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ORIGINAL RESEARCH

# Superhydrophobic bio-based polybenzoxazine-silica coatings on cellulose and mild steel for oil–water separation and anticorrosion properties

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**Abstract** Due to rising environmental concerns and the necessity to reduce the use of fossil-based resources, the development of fully/partially bio-based polymer composites have gained considerable attention. In this connection, an attempt has been made to develop partially bio-based vanillin-based polybenzoxazine-silica (PBZ-Si) hybrid nanocomposites by simple sol–gel approach for multifunctional applications, including oil–water/ oil–water emulsion separation, anti-icing, thermal, and corrosion resistance. The benzoxazine monomers (V-fa and V-sa) were prepared through Mannich reaction using vanillin (V), stearylamine (sa)/ or furfuryl amine (fa) and paraformaldehyde. The synthesized benzoxazines were confirmed by FT-IR, $^{1}H$ NMR, and DSC. To enhance the hydrophobic, and thermal properties of the neat PBZ, silica was introduced to develop PBZ-Si hybrids by an in-situ sol–gel approach using V-fa/ or V-sa, 3-aminopropyl triethoxysilane (3-APTES) and tetraethyl orthosilicate (TEOS) followed by thermal ring-opening polymerization. The incorporation of silica into PBZ hybrid composites enhanced the thermal stability, good oil–water/ oil–water emulsion separation and anti-corrosion properties. Notably, the PBZ-Si hybrid composites coated cellulose substrate showed a higher value of water contact angle of $156 \pm 1°$ and achieved a high oil flux value of 27,283 $Lm^{-2}$ $h^{-1}$ and separation efficiency of 99.5% even after 20 cycles. The PBZ hybrid coated on cellulose substrate exhibited better separation ability even after the substrate was treated with adverse conditions, including acidic, basic, abrasion, and temperature. Further, the PBZ-Si hybrids coated on MS substrates revealed good corrosion-resistant behaviour with an inhibition efficiency of 96%. As research and development continue, these bio-based, sustainable PBZ hybrid materials may play a pivotal role in advancing separation technologies and corrosion-resistant applications.

**Keywords** Oil–water separation · Oil–water emulsion separation · Anti-corrosion · Polybenzoxazine · Sol–gel technique

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## Introduction

The ecology is severely damaged by the fast development of the chemical and petrochemical industry (Bai et al. 2020; Grabowski et al. 2017), oil spills (Hu et al. 2020), and oil drilling operations beneath the sea (Pendergast et al. 2011; Zhang et al. 2018), endangering not just human society but all living things. Oil spills lead to environmental degradation, including damage to marine ecosystems, toxicity to marine organisms, and a decline in biodiversity (Gupta et al. 2017; Chen et al. 2018). Similarly, the petrochemical industry contributes to environmental pollution through the accumulation of hazardous waste, groundwater contamination, and air and soil pollution. As a result, both academic and industrial sectors urgently necessitate the development of innovative oil–water separation methods (Bai et al. 2020; Grabowski et al. 2017; Hu et al. 2020) and anticorrosion materials (Chernykh et al. 2009; Zhou et al. 2014). Classical methods (Bai et al. 2020; Grabowski et al. 2017; Hu et al. 2020) like centrifugation, coalescers, skimming, coagulation-flocculation, in-situ burning, microbiological degradation, gravity settling, and electrochemical treatments are used to address the oil–water separation problems. However, they have significant drawbacks (Bai et al. 2020; Grabowski et al. 2017), including high operating costs, poor separation efficiency, low flux, a need for excessive energy for operations, and seriously induce the secondary pollutants. To address these challenges, superhydrophobic surfaces inspired by nature-such as lotus leaves, rose petals, butterfly wings, peacock feathers, water strider legs, and gecko skin-have attracted significant interest. (Bai et al. 2020; Zhou et al. 2014). Superhydrophobic materials constructed from various substrates (Bai et al. 2020; Hu et al. 2020) such as fabric, mesh, sponge, foam, filter paper, metallic mesh, polymeric membrane, and textiles have also been explored due to their superwetting porous nature. At present, two primary approaches are being developed for the separation of oil–water mixtures: filtration (Pandi et al., 2024; Bai et al. 2020) and absorption (Peng et al. 2019; Periyasamy et al. 2022). The absorption method faces several drawbacks, including difficulty in removing emulsified oil–water mixtures, low absorption capacity, limited ability to treat large-scale contamination, challenges in recycling, and reduced overall efficiency. In comparison, the filtration method overcomes these shortcomings effectively.

