **BHT** allows to improve the protection performance especially when lowering the ageing temperature [20].

Approaches that can dramatically improve polyolefin thermal-oxidative stability have been developed by chemically binding antioxidant groups along the polymer chain. The addressed synthetic strategies are based on (i) post-polymerization modification (PPM) [21-23], and (ii) copolymerization of an antioxidant-containing comonomer with olefin or vinyl monomers [24-26]. This latter approach is the most suitable one for **PDCPD**, according to its cross-linked nature.

The copolymerization of **DCPD** with a functionalized norbornene-based monomer has been already reported to access low density polymeric aerogels [27], metal-cation-based anion exchange membranes [28, 29], as self-healing agents in microcapsules [30], and films [31].

In our group, we have studied the copolymerization of **DCPD** with an hindered phenol-containing norbornene (Scheme 2A). Thermal ageing of the resulting resin has shown an induction period while virgin **PDCPD** oxidized instantly [32]. Furthermore, we have for the first time shown the efficiency of 2,2,6,6-tetramethylpiperidine-1-oxyl (**TEMPO**)-containing dicarboximide polynorbornenes as stabilizing agents in polypropylene [33].

Considering these encouraging results, this study details preparation of **TEMPO**-functionalized **PDCPD** materials by bulk copolymerization between **DCPD** and a nitroxide radical-containing norbornene (Scheme 2B) followed by examination of their thermal ageing behavior. Finally, impact of the thermal ageing on the mechanical properties of **TEMPO**-functionalized **PDCPD** materials have been investigated, and compared to those of a **BHT**-stabilized **PDCPD**.



Scheme 2. Copolymerization of **DCPD** with (A) an hindered phenol- and (B) a nitroxide radical-containing norbornene.

Experimental Section

Materials

2,6-Di-*tert*-butyl-4-methylphenol (**BHT**, ≥ 99%, Sigma-Aldrich), dicyclopentadiene (**DCPD**, TELENE SAS), and ruthenium salicylaldimine phenylindenylidene complex (TELENE SAS), were used as received. *Exo*-5-norbornene-2,3-dicarboximido-*N*-(TEMPO)butanamide (**NB-TEMPO**) was synthesized according to a literature procedure **[**33**]**.

General procedure for preparation of PDCPD films. In a typical experiment, stabilized bulk **PDCPD** materials were prepared in a 100 mL plastic beaker by mixing 10 g of **DCPD** and the desired quantity of **BHT** or nitroxide radical-containing norbornene (1.044 mmole/100 g of **DCPD**). 0.1 g of a solution of the ruthenium salicylaldimine phenylindenylidene complex purchased by TELENE SAS was then added to the mixture. The polymerization occurs immediately at room temperature in 10 min. After polymerization, material was cut in 15-25 µm slices using a Reichert Jung microtome. Samples were stored at -20 °C before ageing for a maximum of a week.

Thermo-oxidative ageing. Samples were subjected to thermo-oxidative ageing in air-circulating ovens at atmospheric pressure at 60°C and 90 °C up to 1660 h.

General Characterization

ThermoGravimetric Analyses (TGA) were performed on a TA Instruments Q500 apparatus and the testing conditions were as follows: the chamber was purged at 30°C by nitrogen at a flow rate of 90 $mL.min^{-1}$ for 5 min and the sample was then heated at a heating rate of 10 $°C.min^{-1}$ to 120°C under pure oxygen flow rate of 90 mL min^{-1}.

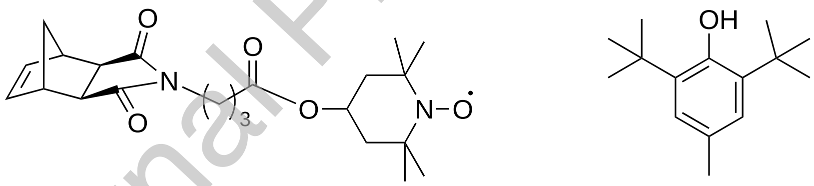
Fourier Transform Infra-Red (FT-IR) spectra were obtained using a Nicolet avatar 370 DTGS system. Spectra were obtained at regular time intervals in the MIR region of 4000-500 cm^{-1} at a resolution of 4 cm^{-1} (640 scans) and analyzed using OPUS software.

