Caryophyllene as a precursor of cross-linked materials

Anderson M. M. S. Medeiros, a Cédric Le Coz, a Etienne Grau a *

a. Univ. Bordeaux, CNRS, Bordeaux INP, LCPO, UMR 5629, F-33600, Pessac, France

* For correspondence: egrau@enscbp.fr

Abstract
This paper aims at the synthesis of a new type of elastomers from caryophyllene. The adopted strategy was to cross-link the polycaryophyllene, which was synthesized by ring-opening metathesis polymerization (ROMP). The polycaryophyllene obtained showed \( M_n = 2 \times 10^4 \text{ g.mol}^{-1} \) (\( \mathcal{D} = 1.5 \)) with a glass transition temperature (\( T_g \)) of -35 °C. On the first hand, thermal crosslinking was performed in the presence of organic peroxides or sulfur system. On the second hand, thiol-ene coupling initiated by UV-light at room temperature was also investigated as an alternative pathway to cross-link the polycaryophyllene. The materials obtained were analyzed by TGA, DSC, and DMA. The \( T_g \) of cross-linked polycaryophyllene could be easily modulated from -35 °C to a range between -25 and 10 °C by changing the type of cross-linking agent. The curing process led to the improvement of thermal stability ranging from 200 °C to around 340 °C. Finally, the network storage modulus varied from 1 to 100 MPa at room temperature.

Introduction
New strategies to develop materials from renewable feedstock have been continuously sought as greener alternatives to commercial oil-based materials. There is a significant interest in polymeric materials, taking into consideration their wide range of applications, especially for elastomers. The elastomers market has witnessed significant growth in the global production in recent years, with an estimated increase in revenue from current US$ 80.73 billion to close to US$ 104.17 billion by 2026.1,2 The adoption of vulcanized thermoplastics (TPV) in various application sectors has led to this development. Among several categories of thermoplastics, the natural rubbers (NR) emerge as a major players. The NR segment plays an important role in the TPV global market since the NR is one of the most used thermoplastic thanks to their versatility.2 Due to their properties such as high thermal stability, good chemical resistance, high tensile strength, low shrinkage, and greater design flexibility, they can be employed as devices and/or tools for automotive, medical, consumer goods, industrial, and other applications.3,4 In the framework of looking for an alternative to oil-based consumer goods, an important number of research groups have concentrated their studies and described the synthesis of vegetable-oil-
based thermoplastics, such as polyester, polyurethanes, polyamides, and many other bio-based polymers. Terpenes and terpenoids have drawn considerable attention as potential starting precursors in the synthesis of elastomers. Studies on the synthesis of elastomers from pinene, myrcene, and limonene can be readily found in the scientific literature and some commercially available resins and adhesives (e.g. Piccolyte®) derived from polypinenes are already reported. However, there is little exploitation of sesquiterpenes by the scientific community. Among molecules defined as sesquiterpenes, caryophyllene and humulene stand out, since these molecules are made of interesting structural elements. These molecules are found in many essential oils such as rosemary, cannabis sativa, hops, and mostly clove oil.

The cheapest and most abundant sesquiterpene, the caryophyllene, is a versatile and significant molecule due to a bicyclic and a cyclobutane rings as well as unsaturated bonds present in its chemical structure. Thanks to them, the caryophyllene can be easily modified by attaching different moieties to its backbone chain. Moreover caryophyllene is, to the best of our knowledge, the only readily available bio-based molecule that can be polymerized by ring-opening metathesis polymerization (ROMP) leading to polycaryophyllene (PCar). PCar exhibits two carbon-carbon double bonds in its structure which can be further used to cross-link it.