Corrosion is another significant global issue, leading to substantial economic losses and environmental challenges each year (Cao et al. 2021; Mahdy et al. 2023). It poses serious environmental concerns, including soil and groundwater pollution caused by the leakage of toxic chemicals, oil, and petrochemical waste from deteriorating pipelines. Corrosion is a natural phenomenon in which metallic materials degrade due to electrochemical and chemical reactions with their surrounding environment (Hariharan et al. 2020; Xu et al. 2019). It creates several struggles for the marine, transport, chemical/petrochemical, production, and construction industries. Corrosion is estimated to cost the global economy over $2.5 trillion annually, posing a significant economic burden worldwide. Various approaches have been adopted widely and explored to resolve the corrosion problems (Peng et al. 2019; Lee et al. 2016). Generally, coatings of organic materials are considered as one of the best approaches to resist the corrosion, definitely enhancing the longevity of the metallic substrates and lowering the financial costs (Hariharan et al. 2020; Xu et al. 2019). Though the anti-corrosion efficacy of organic coatings is mostly inadequate for use in extremely violent environments. Polymer-based coatings are an efficient method to resolve these issues. Polymer coatings primarily function as effective physical barriers, providing high resistance to ionic transport and electrical conductivity. They prevent the penetration of corrosive agents such as water, ions, and oxygen to the metal surface, thereby offering protection against corrosion (Mahdy et al. 2023; Peng et al. 2019). Consequently, addressing the challenges of efficient oil–water separation and the development of anticorrosion materials has become a significant global priority. Researchers have focused on developing superhydrophobic materials with anticorrosion properties, such as fluoropolymers, organosilanes, siloxanes, and polybenzoxazines. Among these, polybenzoxazine has shown particularly promising properties, including superhydrophobicity, low water absorption, insulating properties, high glass transition temperature ($T_g$), minimal shrinkage, lightweight, flexibility, and thermal stability. These characteristics make polybenzoxazine an excellent choice for various multifunctional applications (Bai et al. 2020; Pendergast et al. 2011; Cao et al. 2021) such as