Tensile tests were carried out using an Instron tensile machine. Experiments were performed using 60 µm thick samples in order to obtain homogeneous oxidation through the sample thickness. Samples were cut in a dog-bone shape with an initial working length of 10 mm. They were tested after several ageing durations using an Instron test machine with a 50 N load cell. Tests were performed at 2 $mm.min^{-1}$ and strain measured by Digital Image Correlation. The reported values are the average ±1 standard deviation of at least eight measurements.

Essential Work of Fracture (EWF) measurements were performed on an InstronTM test machine with a 50 N load cell, in double notched tensile mode, with a loading rate of 2 $mm.min^{-1}$. Samples were 60 mm thick with a width of 10 mm. They were notched on each side using a scalpel, the distance between the two notches (ligament length, L) was in the range between 3 and 9 mm. Tests were recorded with a high resolution camera (Camera BaslerTM PIA 2400-12 GM). Images from the camera were used to measure the actual ligament length (L) before testing and fracture energy was measured from the area of the load/displacement curve. The reported values are the average ±1 standard deviation of at least eight measurements. More details about concept and methodology are available in Refs. [34-36]. The fracture energy (Wf) is measured from the area of the load/displacement curve and then plotted as a function of ligament length, see Figure 4.

Results and discussion

Preparation of stabilized PDCPD films. Stabilized bulk **PDCPD** materials were obtained by bulk copolymerization between **DCPD** and the nitroxide radical-containing norbornene (**NB-TEMPO**, Scheme 1) used both as comonomer and stabilizing agent using a ruthenium salicylaldimine phenylindenylidene complex as the initiator. The concentration of the stabilizing agent has been set at the same concentration as in the industrial formulation (see experimental section) when 2,6-di-*tert*-butyl-4-methylphenol (**BHT**) is used, i.e. 1.044 mmol in phenol function per 100 g of **DCPD**. Indeed, previous studies have shown that the use of more stabilizing agent in **PDCPD** does not improve its efficiency [20]. For comparison, incorporation of antioxidant in the **PDCPD** formulation has then been performed by bulk polymerization of **DCPD** in the presence of the commercially available stabilizing agent: hindered phenol **BHT** (Scheme 3).

