



Science Arts & Métiers (SAM)

is an open access repository that collects the work of Arts et Métiers Institute of Technology researchers and makes it freely available over the web where possible.

This is an author-deposited version published in: <https://sam.ensam.eu>
Handle ID: <http://hdl.handle.net/10985/22241>

To cite this version :

Clémence NICOLAS, Jing HUANG, Adelina DAVID, Pierre-Yves Le GAC, Wendy MINNE, Renata DROZDZAK, Gilles RECHER, Laurent FONTAINE, Véronique MONTEMBAULT, Emmanuel RICHAUD - Enhanced thermo-oxidative stability of polydicyclopentadiene containing covalently bound nitroxide groups - Polymer Degradation and Stability - Vol. 195, p.109765 - 2022

Any correspondence concerning this service should be sent to the repository

Administrator : scienceouverte@ensam.eu



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

Clémence Nicolas^a, Jing Huang^b, Emmanuel Richaud^b, Adelina David^c, Pierre-Yves Le Gac^c, Wendy Minne^d, Renata Drozdak^d, Gilles Recher^d, Laurent Fontaine^{a,*}, Véronique Montembault^{a,*}

^a Institut des Molécules et Matériaux du Mans (IMMM), UMR 6283 CNRS – Le Mans Université, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

^b Laboratoire PIMM, Arts et Métiers Institute of Technology, CNRS, CNAM, HESAM Université, 151 boulevard de l'Hôpital, F-75013, Paris, France

^c IFREMER, Service Matériaux et Structures, Centre de Brest BP70, F-29280, Plouzané, France

^d TELENE SAS, 2 rue Marie Curie, 59910 Bondues, France

A B S T R A C T

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 behaviour 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.

1. 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 moulding (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 moulded 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

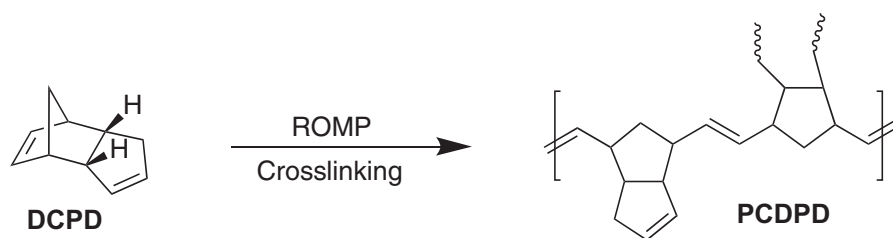
to other hydrocarbon polymers [11], limiting its use in severe environments such as the marine environment for deep-sea oil extraction [12].

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].

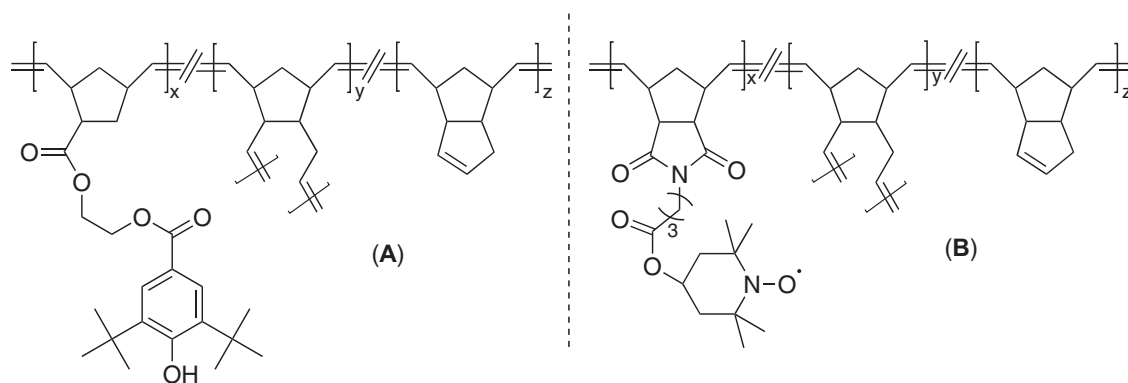
Approaches that can dramatically improve polyolefin thermal-oxidative stability have been developed by chemically binding antioxidant groups along the polymer chain. The addressed synthetic strategies are based on (i) post-polymerization modification (PPM) [21–23], and (ii) copolymerization of an antioxidant-containing comonomer with olefin or vinyl monomers [24–26]. This latter

* Corresponding author.