Keeping in mind this context, the present research has aimed to the cross-linking of polycaryophyllene by using different routes and investigating the thermo-mechanical properties of the newly produced cross-linked bio-based elastomer. Two main pathways have been considered to reach three dimensional cross-linked polycaryophyllene: i) thermal pathways: in the presence of organic peroxides [benzoyl peroxide (BPO) or dicumyl peroxide (DCP)], or by classical vulcanization based on sulfur (SS) and ii) via UV light initiated thiol-click reactions at room temperature (see diagram in Fig.1). As far as we know, this is the first study about the cross-linking of polycaryophyllene.
Fig. 1 Scheme of caryophyllene ROMP and subsequent cross-linking of polycaryophyllene by different pathways

Results and discussions

ROMP of caryophyllene was performed by dissolving Grubbs’ 2nd Generation catalyst ((tricyclohexylposphine) (1.3-dimesitylimidazolidine-2-ylidene) benzylideneruthenium dichloride) (0.2 mol % to monomer) in caryophyllene without any solvent at room temperature for 24 hours under N₂ atmosphere. The obtained polycaryophyllene (Mn=23 kg.mol⁻¹, D=1.5) was used without any further purification for thermal crosslinking or UV crosslinking. For thermal crosslinking, the polymer was homogenized with the selected cross-linker and the mixture was kept at 160 °C under 30 bar for 1 hour in a machine press. For UV-light initiated cross-linking, the polycaryophyllene was mixed with dithiol and IRGARCUR 2959 (photo-cross-linker), placed into a Teflon mold and left in a UV-reactor (λ= 320-380 nm) for 4 hours.

To confirm the crosslinking, the gel fractions were quantified by extraction in THF at 50 °C for 48 hours. The resulted gel fractions were 65 %, 90 %, and 72% for BPO, DCP, and SS respectively, as summarized in Table 1. The gel fraction appears to be limited for BPO cross-linking at 65% since even an increase of the curing temperature to 180 °C does not improve the gel fraction (see Table S1).

Obtaining a higher amount of gel fraction with DCP compared to with BPO was already identified in other studies.²⁶,²⁷ Indeed, DCP is the most frequently used cross-linking agent since it is an organic peroxide which is more selective to vinyl moieties than benzoyl peroxide.²⁸,²⁹ The ability of cumyloxy radical from DCP to react with non-activated vinyl moieties in a free-radical cross-linking pathway via H
abstraction may be a possible explanation of its higher reactivity compared to BPO. Additionally, the cumyloxy radical can undergo β-scission resulting in radical fragments (methyl radical and acetophenone) with high mobility. Furthermore, the unsaturated bonds are not easily accessible by benzoyloxy radicals due to the steric hindrance around double bonds as the increase of formation of cross-linked networks.

The SEC analysis of the BPO soluble fraction testified to the presence of oligomers (see Fig. S7, Mn=320 g.mol⁻¹, D=1.5) which indicated that some polymer backbone cleavage also takes place during the cross-linking. In the case of the sulfur system, the soluble fraction is mainly constituted of the accelerator and the catalyst used. Finally, the IR analysis of the materials obtained (see Fig. S8) shows that whatever the cross-linker, the vibration characteristics the carbon-carbon double bond (i.e. =CH₂ bending 887 cm⁻¹, C=C stretching at 1645 cm⁻¹, C-H stretching at 3115 cm⁻¹) are still present indicating a crosslinking by hydrogen abstraction mechanisms.

In order to confirm the occurrence of cross-linking reactions, on-line rheology measurements were carried out, they are shown in Fig.2. The visco-elastic analysis also provided an estimation of the initial temperature of the cross-linking process.

![Rheology curves of polycaryophyllene with (black) or without (red) DCP, and temperature (blue). The solid line represents the loss modulus (G'') and dashed line corresponds to storage modulus (G').](image)

As expected, polycaryophyllene in the absence of a crosslinker behaves as a liquid for temperatures up to 160°C with the loss modulus (G'') higher than the storage modulus (G'). Classically, as the temperature increases, both moduli continuously decrease and no cross-linking reaction takes place at 160°C since no change in moduli was observed over time.

