Environmentally Friendly, Low Thermal Conductivity, Fire Retarding, Mechanically Robust Cellulose Nanofibril Aerogels and their Use for Early Fire Alarm Sensors in Thermally Insulating Sustainable Building Applications

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As a way to reduce carbon emissions, manufacturing an environmentally friendly and biodegradable cellulose aerogel material with low thermal conductivity, excellent mechanical, and flame retarding property to replace conventional foams is of significant interest in thermally insulating building applications. Primary questions to be addressed include how to design fire retarding and mechanically robust wood derived cellulose nanofibril aerogels as alternatives of expanded polystyrene and rigid polyurethane foams; how to develop aerogel materials in industrial-level manufacturing; and whether it is possible to further develop its early fire alarm sensors with ultra-low temperature sensitive limit and long signal durability by experimental and machine learning artificial intelligence approaches for thermally insulating sustainable building applications.

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Design Strategies

The question at hand is how to design sustainable, fire retarding, and mechanically robust cellulose nanofibril aerogels as alternative materials of polyurethane and expanded polystyrene foams in thermally insulating sustainable building application. Petroleum-based polyurethane (PU) and expanded polystyrene (EPS) foams as thermal insulation materials are widely utilized for thermal management of buildings to maintain a mild indoor temperature. However, these waste PU and EPS foam materials are difficult to degrade. It is necessary to develop alternative materials with the prerequisite of sustainability and energy efficiency to replace EPS and PU foams. An aerogel is an ideal alternative material, as it has nanostructured networks with air in the pores and its mesoporous size (2 to 50 nm) is less than air molecules' free path (70 nm), thereby effectively blocking its gas phase thermal conduction. The aerogel made from cellulose biopolymer materials is also biodegradable and thermally insulating [low thermal conductivity at 40 to 50 mW/(m·K)] (Zhao *et al.* 2023). This is along with good mechanical properties and low density, such that they can be regarded as an ideal alternative material for EPS and PU foams. Supercritical CO_2 drying and freeze-drying are two primary methods for fabrication of aerogel materials. Compared to its open pore structures fabricated from the freeze-drying method, the supercritical CO_2 drying method can maintain the nanostructured porous network of aerogels, which is attributed to the absence of surface tension and capillary stress. However, it is highly necessary to further tailor its thermal conductivity properties as alternatives of petroleum-based foams in sustainable building insulating material application, *e.g.*, thermal conductivity of EPS [30 to 40 mW/(m·K)] and PU Foams [20 to 50 mW/(m·K)]. Inspired by the closed-pore structure of EPS foams, which have superinsulating ability, it makes sense to strive for a similar structure in environmentally friendly foams. However, most cellulose nanofiber (CNF) mesoporous aerogels are open-pore structures made either with supercritical CO_2 drying or freeze-drying approaches. The structure follows from CNF's fibrous morphology and aqueous processing methods. Therefore, how to design CNF aerogels having closed pore structures is a challenging issue. The Pickering emulsion template approach is promising for the design of CNF aerogels with closed pore morphology and superinsulating property [thermal conductivity at 18 mW/(m·K)] (Jiménez-Saelices *et al.* 2018). In addition, fibers are potential candidates for fabrication of aerogels. Whether cellulose nanofibrils can be used is a following-up question. Considering the plastic pollution issues, the development of recycled polyethylene terephthalate (PET) fiber aerogels from waste PET bottles with excellent thermal conductivity as sustainable and thermal insulating materials and CO_2 capture application has attracted attention. Except for waste polypropylene and PET plastics, aerogel materials derived from textile waste and waste tire fibers, *etc*. are also worthy of study. In addition to thermal conductivity, mechanical and fire retarding properties of CNF aerogels also hinder its further application. Phosphorous and halogen compounds as fire additives of EPS and PU foams are required to satisfy fire regulatory standards. However, these fire additives release large amounts of smoke during combustion. By comparison, inorganic flame retardants are more suitable to achieve its environmentally friendly application, as these fire additives release water instead of toxic smoke, and the degraded products are metal oxides. However, much higher loadings of these fire additives are required to achieve satisfied flame retarding performance, while the mechanical property of resulted materials has an obvious reduction. Therefore, it is required to find new fire additives to achieve trade-off between fire retardancy and mechanical properties of aerogel materials. Inspired from the covalent bond interactions of borates and oxygen-involving functional groups in plant tissues, borate cross-linking agent at low concentration maintains both mechanical property of plant fiber structure and retards flame spread on the fiber surfaces. Therefore, inorganic borate is promising for achieving excellent fire retarding and mechanical property of CNF aerogel materials and maintaining its low thermal conductivity. However, the covalently cross-linking structure should be unfavorable for recycling and degradation, so its degradable and recyclable property is also attracting increased attention for sustainable insulating building application considering its disposal of end-of-life materials. Pure CNF aerogel materials are easily degradable in natural environments, while chemically treated ones present difficulties. Thus, biobased phytic acids as a promising alternative to borates have been developed recently for CNF aerogel design with highly efficient flame retarding, excellent mechanical and low thermal conductivity performance (Ren *et al.* 2022).

