Design of flexible Cardanol-derived Poly (benzoxazines) for Advanced Coatings: Superhydrophobicity, Self-Cleaning, Oil–Water Separation and Corrosion Resistance

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Abstract

In the present work, an attempt has been made to develop flexible, partially bio-based polybenzoxazine matrices with superhydrophobic behaviour for improved oil-water separation, self-cleaning and anti-corrosive properties. A new type of card-bisphenol (COBP) has been synthesized using cardanol and octanaldehyde as eco-friendly, natural precursors to substitute fossil-based materials to maintain environmental sustainability. Four distinct benzoxazines (COBP-oa, COBP-dda, COBP-oda, and COBP-fa) were synthesized using COBP and different types of amines viz., octylamine (oa), dodecylamine (dda), octadecyl amine (oda) and furfurylamine (fa) with para formaldehyde through Mannich condensation reaction. The non-polar nature of these long aliphatic chains present in the benzoxazine molecules contributes to an enhanced superhydrophobic behaviour. Structural characterization of the synthesized monomers was confirmed through FT-IR and 1 H NMR spectroscopic analyses. DSC analysis infers that the curing temperature of benzoxazine monomers is increased with increasing the aliphatic chain length. Data from TGA ascertain that the poly (COBP-fa) exhibited the highest thermal stability and char residue, among the synthesized polybenzoxazines (PBZs). The COBP-oda possesses a higher value of water contact angle of 155 ◦ which in turn contributes to superhydrophobic behaviour. The superhydrophobic behaviour also contributes to superior corrosion resistance, with an inhibition efficiency of 95.87 %. Further, it was also observed that the PBZ-coated cotton fabric achieved an oil-water

separation efficiency of >90 %. The oil-absorption properties of the PBZ-modified foams showed 96–99 % oil absorption efficiency. Data obtained from different studies ascertain the versatility of the developed materials and suggest their utility towards high- performance coating applications, under adverse environmental conditions.

Keywords: Card-bisphenol, bio-based polybenzoxazines, superhydrophobic behavior, oil-water separation, corrosion-resistance.

1. Introduction

Superhydrophobic behavior has recently gained fascinating attention due to its excellent water repellency (water contact angle >150º), leading to enhanced oil-water separation, self-cleaning, anti-corrosion and anti-fouling properties. This phenomenon is ubiquitous, as it is found in natural lotus leaves, mosquito eyes, butterfly wings, water-strider legs, taro leaves, etc., [1]. The development of superhydrophobic polymeric coatings is easier when compared to that of inorganic materials due to the requirement of complex techniques (lithography, laser ablation, chemical etching, etc.). Polybenzoxazines (PBZs) replace the conventional phenolic thermoset polymers due to their flexibility in modifying the chemical structures, which enhances the superhydrophobic nature and other properties including high glass transition temperature (T_g), thermal stability, no need for the catalyst or curatives for polymerization, no shrinkage during curing, better chemical resistance, flame retardancy and low moisture absorption [2]. Despite these advantages, limited toughness, the requirement of high cure temperature and brittleness need to be addressed in order to utilize them for wide range of high performance applications [3].

However, petroleum-based PBZs are facing challenges due to economic and environmental concerns. Concerning these drawbacks, the precursors and monomers derived from natural and renewable resources have been focused in recent years on synthesizing eco-friendly PBZs [4]. As the benzoxazine monomer is synthesized from phenol, primary amine and formaldehyde through Mannich condensation reaction [5], various naturally available phenols and amine sources have been widely used for synthesizing bio-based benzoxazines [6]. Bio-based phenols such as cardanol [7–9], eugenol [10–12], vanillin [13,14], magnolol [15], sesamol [16,17], coumarin [18,19], urushiol [20–22], resveratrol [23], etc., and bio-based amines such as furfuryl amine, stearylamine [24,25], etc., were commonly utilized for synthesizing bio-based benzoxazines. Cardanol is one of the widely used agro-waste bio-phenols, extracted from cashew nut shell liquid. As it contains a long unsaturated side chain, it is commonly used in coating industries, diesel engine fuels, lubricants, additives and flame retardants [26].

Bifunctional benzoxazines offer several advantages over monofunctional benzoxazines, including improved cross-linking density and enhanced thermal stability, required for high-performance applications [27]. Further, to overcome the problems in processability and to improve mechanical strength, additional functionalities and novel polymeric precursors have been incorporated into the benzoxazine monomer to develop high-performance polybenzoxazines [8,28,29]. Specifically, to enhance the superhydrophobic properties, certain surface modifications, chemical functionalities, hydrophobic moieties and nanoparticles like silica and carbon materials have been incorporated which improves roughness and low surface energy [30,31]. This contributes to resisting aggressive species and acts as an anti-corrosive coatings. Metallic corrosion can be prevented by polymeric coatings possessing hydrophobicity, high crosslinking, etc., which prevents the corrosion reaction by acting as a barrier against electrolytes [32–34].

