

## Nanolignin for Fire Retardant Composite

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Composites, whether wood-based or polymeric, play a significant role in our daily lives due to their diverse applications [1]. Regrettably, most of these composites are very combustible and generate significant heat and smoke during combustion, so restricting their use in fire-resistant contexts. Flame retardants and smoke suppressants are thus to be developed in response to contemporary needs. Nonetheless, the bulk of flame retardants are halogen- and petroleum-derived, raising concerns regarding their detrimental environmental effects and reliance on fossil resources [2]. Consequently, the development of flame retardants derived from sustainable and renewable biomass resources is garnering heightened interest. Lignin, one of the most prevalent aromatic polymers worldwide, has attracted significant attention in the development of flame retardants.

Due to their highly analogous chemical structures, nanolignin can be utilized in the same manner as lignin in the domain of flame retardants. In contrast to lignin, nanolignin exhibits greater potential owing to its nanoscale dimensions. Nanolignin, due to its exceptionally high specific surface area and porosity, along with its carbon structure and multi-reactive functional groups, has been identified as a potential and effective flame retardant [3]. These properties facilitate the dispersion of nanolignin at a nanometer scale within polymers, thereby enhancing its efficacy [4]. Lignin serves as a flame retardant and functions as a carbonizing agent that promotes char formation during combustion [4]. Nonetheless, the application of nanolignin as flame retardants remains inadequately investigated, despite their potential.

Although limited, literature is available concerning the use of nanolignin and its effects on the flame retardancy of polymers or composites. Chollet *et al.* [5] synthesized lignin nanoparticles (LNP) from Kraft lignin. To improve its flame-retardant characteristics, the LNP was treated with diethyl chlorophosphate and diethyl (2-(triethoxysilyl)ethyl) phosphonate before being blended with polylactic acid (PLA). The treatment with diethyl (2-(triethoxysilyl)ethyl) phosphonate was found to be effective, as it enhances the phosphorus content, which is closely associated with the flame retardant properties of the LNP. The research concluded that the treatment is essential, as untreated lignin offered no flame-retardant advantages. With a modest incorporation load of 10 wt%, the treated LNP significantly reduces the peak heat release rate (pHRR) and extends the time to ignition of the PLA composite. Even with a reduced incorporation load of 5 wt%, the flame retardant properties of the PLA composite were significantly enhanced, illustrating the potential of utilizing LNP, particularly when chemically modified, as a sustainable and effective means of enhancing fire safety.

Meanwhile, Yu *et al.* [6] synthesized two varieties of highly hydrophobic melamine formaldehyde (MF) sponges by depositing lignin and/or acetylated LNP onto the sponge framework. In the combustion test, polyurethane foam (PUF), utilized as a control, ignited entirely, leaving minimal residue. In contrast, following the integration of unmodified and acetylated LNP, the MF sponges extinguish within 3 s, leaving a black residue and preserving 90% of their original weight. The findings

indicated that the integration of LNP can mitigate the risk of fire and explosion. On the other hand, Wang *et al.* [7] produced a composite film from boron nitride (BN), polyvinyl alcohol (PVA), and LNPs. The composite film containing 2.5 vol% LNPs exhibited a marked enhancement in thermal conductivity relative to the film devoid of LNPs. Additionally, the thermal stability of the composite film has also exhibited enhancement. The incorporation of 7.1 vol% LNPs elevated the film's decomposition temperature from 260 °C to 310 °C. During the burn test, the PVA film exhibited a self-propagating flame post-ignition, whereas the BN-OH/PVA composite films did not propagate flames even after 5 s. The incorporation of LNPs resulted in enhanced flame retardancy of the composite film. The findings demonstrated that the LNPs function as superior flame retardants.

Functionalized LNPs as flame retardants have garnered considerable interest recently. He *et al.* [8] prepared functionalized LNP incorporating both nitrogen and phosphorus moieties to address the challenges of poor dispersion and detrimental effects on the mechanical properties of the composite. He *et al.* [8] synthesized functionalized lignin (FL) through a nitrogen-phosphorus grafting reaction. Subsequently, functionalized LNPs were synthesized through solvent exchange and subsequent ultrasonication. The functionalized LNPs were subsequently integrated into polyurethane elastomers, serving as crosslinking agents and flame retardants. The findings indicated that the tensile properties of the polyurethane elastomers were enhanced due to the exceptional compatibility and dispersibility of LNPs within the matrix. The flame retardancy of the polyurethane elastomers was significantly enhanced, as evidenced by a high limiting oxygen index of 30% and achieving a UL-94 V-0 rating. Additionally, the total smoke production rate during combustion was reduced, indicating that the functionalized LNPs can act as environmentally friendly functional additives for various polymers. A study by Meng *et al.* [9] reported the functionalization of LNPs through a stepwise grafting process utilizing phenyl dichloro phosphine oxide and 1,4-dimethoxyacetylene on lignin. The functionalized LNPs were subsequently utilized to fabricate thermoplastic polyurethane (TPU) composites. Mechanical properties of the TPU composites such as tensile strength, elongation at break, and toughness showed improvement after the addition of functionalized LNPs. Additionally, notable reductions in flammability were observed, as evidenced by diminished PHRR and smoke production rate.

The aforementioned studies have demonstrated the promising potential of employing nanolignin in the field of flame retardants for composite fabrication. Nevertheless, several challenges impede its widespread adoption. Firstly, the chemical structures of lignin vary significantly based on their sources, influencing their performance in various applications and requiring meticulous selection and modification for specific uses [10]. Furthermore, the method for LNP production also results in various specific characteristics in turn influencing the fire resistance properties of composites. Conversely, obstacles persist in enhancing their compatibility with diverse substrates and augmenting their dispersion in nonpolar matrices. Future research may concentrate on improving the functional properties of LNPs via advanced chemical modifications, as indicated by certain studies referenced by previous researchers [11]. Notwithstanding these challenges, the prospects for nanolignin as a flame retardant remain promising, as it aligns with global initiatives to diminish dependence on halogenated flame retardants and advocate for sustainable materials and sustainable development goals [12]. Nanolignin flame retardants signify a promising direction for environmentally sustainable fire safety solutions, warranting further research and development.

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