Large-scale Manufacturing

The next question to consider is, what are the large-scale manufacturing methods of functional aerogel materials with promising industrial application in thermally insulating sustainable building. Although the supercritical CO_2 drying method fabricates aerogel materials with more uniform mesoporous structure, it has limitations in industrial-scale manufacturing of aerogels to replace EPS and PU foams for sustainable insulating building application, such as long processing time and large amount of solvent waste. Fortunately, due to its amphiphilic property, CNF is an ideal stabilizer in emulsions and then forms a gel *via* a solvent exchange process. This gel as a template forms aerogels after freeze-drying. For instance, an aerogel in an alveolar texture structure was fabricated *via* the CNF Pickering emulsion template, and a closed porous structure was also formed inside of its cell wall, contributing to its superinsulating ability and toughness (Jiménez-Saelices *et al.* 2018). Therefore, use of a Pickering emulsion template integrated with freeze-drying method is promising in fabrication of aerogels in mass-scale. In addition to aerogel fabrication, dip and spray coating is a general and industrial promising method to tailor its fire retardancy and mechanical properties. However, for conventional dip coating, the sample size is highly dependent on the reaction vessel in coating process, which has limitations as a truly industrially compatible method. Therefore, there is a need for the development of vessel-free and highly efficient coating strategy to tailor aerogel material surface properties, such as spray coating. For instance, ultrafast spray coating polydopamine (PDA) on diverse substrates as a simple and industrially miscible strategy has been reported (Hong *et al.* 2016). One question is how to achieve excellent adhesive strength among PDA coating materials and CNF aerogel substrates and solvent-resistance and long durability of coating materials. Oxygen plasma surface treatment as a physical modification method can easily tailor aerogel surfaces with polar groups, and these surface functional groups enable interaction with coating surfaces and thus enhance adhesive strength. Post-modification or thermal annealing treatment enables further tailoring of its surface chemically resistant performance. The follow-up question is how to achieve the trade-off in fire retarding, mechanical, and interfacial adhesive performance of functional coating aerogel materials. Inspired from the synergistic fire retarding wood and plastic composites, the synergistic PDA, MXene, and ammonium polyphosphate fire additives *via* physical crosslinking with metal ions and the spray coating method together is highly promising to achieve satisfactory comprehensive performance. MXene sheets work as physical barriers and its released titanium dioxide along with phenol groups of PDA particles as synergistic effects make it possible to capture oxygen radicals during combustion. The overall effect is to enhance fire retarding performance and reduce smoke release. Interestingly, ferric ions as cross-linkers and catalysts allow for the maintenance of mechanically robust coatings and enhance its fire retardancy property by promoting dense char layer formation. Besides, PDA coatings with structure color make it possible to tailor aerogel surfaces for aesthetic functions as the controlled PDA coating thickness in nanoscale *via* catalysts can endow aerogels with different colours. Fortunately, both PDA and CNF are biodegradable (Jiang *et al.* 2017). Another promising approach for flame retarding CNF aerogel fabrication is through phosphorylated CNFs, and the resulted aerogels can be self-extinguishing (Ghanadpour *et al.* 2015).