In the presence of DCP, a shoot up in moduli is clearly observed with a gel point (intersection point) at 160°C. Similar curves were obtained for the curing of polycaryophyllene with BPO and SS (see Fig S9-10)
with gel points occurring at 118°C and 160°C respectively and are in agreement with DSC online curing curves (Fig S11-12).

After the gel point, both loss and storage moduli reached constant plateaus and no more significant changes are observed. The magnitude of storage modulus increased up to 0.6, 0.5, and 0.5 kPa and the loss modulus to 1.2 MPa, 40, and 60 kPa respectively for polycaryophyllenes cross-linked by DCP, BPO, and sulfur system.

Concerning the UV cross-linking by thiol-ene coupling, the soluble fraction remains between 0% and 11% depending of the dithiol used (see Table 1). Interestingly, when the crosslinking is performed with 0.5 eq. of thiol per carbon-carbon double bond (db), a slight improvement of the gel fraction is observed (see Table S2). This may be to the presence of free dithiol in the soluble fraction. IR analysis of the polycaryophyllene obtained with 0.5 eq. of thiol per db shows no regioselectivity of the thiol-ene addition since the bands which are characteristic of the two carbon-carbon double bonds decrease (see Fig. S13). For 1 eq. of thiol per db, double bonds appear to have totally disappeared whatever the dithiols used (see Fig. S14).

To obtain further information about cross-linked polycaryophyllenes, TGA and DSC measurements were performed in order to investigate their thermal properties, as shown in Fig. 3, Fig. 4 and Table 1.

Table 1 Thermo-mechanical properties of cross-linked polycaryophyllenes

| Entry          | Insoluble Fraction a (%) | T_g b (°C) | T_10% c (°C) | Tanδ e (°C) | E’ e (MPa) | Cross-linking degree x 10^3 f (mol.m⁻³ of elastomer) |
|----------------|--------------------------|------------|--------------|-------------|------------|-----------------------------------------------------|
| Polycaryophyllene | 0                        | -35        | 200          | NA          | NA         | 0                                                   |
| PCar/DCP       | 90                       | 12         | 335          | 4           | 28         | 11                                                  |
| PCar/BPO       | 65                       | -6         | 245          | -12         | 0.7        | 0.4                                                 |
| PCar/SS        | 72                       | -9         | 315          | -5          | 0.9        | 0.3                                                 |
| PCar/EDT       | 100                      | -22        | 338          | -16         | 0.9        | 1.1                                                 |
| PCar/BDT       | 100                      | -16        | 325          | -17         | 2.0        | 0.8                                                 |
| PCar/HDT       | 95                       | -15        | 332          | -15         | 8.2        | 3.1                                                 |
| PCar/DDT       | 98                       | -6         | 336          | -2          | 4.6        | 1.9                                                 |

a Extraction in THF at 50 °C for 48 h; b Obtained by DSC; c Obtained by TGA; d Obtained by DMA; e Determined using the rubber-like elasticity theory.
According to TGA (see Fig 3 and Fig S15-S16), the crosslinking of polycaryophyllene increases its thermal stability. Indeed, the temperature of 10% of degradation (T\textsubscript{10%}) for polycaryophyllene is around 200 °C. After cross-linking, the T\textsubscript{10%} take place at temperature ranging from 310 to 340 °C.

DSC measurements were performed to evaluate the effect of newly formed cross-linked structures on the glass transition temperatures (T\textsubscript{g}) of polycaryophyllene (See Fig. 4 and Fig. S17).

The T\textsubscript{g} of cross-linked polycaryophyllene increased significantly compared to non-cross-linked polycaryophyllene (T\textsubscript{g} = -35°C). The curing by DCP provided more rigidity to polycaryophyllene (T\textsubscript{g} = 12 °C) than the one by sulfur system (T\textsubscript{g} = -9 °C) or DDT (T\textsubscript{g} = -6 °C). Moreover the T\textsubscript{g} of the network gradually increases with the chain length of the dithiol from -22°C for EDT to -6°C for DDT.
The mechanical properties of cross-linked polycaryophyllene were evaluated by dynamic mechanical analyses (DMA), displayed in Fig. 5 and Fig. S18.