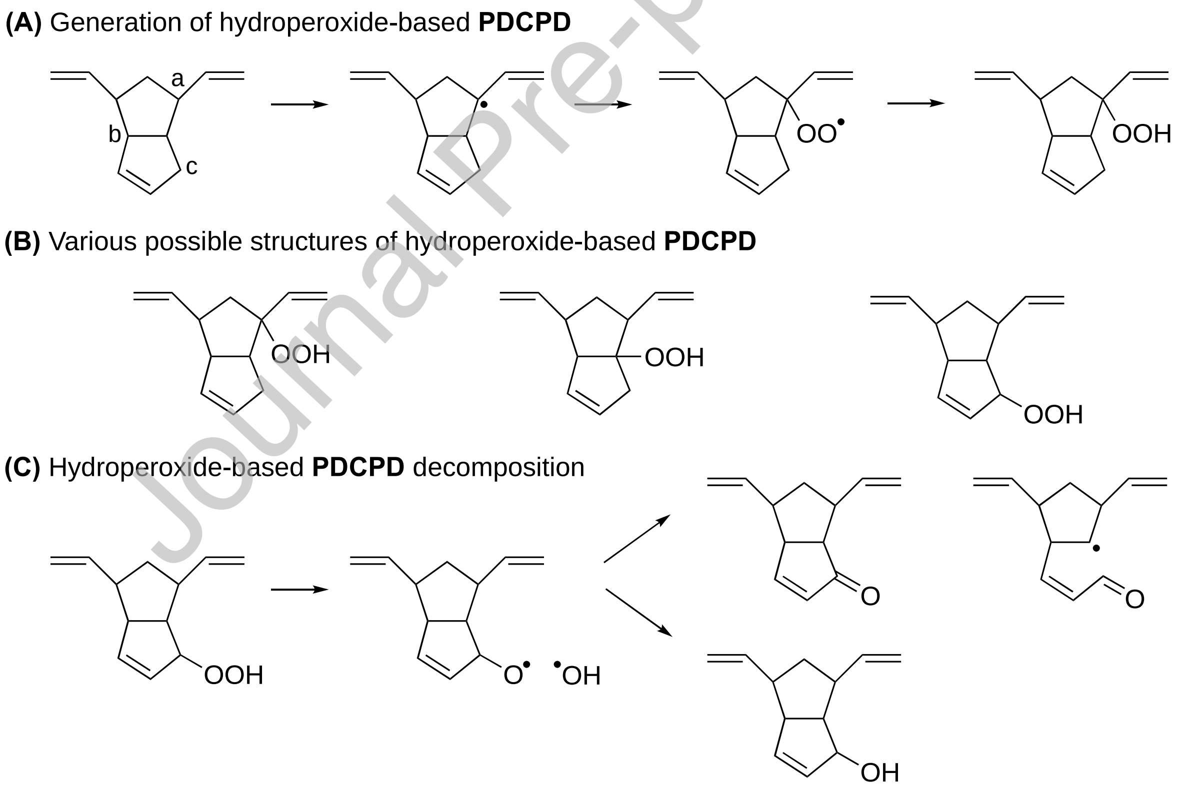


NB-TEMPO **BHT**

Scheme 3. Structures of the commercially available stabilizing agent **BHT** and the nitroxide radical-containing norbornene used as comonomer and stabilizing agent incorporated in the **DCPD** formulation.

Stabilized PDCPD films thermo-oxidation. The effect of stabilizers was evaluated by accelerated ageing tests. For that purpose, a **BHT**-stabilized bulk **PCDPD** (**PDCPD-BHT**) film, a purified **PDCPD** film, i.e. a **PDCPD-BHT** film from which the antioxidants have been removed by extraction according to a literature procedure [37], and a **NB-TEMPO**-stabilized bulk **PCDPD** (**P(DCPD-NB-TEMPO)**) film were *in situ* aged in ThermoGravimetric

Analyses (TGA) apparatus under pure oxygen flow at 120°C. During ageing, thermal oxidation has been shown to occur according to the following process [38]. Allylic radicals are generated by the abstraction of hydrogen from the allylic C-H of the **PDCPD** (labelled a, b and c in Schema 4A) by radical species. These allylic radicals react with oxygen to give peroxy radicals POO°. These in turn abstract a hydrogen from another allylic C-H to form hydroperoxides POOH (Scheme 4B). They then undergo decomposition by a unimolecular or bimolecular mechanism [39], leading to alkoxy PO° radicals, which rearrange into unsaturated ketones, with or without cleavage of the vicinal C-C bond, or to alcohols (Scheme 4C). Thermal oxidation of **PDCPD** thus leads to a progressive increase in the mass of the film, which is monitored by TGA.



Scheme 4. PCDPD thermo-oxidative pathways: (A) hydrogen abstraction, (B) various possible structures of hydroperoxide-based **PDCPD**, and (C) the resulting alcohol- and

carbonyl-based **PDCPD** after decomposition by a unimolecular or bimolecular process of hydroperoxide-based **PDCPD**.

As observed in Figure 1A, kinetic curves for mass increase display the classical behavior with an induction period followed by an auto-acceleration stage classical for the oxidation of hydrocarbon polymers. As previously described [37], induction period for purified **PDCPD** is almost close to 0, due to the relatively high instability of this polymer at the considered temperature. This induction period is significantly increased (Figure 1B) by adding the stabilizing agent usually used in industrial **PDCPD** formulations: hindered phenol **BHT**.