Fire Alarm Sensor Applications

A final question is whether it is possible to further develop excellent fire retarding and mechanically robust cellulose nanofibril aerogel fire alarm sensor in sustainable building material applications. The fire safety of building materials is a major issue because fire accidents result in the loss of large amounts of property and loss of human life. In 2021 alone, more than 1.3 million fires caused about 3,800 civilian deaths and more than 14,000 injuries in the United States (Hall and Evarts 2022). Therefore, motivated by the fire safety issues in construction building materials, it is important to explore the early warning fire alarm aerogel sensor materials. The basic principle of such devices is according to the resistance transition of functional fillers inside of aerogel materials in response to external temperature stimuli. However, one critical question is how to design fire warning aerogel materials with ultralow temperature limits for activating fire warning signals and long signal durability. The development of CNF aerogels with MXene as thermally stimuli responsive fillers is promising, as the resistance transition from conductive to insulating state can be easily detected by the on-off state of the alarm light attributed to the thermal oxidation of MXene sheets during burnings (Zhao *et al.* 2023). Machine learning is also a promising approach for precise design of ultralow responsive temperature and long sensitive durability of CNF aerogel early fire alarm sensors with wireless communication functions.

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REFERENCES CITED

Ghanadpour, M., Carosio, F., Larsson, P. T., and Wågberg, L. (2015). "Phosphorylated cellulose nanofibrils: A renewable nanomaterial for the preparation of intrinsically flame-retardant materials," *Biomacromolecules* 16, 3399-3410. DOI: 10.1021/acs.biomac.5b01117

Hall, S., and Evarts, B. (2022). *Fire loss in the United States during 2021*, National Fire Protection Association, (https://www.nfpa.org/).

Hong, S. H., Hong, S., Ryou, M. H., Choi, J. W., Kang, S. M., and Lee H. (2016). "Sprayable ultrafast polydopamine surface modifications," *Advanced Materials Interfaces* 3, article 1500857. DOI: 10.1002/admi.201500857

Jiménez-Saelices, C., Seantier, B., Grohens, Y., and Capron I. (2018). "Thermal superinsulating materials made from nanofibrillated cellulose-stabilized Pickering emulsions," *ACS Applied Materials & Interfaces* 10, 16193-16202. DOI: 10.1021/acsami.8b02418

Jiang, Q. S., Derami, H. G., Ghim, D., Cao, S. S., Jun, Y. S., and Singamaneni, S. (2017). "Polydopamine-filled bacterial nanocellulose as a biodegradable interfacial photothermal evaporator for highly efficient solar steam generation," *Journal of Materials Chemistry A* 5, 18397-18402. DOI: 10.1039/C7TA04834C

Ren, X. Y., Song, M. Y., Jiang, J. G., Yu, Z. Y., Zhang, Y. F., Zhu, Y. L., Liu, X. L., Li, C. M., Oguzlu-Baldelli, H., and Jiang, F. (2022). "Fire-retardant and thermal-insulating cellulose nanofibril aerogel modified by *in situ* supramolecular assembly of melamine and phytic acid," *Advanced Engineering Materials* 24, article 2101534. DOI: 10.1002/adem.202101534

Zhao, Y. N., Zeng, Q. T., Lai, X. J., Li, H. Q., Zhao, Y., Li, K. Q., Jiang, C. C., and Zeng, X. R. (2023). "Multifunctional cellulose-based aerogel for intelligent fire fighting," *Carbohydrate Polymers* 316, article 121060. DOI: 10.1016/j.carbpol.2023.121060