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Short Review

Bio-Based Oligomers: Progress, Applications, and Future Perspectives

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Abstract: In response to escalating environmental concerns, the coatings industry is experiencing a profound shift towards sustainability. Central to this transformation are advanced technologies such as water-borne coatings, radiation-curable solutions, and high-solid powder coatings. These innovations are complemented by the increasing use of bio-based materials derived from biomass or biomass-dependent processes, which serve as eco-friendly alternatives to traditional fossil fuel-based materials. These bio-based materials not only provide versatility through chemical modifications but also facilitate advanced curing techniques, significantly enhancing the sustainability profile of coatings. Recent research has made notable strides in developing coatings with a high bio-renewable content, highlighting the sector's commitment to reducing environmental impact. This review comprehensively examines recent advancements in this field, focusing on the integration of bio-based oligomers into various coating formulations. It discusses progress in creating durable and eco-friendly coatings, explores diverse applications, and provides insights into emerging trends and future directions. Key areas of exploration include the use of essential oils, vegetable oils, and bio-based polymers in wood coatings; advancements in flame-retardant bio-based materials; and the development of solvent-free solid polymers using deep eutectic solvents. Additionally, the review covers innovative applications such as electrochromic devices using biomass-derived materials, the use of biomass-derived functional materials for enzyme immobilization, and the challenges and breakthroughs in lignin depolymerization. The integration of bio-based materials with UV-curable technology and the development of aqueous two-phase extraction processes for bio-based monomers further underscore the sector's shift towards sustainable practices. By synthesizing and analyzing these advancements, this study contributes to the ongoing discourse surrounding sustainable coatings, highlighting opportunities for further innovation and providing a roadmap for future research in the development of environmentally friendly coating solutions.

***Keywords*:** bio-based oligomers, coatings, organic-inorganic hybrid system, sustainability, eco-friendly materials

1. Introduction

Binders are critical components in coatings, influencing their characteristics, performance, curing methods, sustainability, and end-use applications. They determine essential properties such as adhesion, durability, film formation, and cohesion, which are crucial for effective performance across diverse applications. Historically, conventional coatings have relied on organic polymers like acrylics, polyurethanes, polyesters, and epoxies, primarily derived from petroleum-based sources.[1,2] Figure 1 presents the structure of the commonly used polymers in the coating industry.

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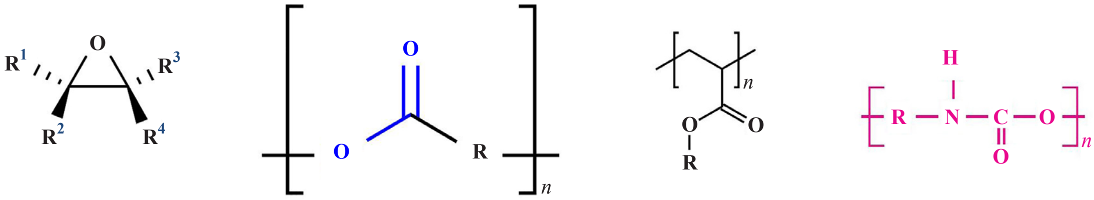

Epoxy Polyesters Acrylics Polyurethanes

Figure 1. Structure of the polymers commonly used in the coating industry

However, there is a growing shift towards renewable and bio-based polymers, driven by concerns about environmental sustainability, economic feasibility, and effective waste management.[3] This transition is prompted by the depletion of fossil fuel reserves, the environmental impact associated with their extraction and use, and the adverse effects of volatile organic compounds (VOCs), which have significant ecological and health implications.[4,5] As a result, both industry and academia are actively exploring alternatives to petroleum-derived chemicals, focusing on green and sustainable materials.[6-8] Bio-based materials, sourced from biomass such as plant oils, lignin, cellulose, and other agricultural by-products, offer a versatile and customizable solution. These materials can be chemically modified to enhance curing techniques, reduce dependency on fossil fuels, and provide lower toxicity and biodegradability, aligning with global sustainability goals.[9,10] Integrating these green materials into coatings represents a significant advancement towards sustainable synthesis, meeting the demand for economically viable and environmentally friendly products.[11] The U.S. Department of Energy has set a goal for 50% of chemical building blocks to be derived from plant-based sources by 2050, emphasizing the need for innovative approaches in developing bio-based binders and polymers.[12,13]