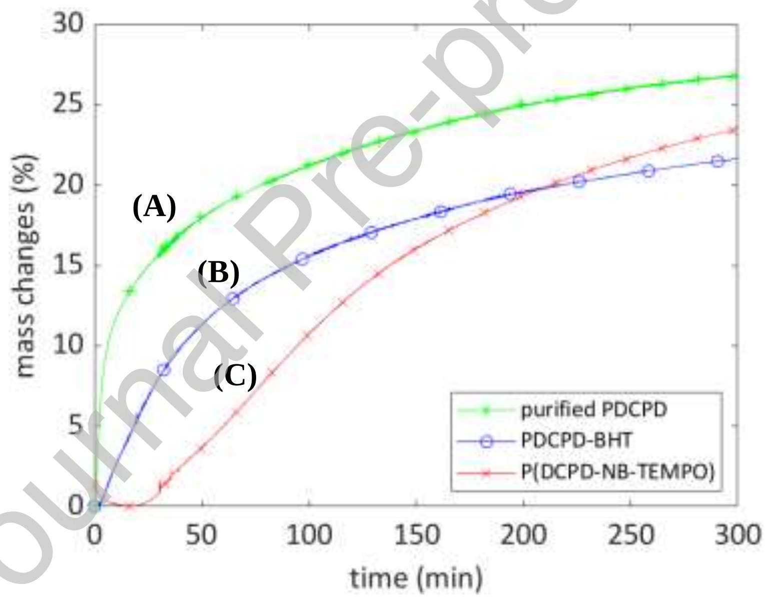


Figure 1. Kinetics of mass uptake at 120°C under pure oxygen flow for (A) purified **PDCPD**, (B) **PDCPD-BHT**, and (C) **P(DCPD-NB-TEMPO)** films.

The replacement of free stabilizer **BHT** by the covalently bounded **NB-TEMPO** in **PDCPD** films with the same concentration in active groups allows to increase the induction period (Figure 1C), demonstrating the greater efficiency of the TEMPO stabilizing agent. This implies (i) that the **TEMPO** group displays a better radical trapping capacity and/or (ii) that the **BHT** migration out of the polymer limits its antioxidant behavior. The greater efficiency of mobile (non-grafted) hindered amine stabilizers compared to **BHT** to stabilize **PDCPD** supports the second hypothesis [20]. The thermal ageing of these films at 60°C and 90°C has also been monitored by Fourier Transform Infra-Red (FT-IR) spectroscopy by converting carbonyl absorbances appearing at 1650-1750 cm^{-1} (stretch vibration mode of C=O) into concentrations using Beer-Lambert's law with ε_{CO} = 300 $L.mol^{-1}.cm^{-1}$ [40] (Figure 2). The results confirm the higher efficiency of amine-based stabilizers compared to hindered phenols.

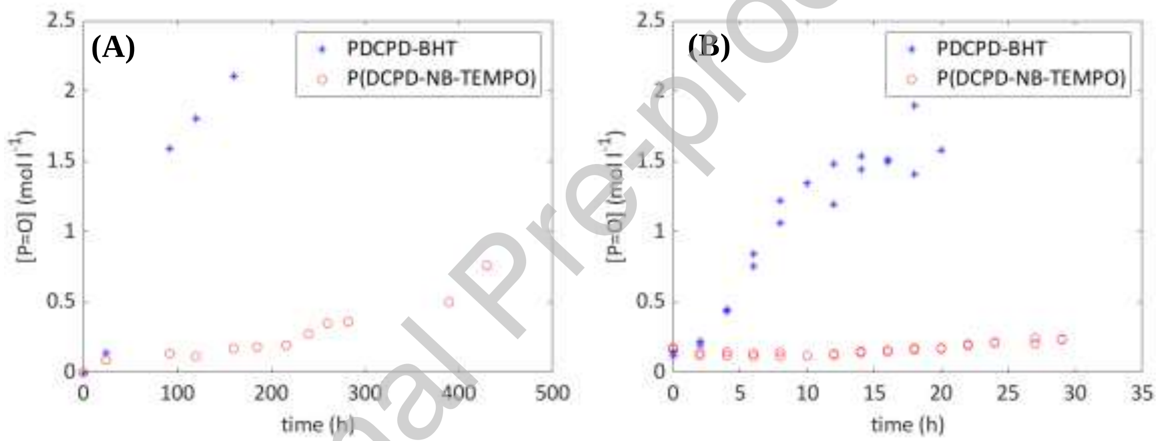


Figure 2. Carbonyls concentration-time profiles during ageing under air of **PDCPD-BHT** and **P(DCPD-NB-TEMPO)** films at (A) 60°C and (B) 90°C.