The DMA curves show a typical behavior for cross-linked materials with a glassy plateau before the alpha transition temperature ($T_\alpha$) followed by a rubbery zone after this point.

![DMA analysis of cross-linked polycaryophyllene by DCP, DDT and SS. Storage modulus in solid line, tan $\delta$ in dashed line](image)

Polycaryophyllene crosslinked by DCP exhibits the highest glassy storage modulus (over 1 GPa). The $T_\alpha$ values were 4 °C, -2 °C and -5 °C for Pcar/DCP, Pcar/DDT and Pcar/SS respectively, and can be considered in agreement with the one obtained by DSC (12 °C, -6 °C and -9 °C respectively). Finally, the rubbery plateau confirms the cross-linking of the materials and its value is directly proportional to the cross-linking density. Polycaryophyllene crosslinked by DCP exhibits significantly higher storage modulus above glass transition temperature (27 MPa) compared to SS or BPO systems (0.7 and 0.9 MPa respectively) (see Table 1) or even DDT cross-linking (4.6 MPa).

**Conclusions**

In the present work, caryophyllene was polymerized by ROMP and the polymer obtained was cross-linked using different routes: organic peroxides, sulfur system or dithiol. Rheological analyses confirmed the occurrence of cross-linking reactions in agreement with the extractions by THF results. Swelling experiments showed that the polycaryophyllene was entirely cross-linked by DCP or dithiols with an insoluble fraction over 90%. Cross-linking by sulfur system resulted in a gel content of 72%.

The cross-linked materials were in-depth analyzed by TGA, DSC and DMA. Materials were obtained with $T_\beta$ between -22°C and 12°C with improved thermal stability compared to non-cross-linked polycaryophyllene ($T_{10\%} > 300°C$). At room temperature (20°C) storage modulus of the cross-linked
polycaryophyllene were between 1 MPa to 100 MPa. Based on the achieved results, they could potentially find applications as replacement of synthetic rubbers.

Supplementary Information available: Materials and methods, NMR and SEC of polycaryophyllene, Gel Fractions of polycaryophyllene crosslinked by BPO, SEC of the soluble fraction, IR of cross-linked polycaryophyllene, Online curing of polycaryophyllene followed by rheology and SEC, TGA, DSC and DMA of crosslinked polycaryophyllene with dithiols

Acknowledgement
E.G. thanks Emergence@INC2019 for the research funding. This work was supported, as part of the Investments for the Future, by the French Government under the reference ANR-001-01. The authors thank Equipex Xyloforest ANR-10-EQPX-16. The financial support from the CPER CAMPUSB project funded by the French state and the Région Nouvelle Aquitaine is gratefully acknowledged.

Conflicts of interest
The authors declare no competing financial or commercial conflicts of interest.