E-mail addresses: laurent.fontaine@univ-lemans.fr (L. Fontaine), veronique.montembault@univ-lemans.fr (V. Montembault).



Scheme 1. PDCPD structure.



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

approach is the most suitable one for **PDCPD**, according to its crosslinked 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 behaviour. 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**.

2. Experimental section

2.1. Materials

2,6-Di-*tert*-butyl-4-methylphenol (**BHT**, $\geq 99\%$, Sigma-Aldrich), dicyclopentadiene (**DCPD**, TELENE SAS), and ruthenium salicylaldehyde phenylindenyldiene 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].

2.1.1. 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 nor-

bornene (1.044 mmole/100 g of **DCPD**). 0.1 g of a solution of the ruthenium salicylaldehyde phenylindenyldiene complex provided 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 $-20\text{ }^{\circ}\text{C}$ before ageing for a maximum of a week.

2.1.2. Thermo-oxidative ageing

Samples were subjected to thermo-oxidative ageing in air-circulating ovens at atmospheric pressure at $60\text{ }^{\circ}\text{C}$ and $90\text{ }^{\circ}\text{C}$.

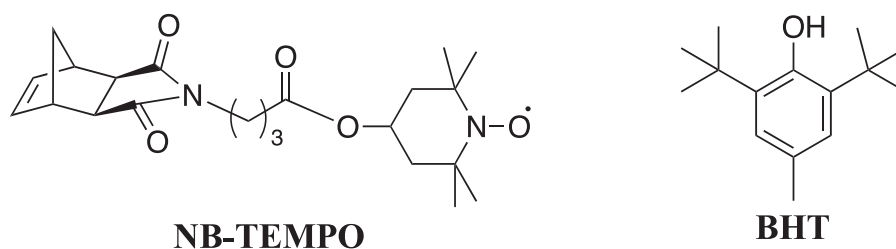
2.2. General characterization

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

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 $4000\text{--}500\text{ cm}^{-1}$ at a resolution of 4 cm^{-1} (640 scans) and analysed using OPUS software.

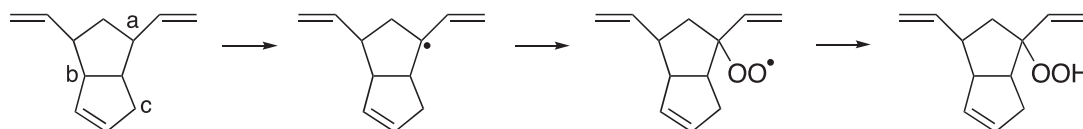
Tensile tests were carried out using an Instron tensile machine. Experiments were performed using $60\text{ }\mu\text{m}$ thick samples in order to obtain homogeneous oxidation through the sample thickness. Samples were cut in a dog-bone shape with an initial working length of 10 mm. They were tested after several ageing durations using an Instron test machine with a 50 N load cell. Tests were performed at $2\text{ mm}\cdot\text{min}^{-1}$ 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 $2\text{ mm}\cdot\text{min}^{-1}$. Samples were 60 mm thick with a width of 10 mm. They were notched on each side using a scalpel, the distance between the

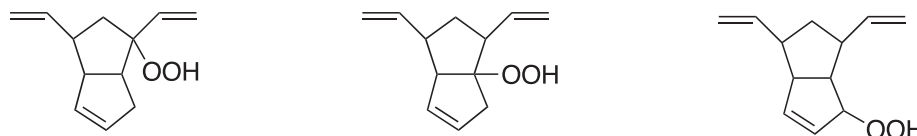


Scheme 3. Structures of the commercially available stabilizing agent **BHT** and the nitroxide radical-containing norbornene used as comonomer and stabilizing agent incorporated in the **DCPD** formulation.

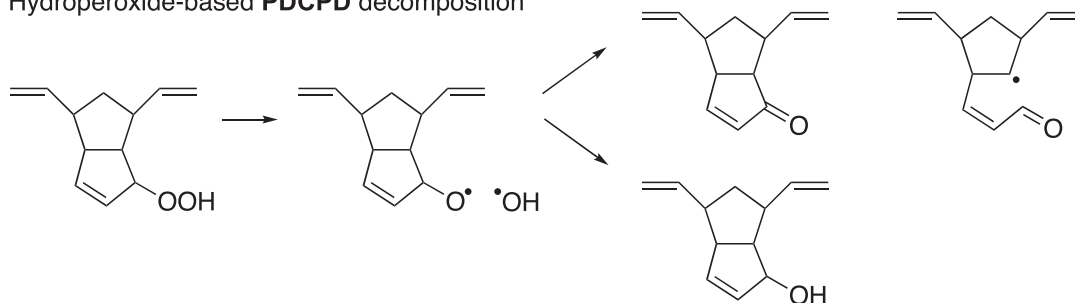
(A) Generation of hydroperoxide-based PDCPD



(B) Various possible structures of hydroperoxide-based PDCPD



(C) Hydroperoxide-based PDCPD decomposition



Scheme 4. PDCPD 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.