To address environmental concerns, technologies such as waterborne coatings and UV curing are being adopted. Waterborne coatings, which offer benefits like reduced air pollution and lower energy consumption, face challenges such as longer drying times and adhesion issues. Advances in waterborne technology aim to overcome these drawbacks through novel formulations and hybrid systems that combine waterborne resins with other eco-friendly components.[14-17] UV-curing technology, known for its environmental benefits and efficiency, also encounters challenges such as reliance on fossil-based prepolymers and issues related to shrinkage and adhesion. Recent research is focused on developing bio-based UV-curable resins, using vegetable oils, soy-based materials, and other bio-renewable resources to enhance sustainability without compromising performance.[18-21] Moreover, the pursuit of sustainability in coatings is driving the development of hybrid coatings that integrate multiple green technologies. Bio-based resins combined with nanotechnology, for instance, offer coatings with improved mechanical strength, thermal stability, and resistance to environmental degradation.[22-27] This review provides a comprehensive overview of recent research efforts aimed at developing bio-based oligomers for various applications. It highlights advancements in sustainable coatings technology, addresses the challenges and opportunities associated with bio-based materials, and outlines key research trends and future directions in the development of sustainable coatings.

2. Bio-based oligomers/binders

Binders are essential components of coatings, influencing their properties, applications, curing methods, and sustainability. The push towards environmentally friendly coatings has led to significant efforts in developing sustainable binders, incorporating high levels of bio-renewable materials. For example, bio-based chemicals like itaconic acid, tartaric acid, isosorbide, vanillin, cyclodextrin, and lignin have been widely used to modify epoxy resins.[28,29] Lopes et al. reviewed recent advancements in stabilizing lignin, a key raw material for bio-based oligomers. Technologies such as hydrogenation (RCF), alkoxylation (Organosolv), and acetal formation have been employed to achieve high depolymerization yields and prevent condensation reactions, enabling the conversion of lignin into valuable aromatic platform chemicals.[30] Similarly, Ali et al. analyzed photo-curable polyurethanes, categorizing them based on solvent and acrylate components over the past five years. Their study covered various performance parameters, including tensile strength, hardness, flexibility, hydrophobicity, solvent resistance, and thermal stability. Bio-based polyurethane (PU) coatings are gaining popularity due to their environmental benefits, cost-effectiveness, and biodegradability. In contrast, water-based PU coatings are preferred for applications requiring wear and friction resistance due to their soft surface feel.[31,32] Kunduru et al. reviewed renewable polyols for creating biodegradable polyesters, highlighting the potential of these materials for various applications, including tissue engineering, drug delivery, and coatings. They discussed how tailored process conditions and chemical modifications can enhance the properties and applications of these polyesters.[33]

In pioneering work, Hardian et al. developed nanofiltration membranes using chemically recyclable polymers such as polyester and poly(cyclic olefin), utilizing γ-butyrolactone as a sustainable solvent. They explored the effects of physical treatments like annealing and hot-pressing on membrane performance, demonstrating stability over a week of continuous testing. They also created a new class of biosourced nanofiltration membranes based on aliphatic polyesters and green solvents, emphasizing their chemical recyclability and potential biodegradability.[34,35] Yang et al. focused on sustainable membranes, developing plant-based thin film composite (TFC) membranes exclusively from renewable resources. Their fabrication platform converts biomass-based building blocks into high-value products, advancing sustainable membrane technologies.[36] In their studies, they also created a biodegradable electrospun nanofibrous support using polylactic acid (PLA) and gelatin as an interlayer for the TFC membranes. This approach enhances solvent stability and overall performance in osmotically-driven processes, offering promising prospects for further developments in eco-friendly membrane manufacturing.[37,38]

Cavalcante et al. utilized nanodomain engineering to develop interpenetrating biopolymer network membranes from natural compounds with opposing polarity in water, avoiding toxic cross-linking agents. These biodegradable membranes offer a sustainable lifecycle from cradle to grave.[39-40] Skoczinski et al. scaled up the development of furan-based polyester oligomer diols through lipase-catalyzed synthesis, demonstrating their excellent flame retardancy and high thermal stability, which are suitable for industrial applications.[41] Dinu et al. synthesized bio-based tris-epoxy monomers from renewable flavonoid and phlorotannin extracts to create sustainable thermosetting resins. These resins exhibited high glass transition values, storage moduli, and crosslinking densities, along with mechanical strength and heat resistance. Their ability to be chemically recycled enhances their sustainability, making them viable alternatives to petroleum-based epoxy resins for various industries.[42] Figure 2 presents a schematic of the preparation of bio-based UV-curable water-borne polyurethane dispersion (UV-PUD) that Zareanshahraki et al. provided.[43]

