# Suberin as a Bio-based Flame-Retardant?

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Fire hazard is a constant risk in everyday life with the use of combustibles such as polymeric materials, wood, and fabrics, to name a few. Halogenated compounds have been widely used as efficient flame-retardants, often being applied as coatings or impregnations. With growing environmental concerns and regional bans on the use of halogenated flame-retardant compounds, bio-based alternatives are garnering significant research interest. Naturally occurring materials such as eggshells, DNA, and certain proteins have developed a self-defense mechanism against fire over millions of years of evolution. Cork, a naturally occurring biological tissue in outer bark, is of interest as it is often used as a heat shield and moisture repellent, specifically in spacecraft. A deeper look into the chemical structure of cork indicates the presence of suberin, a bio-polyester group that makes up as much as 40% of its chemical composition. These bio-polyester groups play a key role as a protective barrier between the plant and the surrounding external environment. Thus, the role of suberin in plants could be mimicked for the design of biobased flame-retardant materials.

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## Flame-Retardancy

Fire risks can be mitigated by preventing the ignition of the combustible materials or by lowering the heat released during combustion using fire-retardant additives such as halogenated, phosphorous-based compounds, or inorganic fillers (*e.g.*, silicates and other minerals) in the form of coatings or impregnations (Costes *et al*. 2017; Wang *et al*. 2023). While minerals efficiently decrease fire hazards, a large amount is typically needed to achieve the desirable outcomes (Costes *et al.* 2017). The halogenated compounds have been widely restricted and avoided due to environmental and health concerns such as releasing corrosive gases and increased smoke. A flame-retardant that can promote the formation of an insulating char layer on the surface of the burning samples/materials is generally considered to be a promising and effective alternative to halogenated flame retardants (Costes *et al.* 2017; Wang *et al.* 2023). Bio-based renewable materials such as lignocellulosics (specifically the constituent biopolymers) typically char and can potentially be exploited as alternatives to halogenated flame-retardants.

Cork is a noteworthy example of lignocellulosic material that has developed a self-defense mechanism against fire aggression. The flame-retardant behavior in certain lignocellulosics, such as cork oak, is due to their ability to undergo a slow combustion process, which results from the presence of a waxy substance called suberin (Costes *et al.* 2017). The chemical composition and the ability to produce thermally stable charred residues dictate the flame-retardant properties in certain lignocellulosics.

## Suberin

Suberin is a naturally occurring polyester group present in the outer tissues of specialized plants (Gandini *et al.* 2006; Graça and Santos 2007). Suberin is typically present in suberized cells, where it can comprise *ca.* 50% of the chemical composition in their cell walls (Bernards 2002). Tissue distribution in suberized cell walls in plants suggests that suberization can occur anytime the plant needs to form a barrier from the external surroundings (Bernards 2002). Deposition of suberin lowers the uncontrolled transport of water, gases, and dissolved ions, further facilitating the protection against environmental aggressions and pathogens (Bernards 2002; Franke and Schreiber 2007). Significant quantities of suberized cells can be found in the outer bark of certain wood species (Franke and Schreiber 2007; Gandini *et al*. 2006). Specifically, it is found in the outer bark tissues of oak and birch wood species, which are more familiarly known as cork (Gandini *et al.* 2006; Şen *et al.* 2014).

It is generally believed that the chemical structure of suberin consists of aliphatic and aromatic domains (Gandini *et al.* 2006; Franke and Schreiber 2007). Most of the suberin's aliphatic domains consist of long chain ω-hydroxy fatty acids, α-, ω-dicarboxylic acids, together with glycerol. The aliphatic groups of this naturally occurring polyester have extensive links to the aromatic domains. Researchers believe that the aromatic domains in suberized cells present in outer bark tissues are dominated by variously substituted phenolic moieties. Although some previous studies have also suggested that the aromatic domains in suberized cells present in outer bark tissues might simply be components of lignin (Bernards 2002), the macromolecular structure of suberin remains unclear to date. Furthermore, the self-organization mechanism of the suberin monomers at the macromolecular level is poorly understood. Similar to the recent efforts in highlighting the self-assembly process in wood/lignocellulosics by Hubbe *et al.* (2023), the development of corresponding insights on suberin might be more beneficial. Nevertheless, attempts to discover the uses of suberin have been ongoing for decades, and with the recent push for a more bio-based material, R&D efforts on suberin have the potential to grow.

## Isolation of Suberin

Suberin can be isolated from cork oak or birch outer bark residues through well-defined depolymerization strategies (Gandini *et al.* 2006; Ferreira *et al.* 2012, 2013). Suberin isolation processes typically involve the cleavage of ester bonds, which are attained through methanolysis (alkaline) in the presence of alkoxide, *e.g.*, sodium methoxide (Gandini *et al.* 2006; Ferreira *et al.* 2013). Gentle processes such as alkaline methanolysis in the presence of calcium oxide have been reported to result in partial depolymerization of suberin. Furthermore, ionic liquids such as cholinium hexanoate have demonstrated successful extraction of suberin from birch outer bark (Ferreira *et al.* 2012).

## Thermal Performance of Suberin

The thermal stability studies conducted on cork samples have highlighted the importance of suberin on the overall thermal performance. Fereiera *et al*. (2013) studied the thermal decomposition behavior of the isolated suberin from the cork oak (using ionic solvent), and the native cork, based on TGA conducted in an $N_2$ atmosphere. The TGA thermograms presented in the report suggested that both the native cork samples and the isolated suberin were thermally stable up to 200 °C. The $T_{onset}$ and the $T_{d,\,max}$ values of the two samples were comparable: for cork $T_{onset}$ of 348 °C and $T_{d,\,max}$ of 407 °C, while $T_{onset}$

of 368 °C and $T_{d, max}$ of 414 °C for isolated suberin. Charred residue content of about 17% of the initial mass was observed for both samples at 600 °C. The ability of suberin to form a charred residue upon burning is encouraging and can potentially be exploited further for designing bio-based flame-retardants.