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 (W_f) is measured from the area of the load/displacement curve and then plotted as a function of ligament length, see Fig. 4.

3. Results and discussion

3.1. 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 3) used both as comonomer and stabilizing agent using a ruthenium salicylaldimine phenylindenyldene 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).

3.2. Stabilized PDCPD films thermo-oxidation

The effect of stabilizers was evaluated by accelerated ageing tests. For that purpose, a **BHT**-stabilized bulk PDCPD (**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 PDCPD (**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^\bullet . These in turn abstract a hydrogen from another allylic C–H to form hydroperoxides POOH (Scheme 4B). They then undergo decomposi-

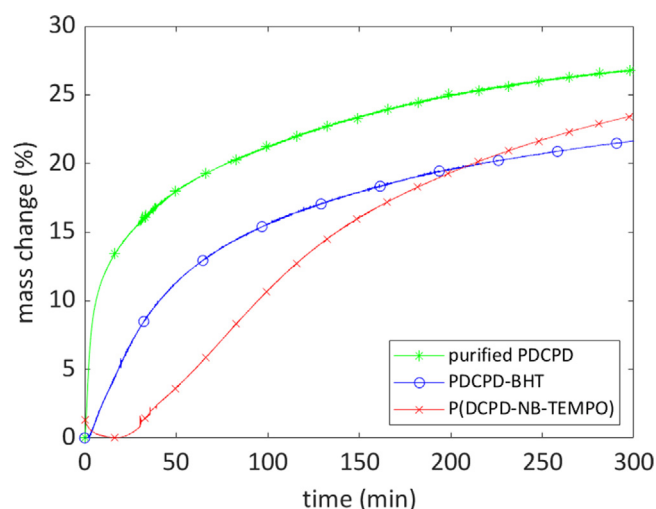


Fig. 1. Kinetics of mass uptake at 120 °C under pure oxygen flow for (A) purified PDCPD, (B) PDCPD-BHT, and (C) P(DCPD-NB-TEMPO) films.

tion by a unimolecular or bimolecular mechanism [39], leading to alkoxy PO^\bullet 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.

As observed in Fig. 1A, kinetic curves for mass increase display the classical behaviour 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 (Fig. 1B) by adding the stabilizing agent usually used in industrial PDCPD formulations: hindered phenol BHT.

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 (Fig. 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 behaviour. 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 $\epsilon_{\text{CO}} = 300 \text{ L.mol}^{-1}.\text{cm}^{-1}$ [40] (Fig. 2). The results confirm the higher efficiency of amine-based stabilizers compared to hindered phenols.

3.3. Impact of the thermal ageing on the mechanical properties of stabilized PDCPD films

Fig. 3 presents typical stress/strain curves obtained during uni-axial 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, Fig. 3A), a linear portion is first observed corresponding to an elastic behaviour. 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, Fig. 3B), the mechanical behaviour 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 behaviour 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 h at 60 °C). The most interesting point here is the fact that even after 408 h at 60 °C, P(DCPD-NB-TEMPO) is not brittle whereas PDCPD-BHT is brittle after 120 h. 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.

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.

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 behaviour could be due to a lower crosslink density in the polymer. During ageing, a clear decrease in βW_p (i.e. the slope in Fig. 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 βW_p even after 120 h at 60 °C.