Despite these advancements, challenges such as brittleness, slow drying, and inadequate adhesion remain in bio-based coatings, highlighting the need for continued innovation.[44] Glucan oligomers, with applications in agriculture and healthcare, are produced efficiently through glucose glycosylation. However, the random formation of glycosidic bonds limits their applications.[45] The integration of organic-inorganic hybrid crosslinkers has emerged as a promising strategy to enhance the mechanical strength and anticorrosive properties of coatings, offering a balance between performance and eco-friendliness.[46-48] Recent studies have explored bio-based organic-inorganic hybrid UV-curable coatings with self-cleaning properties and practical applications,[49,50] and the addition of tetraethyl orthosilicate (TEOS) into non-isocyanate polyurethane (NIPU) coatings to improve corrosion resistance.[51] Novel approaches include developing water-based organic-inorganic nano-hybrid resins through in-situ hydrolysis-condensation reactions.[52] At the Coating Research Institute, Eastern Michigan University, our team is dedicated to advancing sustainable high-solid organic-inorganic hybrid systems, focusing on innovative curing techniques and renewable materials to meet both performance and environmental goals.[53-55] Figure 3 presents the schematic of the curing mechanism of the organic-inorganic hybrid (OIH) system under various curing conditions.

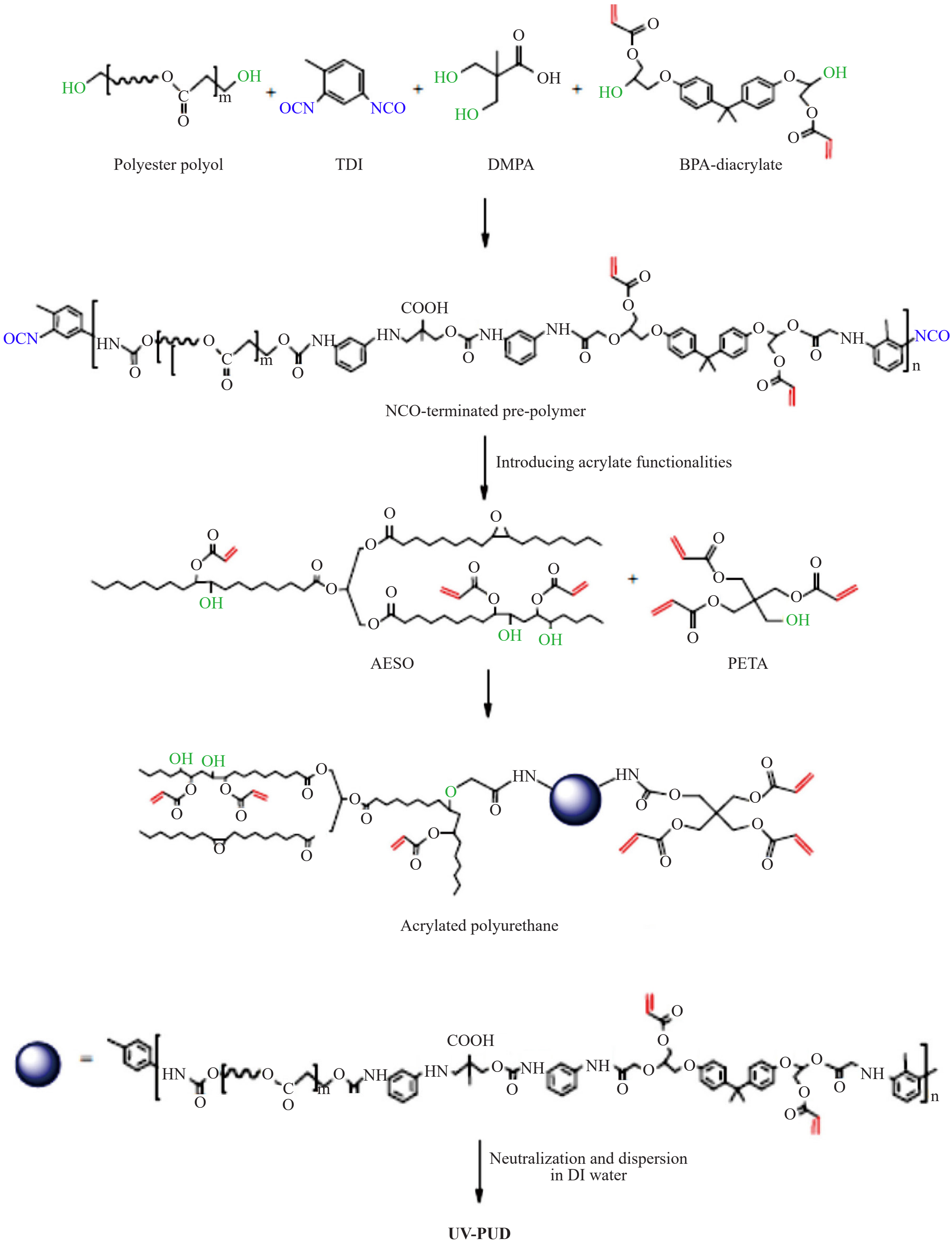

Figure 2. Schematic of the preparation of bio-based UV-curable water-borne polyurethane dispersion (UV-PUD)[43]