Impact of the thermal ageing on the mechanical properties of stabilized PDCPD films. Figure 3 presents typical stress/strain curves obtained during uniaxial tensile test for **PDCPD-BHT** and **P(DCPD-NB-TEMPO)** 60 µm thick dog-bone specimens in order to obtain homogeneous oxidation through the sample thickness. Let us first focus on unaged **P(DCPD-NB-TEMPO)** material **(**black curve, **Figure 3A)**, a linear portion is first observed corresponding to an elastic behavior. Then, at a stress close to 22 MPa, a yield occurs where plastic deformation takes place within the polymer. Finally, an elongation at break can be measured, about 20% for the unaged samples. In presence of **BHT** (black curve, Figure 3B), the mechanical behavior of **PDCPD-BHT** is the same except that maximal stress is about 30 MPa suggesting a higher crosslink density in this material before ageing. During ageing, the same behavior is observed for both materials, i.e. a decrease in elongation at break as well as an increase in maximal stress and finally a complete embrittlement for **PDCPD-BHT** (after 120 hours at 60°C). The most interesting point here is the fact that even after 408 hours at 60°C, **P(DCPD-NB-TEMPO)** is not brittle whereas **PDCPD-BHT** is brittle after 120 hours. These results confirm improvement of the **PDCPD** durability already observed by FT-IR spectroscopy and mass changes using nitroxide radical-containing norbornene both as stabilizer and comonomer.

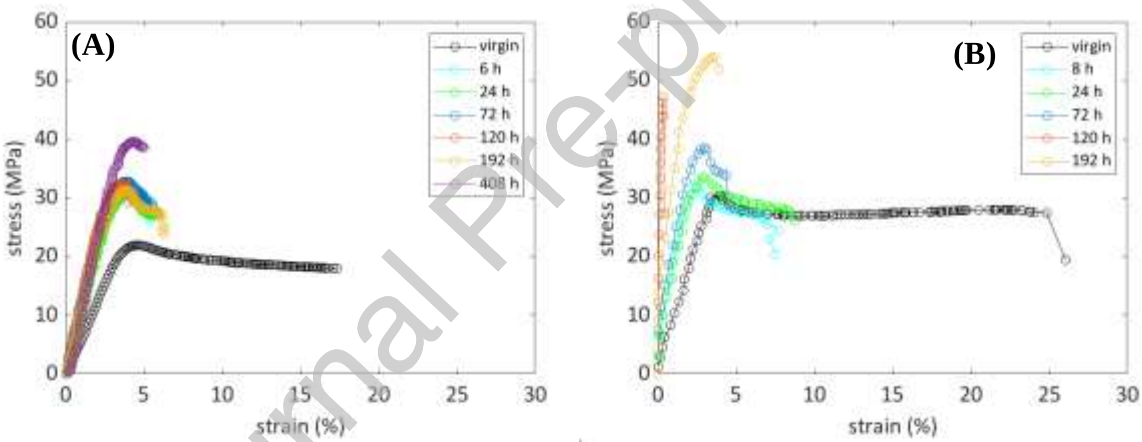


Figure 3. Tensile curves during ageing at 60°C for (A) **P(DCPD-NB-TEMPO)** (left) and (B) **PDCPD-BHT** (right).

As shown in a previous study [19], determination of fracture properties in **PDCPD** can be achieved using DENT (double edge notched specimen) samples through the Essential Work of Fracture specially to understand the decrease in strain at break.