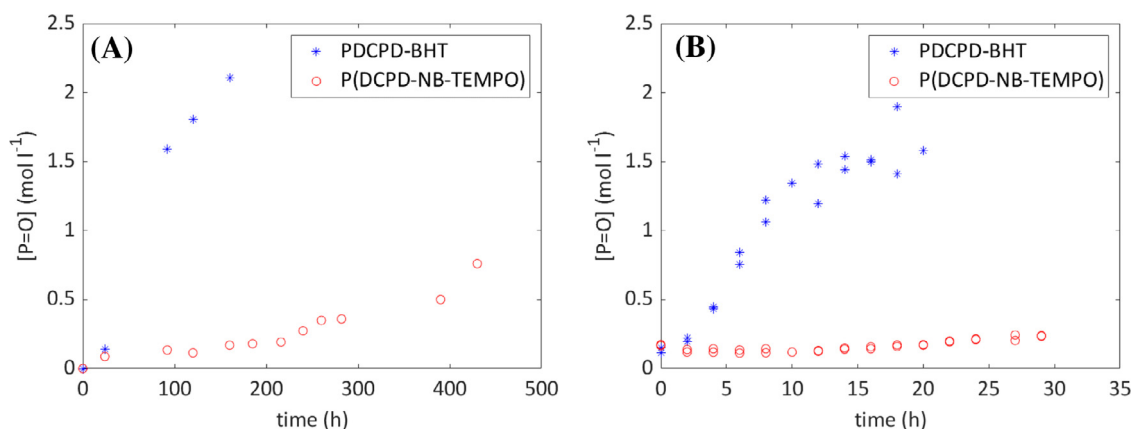


Fig. 2. Carbonyls concentration-time profiles during ageing under air of PDCPD-BHT and P(DCPD-NB-TEMPO) films at (A) 60 °C and (B) 90 °C.

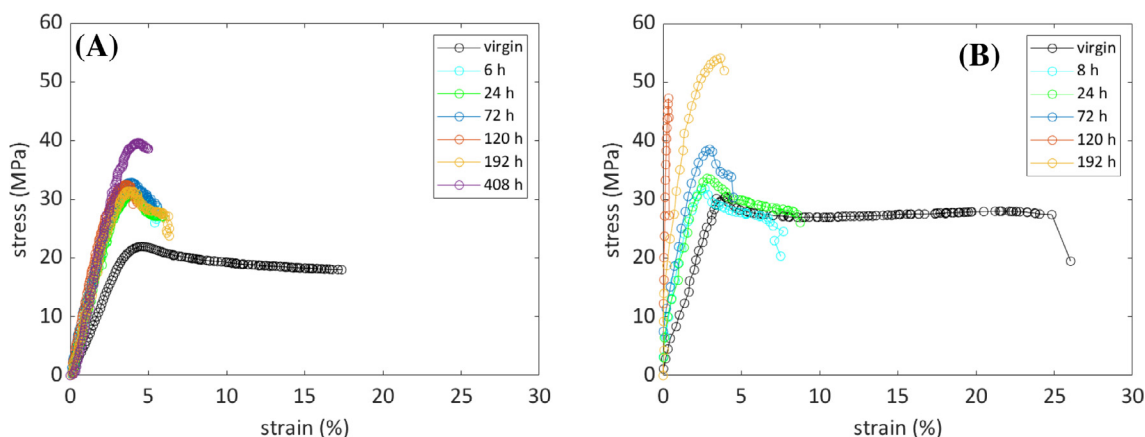


Fig. 3. Tensile curves during ageing at 60 °C for (A) P(DCPD-NB-TEMPO) (left) and (B) PDCPD-BHT (right).

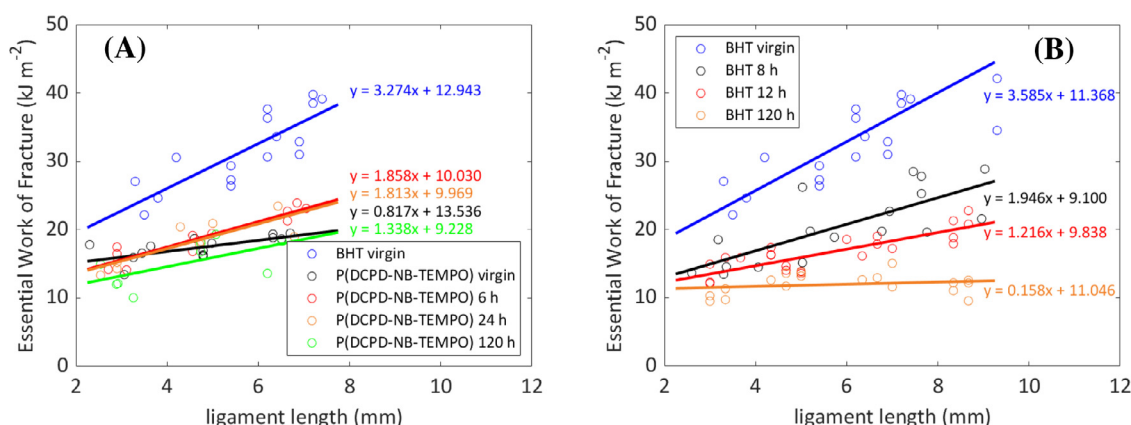


Fig. 4. Impact of oxidation on fracture properties in (A) P(DCPD-NB-TEMPO) (left) and (B) PDCPD-BHT (right) at 60 °C.