Though substantial progress has been achieved in developing suberin applications by trial and error, there is an opportunity for theoretical development. The authors propose the following hypothesis: the chemical intermediates released during the decomposition of suberin have favorable reactive and viscoelastic properties that can lead to the formation of a tough, adherent char layer. In principle, the chemical nature of the released byproducts of heated suberin could be evaluated, making it possible to reveal the important chemical mechanisms of char formation. Beyond suberin itself, the principles learned in such studies could have applications in further developments of natural flame-retardant strategies.

## Potential Routes to Incorporate Suberin for Flame-Retardant Performance

Inspired by the studies using anisotropic foams from cellulose nanomaterials in combination with, *e.g.*, graphene oxide or boric acid (Wicklein *et al.* 2015, 2016), for flame-retardant lightweight materials, the potential of combining isolated suberin with such nanoscale cellulosic materials could be seen as a promising avenue to explore. Cellulose nanomaterials, specifically cellulose nanofibrils (CNFs), can form strong percolating networks (Trovagunta *et al.* 2021), which can be further utilized as scaffolds for engineering hybrid composite foams. Additionally, the combination of isolated suberin with lignin, which also is known to char due to the presence of aromatic/polyphenolic groups, could potentially be exploited for flame-retardant materials. A recent study by Trovagunta *et al.* (2022) provides inspiration for the design of such bio-based composite material, wherein lignin and CNFs were combined for anisotropic foams via freeze-casting.

## References Cited

Bernards, M. A. (2002). "Demystifying suberin," *Canadian Journal of Botany* 80(3), 227-240. DOI: 10.1139/b02-017

Costes, L., Laoutid, F., Brohez, S., and Dubois, P. (2017). "Bio-based flame retardants: When nature meets fire protection," *Materials Science and Engineering: R: Reports* 117, 1-25. DOI: 10.1016/j.mser.2017.04.001

Ferreira, R., Garcia, H., Sousa, A. F., Freire, C. S. R., Silvestre, A. J. D., Rebelo, L. P. N., and Silva Pereira, C. (2013). "Isolation of suberin from birch outer bark and cork using ionic liquids: A new source of macromonomers," *Industrial Crops and Products* 44, 520-527. DOI: 10.1016/j.indcrop.2012.10.002

Ferreira, R., Garcia, H., Sousa, A. F., Petkovic, M., Lamosa, P., Freire, C. S. R., Silvestre, A. J. D., Rebelo, L. P. N., and Pereira, C. S. (2012). "Suberin isolation from cork using ionic liquids: Characterisation of ensuing products," *New Journal of Chemistry* 36(10), 2014-2024. DOI: 10.1039/c2nj40433h

Franke, R., and Schreiber, L. (2007). "Suberin – A biopolyester forming apoplastic plant interfaces," *Current Opinion in Plant Biology* 10(3), 252-259. DOI: 10.1016/j.pbi.2007.04.004

Gandini, A., Pascoal Neto, C., and Silvestre, A. J. D. (2006). "Suberin: A promising renewable resource for novel macromolecular materials," *Progress in Polymer Science* 31(10), 878-892. DOI: 10.1016/j.progpolymsci.2006.07.004

Graça, J., and Santos, S. (2007). "Suberin: A biopolyester of plants' skin," *Macromolecular Bioscience* 7(2), 128-135. DOI: 10.1002/mabi.200600218

Hubbe, M. A., Trovagunta, R., Zambrano, F., Tiller, P., and Jardim, J. (2023). "Self-assembly fundamentals in the reconstruction of lignocellulosic materials: A review," *BioResources* 18(2), 4262-4331. DOI: 10.15376/biores.18.2.Hubbe

Şen, A., Van Den Bulcke, J., Defoirdt, N., Van Acker, J., and Pereira, H. (2014). "Thermal behaviour of cork and cork components," *Thermochimica Acta* 582, 94-100. DOI: 10.1016/j.tca.2014.03.007

Trovagunta, R., Kelley, S. S., and Lavoine, N. (2021). "Highlights on the mechanical pre-refining step in the production of wood cellulose nanofibrils," *Cellulose* 28(18), 11329-11344. DOI: 10.1007/s10570-021-04226-6

Trovagunta, R., Kelley, S. S., and Lavoine, N. (2022). "Dual-templating approach for engineering strong, biodegradable lignin-based foams," *ACS Sustainable Chemistry and Engineering* 10(46), 15058-15067. DOI: 10.1021/acssuschemeng.2c04056

Wang, M., Yin, G. Z., Yang, Y., Fu, W., Díaz Palencia, J. L., Zhao, J., Wang, N., Jiang, Y., and Wang, D. Y. (2023). "Bio-based flame retardants to polymers: A review," *Advanced Industrial and Engineering Polymer Research* 6(2), 132-155. DOI: 10.1016/J.AIEPR.2022.07.003

Wicklein, B., Kocjan, D., Carosio, F., Camino, G., and Bergström, L. (2016). "Tuning the nanocellulose-borate interaction to achieve highly flame retardant hybrid materials," *Chemistry of Materials*. DOI: 10.1021/acs.chemmater.6b00564

Wicklein, B., Kocjan, A., Salazar-Alvarez, G., Carosio, F., Camino, G., Antonietti, M., and Bergström, L. (2015). "Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide," *Nature Nanotechnology* 10(3), 277-283. DOI: 10.1038/nnano.2014.248