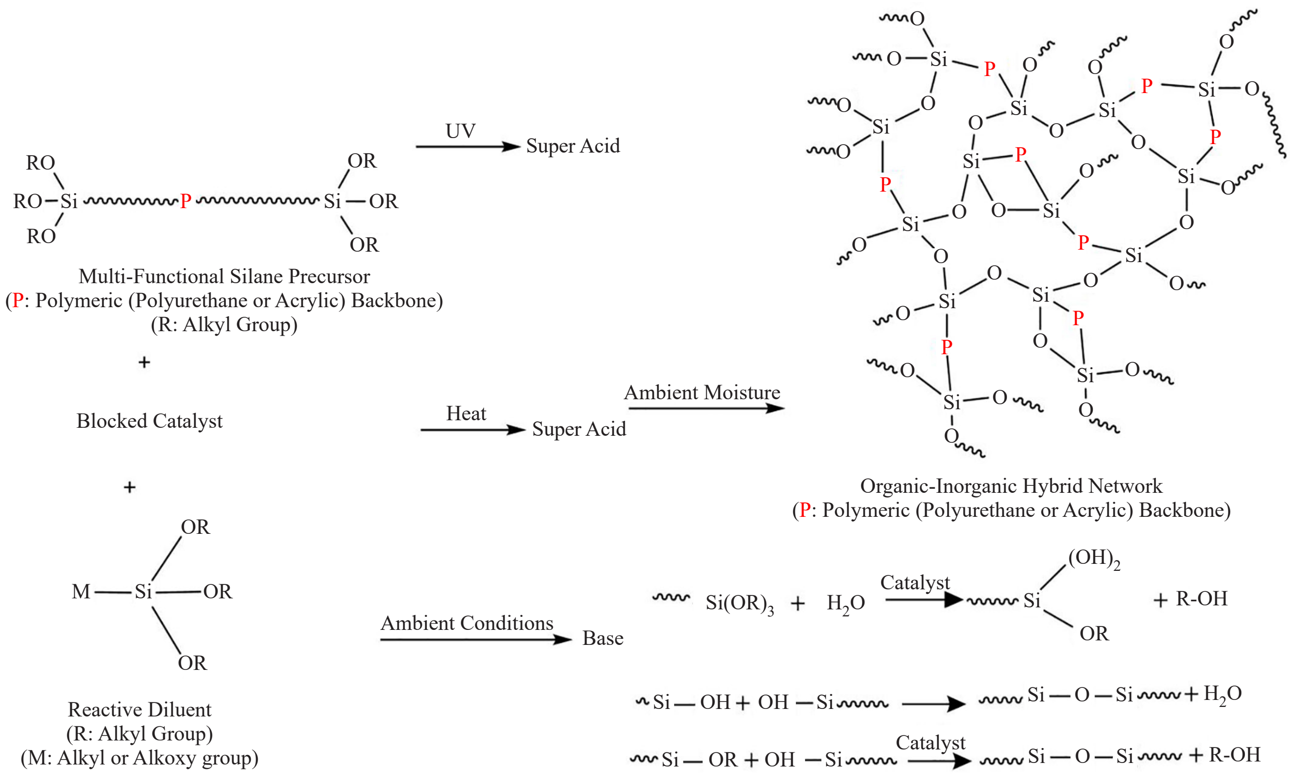

Figure 3. Schematic of the curing mechanism of the OIH system under various curing conditions

3. Applications

Bio-based oligomers have emerged as versatile components in the development of coatings for a wide range of applications. Efforts to create environmentally friendly wood coatings have been extensively reviewed by Calovi et al., who explored the potential of essential oils, vegetable oils, and bio-based polymers in crafting durable and eco-friendly coating matrices. The review also addresses strategies for enhancing weathering resistance and combating biological decay using natural compounds and extracts. It assesses their efficacy as alternatives to traditional chemical preservatives and identifies promising candidates.[56] In another study, Naiker et al. investigated the development of bio-based materials for formulating flame retardant coatings. They explored the use of natural resources, such as phosphorus-based flame retardant systems, to create fire-safe coatings. The study emphasizes the synergistic effects of incorporating elements like nitrogen, silicon, boron, and sulfur alongside phosphorus, highlighting the potential of bio-based phosphorus-containing flame retardants.[57] Additionally, there is growing interest in designing durable flame-retardant epoxy coatings with superior mechanical properties, thermal resistance, and transparency. The introduction of hyperbranched, phosphorus-containing bio-based flame retardants presents a promising avenue for achieving these objectives.[58]