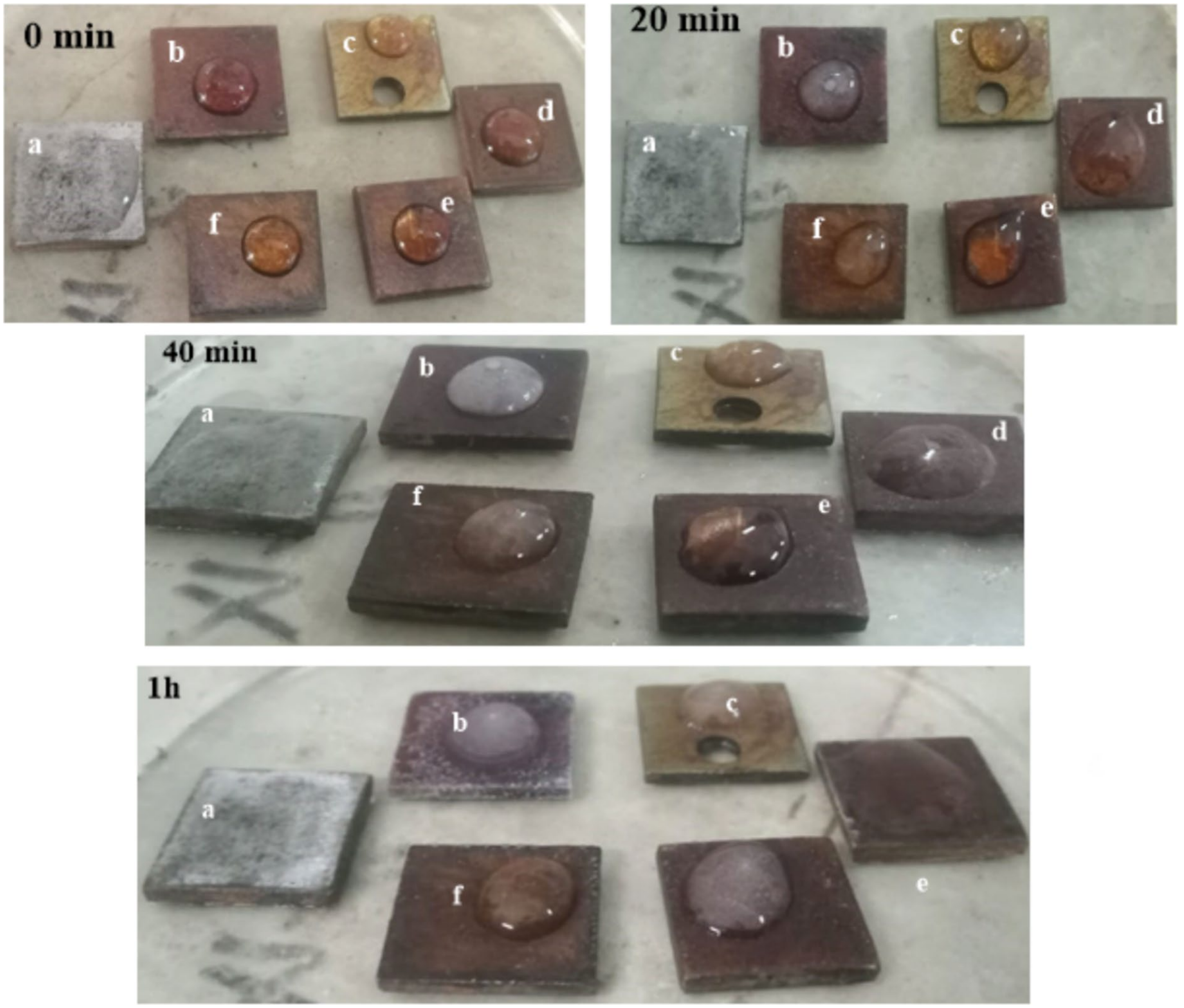


**Fig. 11** Anti-icing study of uncoated and PBZ hybrid-coated MS substrates in different time durations

surface retained the original droplet shape due to its low surface free energy and superhydrophobicity, preventing freezing. After an hour, snow covered the MS substrate, yet the water droplets on the PBZ-coated surface remained distinct, with little to no interaction with the substrate, indicating oleophobic properties. Upon attempting to remove the crystallized water droplets and snow, the uncoated MS surface exhibited strong adhesion, making it difficult to remove frozen ice. Conversely, the PBZ hybrid coated MS surfaces allowed easy removal of snow and droplets, attributed to their low adhesion and hydrophobic properties. These results suggest that bio-based PBZ hybrid materials could be suitable for various applications, including superhydrophobic coatings to prevent ice accumulation on surfaces.

## Conclusion

Successfully developed partially bio-based polybenzoxazine silica hybrid composites from vanillin-based benzoxazines (V-fa and V-sa), 3-APTES and TEOS by the sol–gel approach followed by thermal curing. The prepared PBZ and PBZ-Si hybrids were used to modify the surface of cellulose and MS substrates for oil–water/oil–water emulsion separations and corrosion-resistant applications. PBZ silica hybrid coated on cellulose substrate revealed the water contact value of 156° with the high oil-flux value of 27,283 L $m^{-2}$ $h^{-1}$ (oil–water separation), 17,050 L $m^{-2}$ $h^{-1}$ (oil–water emulsion separation), and 99.5% separation efficiency even after 20 cycles. The silica-reinforced PBZ hybrid composites exhibited superior thermal stability and a higher char yield (68.7%) compared to neat PBZ (46.1%). The corrosion resistance of PBZ-hybrid coatings on MS substrates was evaluated using electrochemical measurements, and it was observed that increasing the silica content in the PBZs significantly improved corrosion resistance, achieving an inhibition efficiency of 96%. Moreover, PBZ coatings on cellulose substrates demonstrated excellent self-cleaning and anti-icing properties, making them highly suitable for separating oil–water mixtures and oil–water emulsions under harsh environmental conditions.

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**Author contribution** PP: Conceptualization, Methodology, Formal analysis, Investigation, Data Curation, Writing—Original Draft DS: Conceptualization, Validation, Resources, Writing—Review & Editing, Supervision, Project administration. KA: Formal analysis, Investigation, Data Curation, Writing—Original Draft.

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**Data availability** The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Declarations**

**Conflict of interest** The authors declare no competing interests.

**Ethics, consent to participate, and consent to publish** Not applicable.

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