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 h vs 120 h with PDCPD-BHT at 60 °C). These results confirm the benefit of using the new stabilizer developed in this study.

4. 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.

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.

CRediT authorship contribution statement

Clémence Nicolas: Methodology, Investigation, Writing – original draft. **Jing Huang:** Methodology, Investigation. **Emmanuel Richaud:** Conceptualization, Supervision, Project administration, Funding acquisition. **Adelina David:** Methodology, Investigation. **Pierre-Yves Le Gac:** Conceptualization, Supervision. **Wendy Minne:** Investigation. **Renata Drozdak:** Conceptualization, Methodology. **Gilles Recher:** Conceptualization, Methodology. **Laurent Fontaine:** Conceptualization, Supervision, Writing – review & editing. **Véronique Montebault:** Conceptualization, Supervision, Writing – review & editing.

Acknowledgments

Agence Nationale de la Recherche is gratefully acknowledged for financial support of this study (VRPOM project – Vieillessement des Réseaux Polymérisés par Métathèse – ANR-15-CE08-0025).

References

- [1] S. Kovacic, C. Slugovc, Ring-opening Metathesis Polymerization derived poly(dicyclopentadiene) based materials, Mater. Chem. Front. 20 (2020) 2235–2255, doi:10.1039/d0qm00296h.