Corrosion poses a significant economic challenge, particularly in the oil and gas sectors. To address this issue, extensive research has been conducted on corrosion mechanisms and alternative polymeric coating materials [35]. Among the corrosion-resistant coatings are biodegradable polymeric coatings based on Mg alloys [36], other biodegradable polymers such as polylactic acid [37], and graphene oxide (GO) nanofiller-reinforced rubber-modified polybenzoxazine [38]. Bio-based polybenzoxazines are alternatives to classic phenolics, and the bio-phenol “cardanol” is widely utilized for preparing biocomposites to produce sustainable and biodegradable reinforcements [39]. This bio-phenol exhibits flexibility and hydrophobicity owing to the presence of either saturated or unsaturated 15 methylene units in its structure [40]. As it is derived from renewable bio-source and is eco-friendly, various applications has been investigated [41,42]. Furthermore, hydrophobicity contributes to oil-water separation, and cardanol-based polybenzoxazine precursors for oil-water separation have been widely utilized [43–47]. To the best of our knowledge, a single polybenzoxazine material possessing superhydrophobicity, corrosion resistance, and oil-water separation has not been explored with bifunctional cardanol combined with long alkyl chain moieties such as aliphatic aldehydes and amines.

The present work focused on the development of toughened, partially bio-based benzoxazines to replace the traditional petroleum-based polybenzoxazines with improved superhydrophobic oa/dda/oda/fa) coated cellulose substrates exhibited self-cleaning properties. Even though juice, milk and tea did not stick on to the surface, they shown stains which were removed by water, as shown in Figure. 16 (a), (b) and (d).

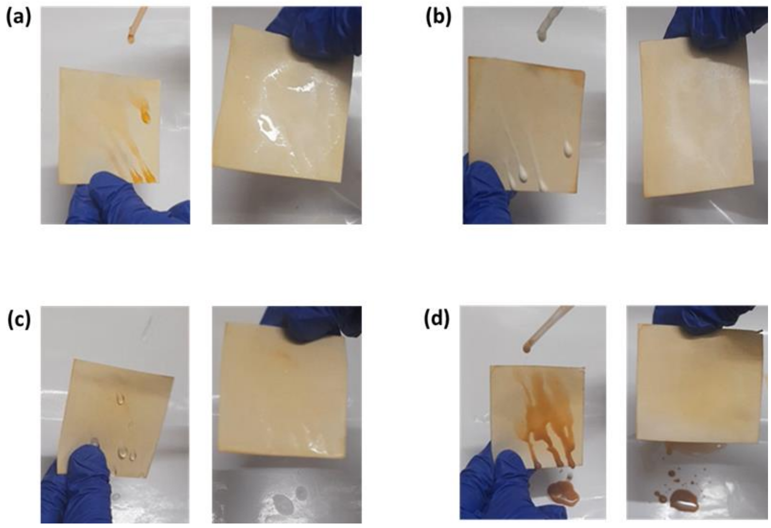

Figure 16. Self-cleaning performance of COBP-based polybenzoxazine matrices coated filter paper with juice **(a)** milk **(b)** water **(c)** and tea **(d)**.

4. Conclusion

Four new types of partially bio-based polybenzoxazine matrices from cardanol-based bisphenol (COBP) with varied nature of amines including octylamine, dodecylamine, octadecylamine and furfurylamine have been developed for corrosion resistant, oil-water separation and self-cleaning applications. The synthesized new type of benzoxazine monomers was confirmed from FT-IR and ^{1}H NMR spectra. The poly (COBP-oa/dda/oda/fa) matrices obtained were used to modify the surfaces of cellulose substrate and MS specimen for oil-water separation and corrosion resistant applications. Poly (COBP-oa/dda/oda/fa) matrices exhibited the water contact value of $\leq 155^{o}$ with the oil-water separation efficiency of $\leq 96\%$ even after many cycles. The developed poly (COBP-oa/dda/oda/fa) matrices possess better thermal stability with the maximum degradation temperature of over 450^{o}C. Further, corrosion-resistant behaviour of poly (COBP-oa/dda/oda/fa) matrices coated on MS specimens was checked with electrochemical measurements. It was found that poly (COBP-oda) matrices coated on MS substrate exhibit a remarkable improvement of corrosion resistance with the inhibition efficiency of 95.87%. Further, the poly (COBP-oa/dda/oda/fa) coated on cellulose and MS substrate possess good self-cleaning and anti-corrosion characteristics. Even though cardanol-based polybenzoxazines have been widely explored, the multiple functionalities (superhydrophobicity, corrosion-resistance and oil-water separation) in a single material system are unconventional. The present work is considered a unique concept in the field of development of partially bio-based benzoxazine materials suitable for separating oil-water mixture towards environmental pollution control and corrosion-resistant coatings to protect the surfaces of iron and steel products.

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Data availability

Data will be available on request.

Declarations

Ethics approval and consent to participate: Not applicable.

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Conflict of interest

The authors declare no conflict of interest.

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