Zhang et al. introduced deep eutectic solvents (DESs) as green alternatives to traditional organic solvents and ionic liquids. They leveraged the formation mechanisms and macroscopic properties of DESs to develop a green strategy for creating solvent-free solid polymers (SPs). This innovative approach enhances the performance of SPs without the use of solvents.[59] Electrochromic devices (ECDs) are materials that can undergo reversible changes in transmittance when exposed to different applied potentials. Eduardo et al. presented a furan trimer as a discrete electrochromic material that transitions from light yellow to red with high coloration efficiency. They attribute this effect to the reversible π-stack formation of the oligomer radical cations, as demonstrated by both experimental and computational results. The ease of synthesizing this oligomer from biomass makes it an appealing alternative to existing organic electrochromic materials.[60] Bisht et al. reviewed advancements, challenges, and future prospects in the field of biomass-derived functional materials (BDFMs) such as cellulose, silk protein, chitin, chitosan, lignocellulose, and combinations of biopolymers like chitin/lignin and chitosan/alginate for enzyme immobilization. They examined the relationship between the structural properties and functionality of enzymes immobilized in BDFMs, and evaluated the impact of factors such as pH, temperature, reusability, storage stability, and enzyme activity.[61] Murnaghan et al. investigated the laccase-catalyzed oxidation of a lignin model hexamer to address key questions regarding lignin depolymerization. They found that the model hexamer effectively represents lignin, including the recalcitrant bond types that hinder the complete depolymerization of lignin into monoaromatics. Their findings suggest that the laccase-catalyzed depolymerization of various types of waste lignin, such as lignosulfonate, organosolv lignin, and Kraft lignin, is inefficient for producing monoaromatic feedstock chemicals.[62]

In a pioneering study, Sarangi et al. explored the use of agricultural residues as renewable biomass for producing green fuels and other sustainable biochemicals. They demonstrated that these residues offer a cost-effective and environmentally friendly alternative to fossil fuels. Their work includes a summary of biorefinery solutions and a life cycle assessment of agricultural waste biomass, highlighting its potential to produce a wide range of value-added products that support the bioeconomy.[63] Chan et al. pioneered aqueous two-phase extraction processes for the separation and purification of furfuryl alcohol monomers and oligomers. By examining variables such as partition coefficients and extractability, they found that deionized water achieved a high oligomer content of approximately 94 wt% in the separated furfuryl alcohol oligomer solution. In contrast, salting-out extraction resulted in a furfuryl alcohol purity of about 92 wt%.[64] The integration of bio-based materials with UV-curable technology represents another significant advancement, particularly in the industrial, cosmetic, and beauty sectors. Ongoing research continues to explore the utilization of bio-based oligomers across various sectors, with the goal of further enhancing their sustainability.[65-67]

4. Summary and future prospectives

The future of bio-based oligomers in coatings is poised for significant advancements as industries increasingly embrace sustainability. As environmental concerns mount, there is a concerted effort to optimize renewable resources such as essential oils and bio-based polymers. These resources are being harnessed to produce coatings that are not only durable but also environmentally friendly. The focus on eco-friendliness is evident in specialized applications, including wood coatings and flame-retardant formulations, where natural compounds are employed to mitigate environmental hazards effectively. Integrating bio-based oligomers with advanced technologies, such as UV-curable coatings and nanotechnology, presents promising opportunities to enhance coating performance across diverse industries. The synergy between bio-based materials and cutting-edge methodologies is paving the way for coatings with superior mechanical properties, improved thermal resistance, and enhanced transparency. This integration not only augments the functional attributes of coatings but also reinforces the industry's commitment to sustainable practices. Looking ahead, collaboration between academia and industry will be essential in driving the development and widespread adoption of bio-based oligomers. Such partnerships can accelerate innovation, facilitating the efficient commercialization of sustainable, high-performance coating solutions. Continued research and technological advancements will be crucial in overcoming existing challenges, such as achieving optimal balance between performance and environmental impact. As bio-based oligomers evolve, they are expected to become a cornerstone of the coatings industry, providing eco-friendly alternatives that address the growing demand for sustainable solutions. The trajectory of bio-based oligomers promises a future where coatings not only meet the functional requirements of modern applications but also align with global sustainability goals, marking a pivotal shift towards a greener and more responsible industry.

Conflict of interest

The author declares no competing financial interest.

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