- [2] T.T.P. Cheung, Cyclopentadiene and Dicyclopentadiene, in: A. Seidel (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Ed., John Wiley & Sons, Inc., Hoboken, New Jersey, 2004, pp. 219–235.
- [3] M. Howe-Grant, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Wiley-Interscience, New York, 1996.
- [4] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis polymerization*, 2nd ed., Academic, New York, 1997.
- [5] L. Matejka, C. Houtman, C.W. Macosko, Polymerization of dicyclopentadiene: a new reaction injection molding system, *J. Appl. Polym. Sci.* 30 (1985) 2787–2803, doi:10.1002/app.1985.070300707.
- [6] M. Perring, T.R. Long, N.B. Bowden, Epoxidation of the surface of polydicyclopentadiene for the self-assembly of organic monolayers, *J. Mater. Chem.* 20 (2010) 8679–8685, doi:10.1039/C0JM01999B.
- [7] J. Chen, F.P. Burns, M.G. Moffitt, J.E. Wulff, Thermally crosslinked functionalized polydicyclopentadiene with a high Tg and tunable surface energy, *ACS Omega* 1 (2016) 532–540, doi: 10.1021/acsomega.6bqm00296h.
- [8] C.J. Mol, Industrial applications of olefin metathesis, *J. Mol. Catal. A* 213 (2004) 39–45, doi: 10.1016/j.molcata.2003.10.049.
- [9] C. Kun, F. Qiang, Z. Liwu, Y. Zhen, Reaction injection molding of dicyclopentadiene, *Prog. Chem.* 24 (2012) 1368–1377.
- [10] Z. Yao, L. Zhou, B. Dai, Ring-opening metathesis copolymerization of dicyclopentadiene and cyclopentene through reaction injection molding process, *J. Appl. Polym. Sci.* 125 (2012) 2489–2493, doi:10.1002/app.36359.
- [11] E. Richaud, P.Y. Le Gac, J. Verdu, Thermooxidative aging of polydicyclopentadiene in glassy state, *Polym. Degrad. Stab.* 102 (2014) 95–104, doi:10.1016/j.polymdegradstab.2014.01.036.
- [12] P.-Y. Le Gac, D. Choqueuse, M. Paris, G. Recher, C. Zimmer, D. Melot, Durability of polydicyclopentadiene under high temperature, high pressure and seawater (offshore oil production conditions), *Polym. Degrad. Stab.* 98 (2013) 809–817, doi:10.1016/j.polymdegradstab.2012.12.023.
- [13] J. Pospišil, Mechanistic action of phenolic antioxidants in polymers—a review, *Polym. Degrad. Stab.* 20 (1988) 181–202, doi: 10.1016/10.1016/0141-3910(88)90069-9.
- [14] I. Vulić, G. Vitarelli, J.M. Zenner, Structure-property relationships: phenolic antioxidants with high efficiency and low colour contribution, *Polym. Degrad. Stab.* 78 (2002) 27–34, doi: 10.1016/S0141-3910(02)00115-5.
- [15] X. Wang, X. Chen, M. Song, Q. Wang, W. Zheng, H. Song, Z. Fan, A.M. Thu, Effects of hindered phenol organic molecules on enhancing thermo-oxidative resistance and damping capacity for nitrile butadiene rubber: insights from experiments and molecular simulation, *Ind. Eng. Chem. Res.* 59 (2020) 11494–11504, doi:10.1021/acs.iecr.0c00528.
- [16] K. Thörnblom, M. Palmlöf, T. Hjertberg, The extractability of phenolic antioxidants into water and organic solvents from polyethylene pipe materials – Part I, *Polym. Degrad. Stab.* 96 (2011) 1751–1760, doi:10.1016/j.polymdegradstab.2011.07.023.
- [17] S. Al-Malaika, in: G. Allen, J.C. Bevington, G.C. Eastwood, A. Ledwith, S. Russo, P. Sigwalt (Eds.), *Comprehensive Polymer Science*, 6, Pergamon Press, New-York, 1989, pp. 539–576.
- [18] T.R. Crompton, in: *Thermo-oxidative Degradation of Polymers*, Smithers Rapra Technology Ltd, Shrewsbury, Shropshire, UK, 2010, p. 21.
- [19] A. David, J. Huang, E. Richaud, P.Y. Le Gac, Impact of thermal oxidation on mechanical behavior of polydicyclopentadiene: case of non-diffusion limited oxidation, *Polym. Degrad. Stab.* 179 (2020) 109294, doi:10.1016/j.polymdegradstab.2020.109294.
- [20] J. Huang, P.Y. Le Gac, E. Richaud, Thermal oxidation of poly(dicyclopentadiene) – Effect of phenolic and hindered amine stabilizers, *Polym. Degrad. Stab.* 183 (2021) 109267, doi:10.1016/j.polymdegradstab.2021.109267.
- [21] T.H. Kim, N. Lee, Melt-grafting of maleimides having hindered phenol group onto polypropylene, *Bull. Korean Chem. Soc.* 24 (2003) 1809–1813, doi:10.3390/polym9120670.
- [22] G. Zhang, C. Nam, L. Petersson, J. Jämbeck, H. Hillborg, T.C.M. Chung, Increasing polypropylene high temperature stability by blending polypropylene-bonded hindered phenol antioxidant, *Macromolecules* 51 (2018) 1927–1936, doi:10.1021/acs.macromol.7b02720.