Notes and references
1. Credence Research, (Summary) Elastomers Market By Product Type (Thermoset Elastomers, Thermoplastic Elastomers), By End-Use Industry (Automotive, Healthcare, Consumer Goods, Construction, Oil & Gas, Others), 2018.
2. MarketsandMarkets™ Research Private Ltd., Description - Elastomers Market by Type (Thermoset (Natural Rubber, Synthetic Rubber (SBR, IIR, PBR, NBR, ACM, EPM)), and Thermoplastic (PEBA, SBC, TPO, TPU, TPV)), Application (Automotive, Consumer Goods, Medical, and Industrial), 2017.
3. M. Biron, in Material Selection for Thermoplastic Parts, ed. M. Biron, William Andrew Publishing, Oxford, 2016, pp. 77–111.
4. P. K. Mallick, in Materials, Design and Manufacturing for Lightweight Vehicles, ed. P. K. Mallick, Woodhead Publishing, 2010, pp. 174–207.
5. E. Nekhavhambe, H.E. Mukaya and D.B. Nkazi J Adv Manuf Process., 2019; 1:e10030. https://doi.org/10.1002/amp2.10030.
6. C. Zhang, T.F. Garrison, S.A. Madbouly and M.R Kessler, Prog Polym. Sci., 2017, 71, 91-143.
7. L. Maissoneuve, T. Lebarbé, E. Grau and H. Cramail, Polym. Chem., 2013, 4, 5472-5517.
8. A. Gandini, T.M. Lacerda, A.J.F. Carvalho and E. Trovatti, Chem. Rev. 2016, 116, 1637-1669.
9. C. Voirin, S. Caillol, N.V. Sadavarte, B.V. Tawade, B. Boutevin and P.P. Wadgaonkar, Polym. Chem., 2014, 5, 3142-3162.
10. A. L. Holmberg, K. H. Reno, R. P. Wool and T.H. Epps, Soft Matter, 2014, 10, 7405–7424.
11. P. Sarkar and A. K. Bhowmick, J. App. Polym. Sci., 2018, 135, 45701.
12. M.R. Thomsett, T.E. Storr, O.R. Monaghan, R.A. Stockman and S.M. Howdle, Green Mat., 2016, 4, 115-134.
13. M. Winnacker and B. Rieger, Chem. Sus. Chem., 2015, 15, 2455-2471.
14. P.A. Wilbon, F. Chu and C. Tang, Macromol. Rapid. Comm., 2013, 1, 8-37.
15. M. Firdaus, L.M. de Espinosa and M.A.R. Meier, Macromolecules 2011, 44, 7253-7262.
16. S. Noppalit, A. Simula, N. Ballard, X. Callies, J.M. Asua and L. Billon, Biomacromolecules, 2019, 20, 2241-2251.
17. H. Miyaji, K. Satoh and M. Kamigaito, Angew. Chem. Int. Ed., 2016, 55, 1372-1376.
18. P. Sarkar and A. K. Bhowmick, Ind. Eng. Chem. Res. 2018, 57, 5197–5206.
19. P. Sarkar and A. K. Bhowmick, RSC Adv., 2014, 4, 61343–61354.
20. P. Sarkar and A. K. Bhowmick, ACS Sustain. Chem. Eng., 2016, 4, 5462–5474.
21. J. Raynaud, J.Y. Wu and T. Ritter, Angew. Chem. Int. Ed, 2012, 51, 11805-11808.
22. I. G. Collado, J. R. Hanson and A. J. Macías-Sánchez, Nat. Prod. Rep., 1998, 15, 187–204.
23 J. Gertsch, M. Leonti, S. Raduner, I. Racz, J.-Z. Chen, X.-Q. Xie, K.-H. Altmann, M. Karsak and A. Zimmer, Proc. Natl. Acad. Sci., 2008, 105, 9099.
24 A. Chicca, D. Caprioglio, A. Minassi, V. Petrucci, G. Appendino, O. Taglialetela-Scafati and J. Gertsch, ACS Chem. Biol., 2014, 9, 1499–1507.
25 E. Grau and S. Mecking, Green Chem., 2013, 15, 1112-1115.
26 S. Suyama, H. Ishigaki, Y. Watanabe and T. Nakamura, Polym. J., 1995, 27, 371–375.
27 S. Wang, Q. Zhou, R. Liao, L. Xing, N. Wu and Q. Jiang, Polymers, 2019, 11, 1149.
28 G. Baquey, L. Moine, O. Babot, M. Degueil and B. Maillard, Polym. Blends Compos. Hybrid Polym. Mater., 2005, 46, 6283–6292.
29 S. Dworakowska, C. Le Coz, G. Chollet, E. Grau, H. Cramail, Eur. J. Lipids Sci. Tech., 2019, 121, 1900264.
30 L. González, A. Rodríguez, A. Marcos and C. Chamorro, Rubber Chem. Technol., 1996, 69, 203–214.
31 I. Di Somma, R. Marotta, R. Andreozzi and V. Caprio, Ind. Eng. Chem. Res., 2012, 51, 7493–7499.