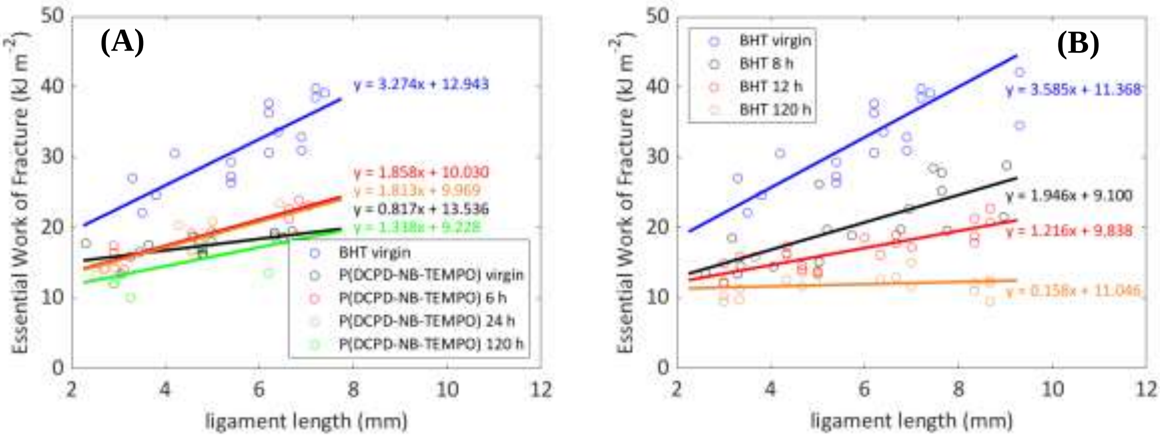


Figure 4. Impact of oxidation on fracture properties in (A) **P(DCPD-NB-TEMPO)** (left) and (B) **PDCPD-BHT** (right) at 60°C.

At the unaged state, the energy necessary to propagate a crack in **P(DCPD-NB-TEMPO)** is lower than for **PDCPD-BHT**. Here again, this behavior could be due to a lower crosslink density in the polymer. During ageing, a clear decrease in βWp (i.e. the slope in Figure 4B) is observed for **PDCPD-BHT** during oxidation at 60°C. When this value is equal to 0 then it means that the polymer is brittle. On the contrary, for **P(DCPD-NB-TEMPO)**, there is no large impact of thermal oxidation on the βWp even after 120 hours at 60°C.

As a conclusion on the study of the impact of thermal oxidation on mechanical properties of two **PDCPD** stabilized with the usually used **BHT** in industrial **PDCPD** formulations and the nitroxide radical-containing norbornene **NB-TEMPO** used both as comonomer and stabilizing agent, it appears that the consequences of oxidation are the same for the two polymers, i.e. an embrittlement of the material. However, with both tensile tests and fracture tests, the embrittlement time is much longer for **P(DCPD-NB-TEMPO)** (more than 400 hours *vs* 120 hours with **PDCPD-BHT** at 60°C). These results confirm the benefit of using the new stabilizer developed in this study.

Conclusion

A new antioxidant moiety was chemically bound to a **PDCPD** matrix by bulk copolymerization between **DCPD** and a **TEMPO**-containing norbornene. The thermal oxidation of resulting thin films studied by TGA at 120°C in pure oxygen shows an improved stability with an increase of the period induction compared with thin films of **BHT**-stabilized **PDCPD** which was confirmed by kinetics of carbonyl concentration built up monitored by FT-IR for ageing at 60 and 90°C under air. While the consequences of oxidation of the **BHT**-stabilized **PDCPD** and **TEMPO**-functionalized **PDCPD** formulations on their mechanical properties both lead to an embrittlement of the material, this embrittlement occurs for this latter after an improved latency of a factor of 3. The opportunity to immobilize an antioxidant to the **PDCPD** matrix gives a new perspective for use in severe environments such as the marine environment for deep-sea oil extraction.

Conflicts of 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.

Acknowledgments

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CRediT authorship contribution statement

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Declaration of interests

☒ 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.