- [23] A. Manteghi, S. Ahmadi, H. Arabi, Enhanced thermo-oxidative stability through covalent attachment of hindered phenolic antioxidant on surface functionalized polypropylene, *Polymer (Guildf)* 138 (2018) 41–48, doi:10.1016/j.polymer.2018.01.048.
- [24] M.C. Sacchi, C. Cogliati, S. Losio, G. Costa, P. Stagnaro, S. Menichetti, C. Viglianisi, Macromolecular non-releasing additives for commercial polyolefins, *Macromol. Symp.* 260 (2007) 21–26, doi:10.1002/masy.200751404.
- [25] S. Menichetti, C. Viglianisi, F. Liguori, C. Cogliati, L. Boragno, P. Stagnaro, S. Losio, M.C. Sacchi, Ethylene-based copolymers with tunable content of polymerizable hindered phenols as nonreleasing macromolecular additives, *J. Polym. Sci., Part A: Polym. Chem.* 46 (2008) 6393–6406, doi:10.1002/pola.22940.
- [26] S. Beer, I. Teasdale, O. Brueggemann, Immobilization of antioxidants via ADMET polymerization for enhanced long-term stabilization of polyolefins, *Eur. Polym. J.* 49 (2013) 4257–4264, doi:10.1016/eurpolymj.2013.10.005.
- [27] S.H. Kim, M.A. Worsley, C.A. Valdez, S.J. Shin, C. Dawedeit, T. Braun, T.F. Baumann, S.A. Letts, S.O. Kucheyev, J.J. Wu, J. Biener, J.H. Satcher, A.V. Hamza, Exploration of the versatility of ring opening metathesis polymerization: an approach for gaining access to low density polymeric aerogels, *RSC Adv* 2 (2012) 8672–8680, doi:10.1039/c2ra21214e.
- [28] Y. Zha, M.L. Disabb-Miller, Z.D. Johnson, M.A. Hickner, G.N. Tew, Metal-cation-based anion exchange membranes, *J. Am. Chem. Soc.* 134 (2012) 4493–4496, doi:10.1021/ja211365r.
- [29] X. Li, Y. Zhao, Z. Feng, X. Xiang, S. Wang, X. Xie, V.K. Rahmani, Ring-opening metathesis polymerization for the preparation of polynorbornene-based proton exchange membranes with high proton conductivity, *J. Membrane Sci.* 528 (2017) 55–63, doi:10.1016/j.memsci.2016.12.050.
- [30] J.K. Lee, S.J. Hong, X. Liu, S.H. Yoon, Characterization of dicyclopentadiene and 5-ethylidene-2-norbornene as self-healing agents for polymer composite and its microcapsules, *Macromol. Res.* 12 (2004) 478–483, doi:10.1007/bf03218430.
- [31] T.K.H. Trinh, G. Schrodj, S. Rigolet, J. Pinaud, P. Lacroix-Desmazes, L. Pichavant, V. Heroguez, A. Chemtob, Combining a ligand photogenerator and a Ru precatalyst: a photoinduced approach to cross-linked ROMP polymer films, *RSC Adv* 9 (2019) 27789–27799, doi:10.1039/c9ra05831a.
- [32] C. Nicolas, J. Huang, E. Richaud, W. Minne, R. Drozdak, G. Recher, L. Fontaine, V. Montebault, ROMP of novel hindered phenol-functionalized norbornenes and preliminary evaluation as stabilizing agents, *Polym. Degrad. Stab.* 186 (2021) 109522, doi:10.1016/j.polymdegradstab.2021.109522.
- [33] C. Nicolas, L. Fontaine, V. Montebault, Nitroxide Radical-Containing Polynorbornenes by Ring-Opening Metathesis Polymerization as Stabilizing Agents for Polyolefins, *Polym. Chem.* 10 (2019) 5487–5497, doi:10.1039/C9PY00769E.
- [34] J. Wu, Y.W. Mai, The essential fracture work concept for toughness measurement of ductile polymers, *Polym. Eng. Sci.* 36 (18) (1996) 2275–2288, doi:10.1002/pen.10626.
- [35] A.B. Martinez, N. Leon, D. Arencon, M. Sanchez-Soto, Essential work of fracture, crack tip opening displacement, and J-integral relationship for a ductile polymer film, *Polym. Test.* 55 (2016) 247–256, doi:10.1016/j.polymer.2016.09.004.
- [36] B. Fayolle, L. Audouin, J. Verdu, Initial steps and embrittlement in the thermal oxidation of stabilised polypropylene films, *Polym. Degrad. Stab.* 75 (1) (2002) 123–129, doi:10.1016/S0141-3910(01)00211-7.
- [37] V. Defauchy, P.Y. Le Gac, A. Guinault, J. Verdu, G. Recher, R. Drozdak, E. Richaud, Kinetic analysis of polydicyclopentadiene oxidation, *Polym. Degrad. Stab.* 142 (2017) 169–177, doi:10.1016/j.polymdegradstab.2017.06.005.
- [38] J. Huang, A. David, P.-Y. Le Gac, C. Lorthioir, C. Coelho, E. Richaud, Thermal oxidation of Poly(dicyclopentadiene) – kinetic modeling of double bond consumption, *Polym. Degrad. Stab.* 166 (2019) 258–271, doi:10.1016/j.polymdegradstab.2019.06.003.
- [39] J. Huang, W. Minne, R. Drozdak, G. Recher, P.-Y. Le Gac, E. Richaud, Thermal oxidation of Poly(dicyclopentadiene) – decomposition of hydroperoxides, *Polym. Degrad. Stab.* 174 (2020) 109102, doi:10.1016/j.polymdegradstab.2020.109102.
- [40] J.F. Rabek, *Polymer Photodegradation: Mechanisms and Experimental Methods*, Chapman & Hall Ed., New York, 1994.