Unlocking the potential of hydroxylated chalcone-based photosensitive benzoxazines: Synthesis, multifunctional properties and theoretical insights from DFT

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Abstract

This work pioneers the synthesis of a new class of benzoxazine monomers incorporating hydroxylated chalcone units (HAN-HB) using 2′-hydroxy-1′-acetonaphthone (HAN) and p-hydroxybenzaldehyde (HB) by following Claisen-Schmidt condensation process. Three types of structurally varied bifunctional benzoxazines were prepared using hydroxylated chalcone (HAN-HB) and paraformaldehyde separately with tyramine (ty), 3-amino-1-propanol (ap) and 2-(2-aminoethoxy)ethanol (aee) by adopting Mannich condensation. Both hydroxylated chalcone and benzoxazines molecular structures were confirmed by different spectroscopic analyses. DSC analysis reveals that HAN-HB-ap benzoxazine showed the lowest T_p value of 214^{o}C. Poly(HAN-HB-ty) possesses the highest values of thermal decomposition temperature and percentage char yield. Further, all the polybenzoxazines exhibit self-extinguishing and good heat-resistant properties. In addition, synthesized benzoxazines showed good anti-microbial behavior. Photosensitive property of the benzoxazines were studied using UV-Visible spectroscopic analysis and the results indicated that the synthesized benzoxazines exhibited both photoisomerization and photocross-linking due to their inherent molecular rearrangement ability. Aggregation caused quenching (ACQ) characteristic was observed for the benzoxazines through fluorescence study. From the water contact angle study (WCA), it was inferred that all the poly(HAN-HB-Bz) exhibited water repellent nature and obtained higher WCA of 151^o. The corrosion resistant behavior of polybenzoxazines towards mild steel (MS) surface was studied and the results obtained infer that these materials exhibit good protection efficiency. DFT studies were performed for all the chalcone based benzoxazines. The incorporation of hydroxyl groups not only improves hydrogen bonding interactions, enhancing thermal stability and also introduces photo-reactivity. This dual functionality is not commonly reported in conventional benzoxazines. The results obtained from various studies suggested that the developed chalcone based benzoxazines to be suitably exploited for advanced photosensitive coating applications.

Keywords: Chalcone based benzoxazines, photosensitive, microbial resistance, corrosion protection, DFT, aggregation caused quenching.

Introduction

Phenolic resins are commercially valuable material toward industrial point of view due to its versatile nature such as excellent mechanical strength, good heat resistance and competitive cost, making them suitable for wide range of applications [1,2]. Polybenzoxazine, represents a promising alternative to traditional phenolic resins, offering improved performance and versatility for various multifaceted applications [3,4]. Polybenzoxazine exhibits excellent thermal stability, low dielectric properties, flame retardancy, low surface energy, low shrinkage on curing, and high char yield [5–10]. The unique combination of properties makes benzoxazine as one of the ideal materials for coatings, adhesives, sealants, potting agents, encapsulating materials, and composites for a wide range of applications, including automotive, aerospace and electronics industries [11–17]. Additionally, the flexible molecular design of benzoxazine allows for tailoring its properties to meet specific application requirements such as photosensitive, corrosion resistance, insulation behavior and antibacterial activities [18–20]. The tailor-made properties of polybenzoxazines can be achieved by utilizing molecular design flexibility and incorporating the specific functional groups into the benzoxazine moiety.

To enhance the properties of polybenzoxazine, researchers have adopted an alternative method of using hydroxylated chalcones instead of traditional phenols [21,22]. By incorporating hydroxylated chalcones, it can potentially improve the properties of the resulting materials to an appreciable extent. This approach not only diversifies the molecular structure of polybenzoxazine, but also opens a new avenue for fine-tuning its properties suitable for indented applications, viz., photocurable materials, semiconductors, fluorescence probes, etc., [23].

Chalcones, as prominent flavonoids found in vegetables and fruits, possess α,β-unsaturated carbonyl groups that endow them with a diverse range of biological activities with inherent chemical behavior [24,25]. The properties of chalcone based benzoxazine make them suitable for coatings to protect metallic surfaces, photoresists in microlithography processes, and printing materials in additive manufacturing processes [26–28]. Further, chalcone-based monomers, undergo photochemical reactions to form cross-linked network structured thermosets with enhanced properties suitable for photolithography, and photopatterning [26].

In the present work, the hydroxylated chalcone was synthesised through Claisen-Schmidt condensation process. Analytical techniques like ATR-FTIR and ^{1}H-NMR were employed to ascertain the formation of targeted bifunctional benzoxazines. DSC and TGA studies were performed to assess the thermal behaviors of the synthesized materials. The synthesised materials were subjected to diversified application studies like optical, hydrophobic, anti-corrosion and anti-microbial coatings and the results are discussed in the subsequent sections.

Table 4. Corrosion parameters obtained from Tafel and Nyquist plots

Sample code	E_{corr} (mV)	I_{corr} (mA)	β_c (mV dec^{-1})	β_a (mV dec^{-1})	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	Corrosion rate (mpy)	η (%)
Blank MS	-2.77	3.11×10^{-3}	-3.16	-2.74	1346.51	5.90×10^{4}	3.61×10^{1}	0
Poly(HAN-HB-ty)	0.06	4.96×10^{-9}	-1.00	1.06	2361.89	1.63×10^{7}	5.76×10^{-5}	100
Poly(HAN-HB-ap)	-0.21	3.46×10^{-8}	-1.29	0.69	1917.61	1.53×10^{7}	4.02×10^{-4}	99
Poly(HAN-HB-aee)	-0.34	1.75×10^{-8}	-1.41	0.06	1632.75	1.34×10^{7}	2.03×10^{-4}	99

Conclusion

The hydroxylated chalcone (HAN-HB) was successfully synthesised as a precursor to prepare three different photosensitive benzoxazines. The molecular mass of hydroxylated chalcone and molecular structure of both chalcone and benzoxazines were characterized using modern analytical techniques. Among the synthesized benzoxazines HAN-HB-ap exhibit the lowest curing temperature of 214^{o}C. Poly(HAN-HB-ty) showed the highest thermal stability with the char output of 44% at 850^{o}C. All the synthesized polybenzoxazines exhibit self-extinguishing behavior. UV-Visible spectroscopic analysis infer that synthesized hydroxylated chalcone based benzoxazines showed both photo-crosslinking and photo-isomerization phenomena. Results from fluorescence study inferred that all the benzoxazines exhibited aggregation caused quenching behavior. Among the benzoxazines, HAN-HB-ap exhibits the greater inhibition zone of 12 mm than rest of the benzoxazines. WCA values ascertain that all polybenzoxazines exhibited good hydrophobic nature and the results from corrosion studies infer that all the synthesized polybenzoxazines showed the corrosion protection efficiency of greater than 99%. On utilizing the DFT technique energy gap, dipole moment were calculated. As discussed from all the results it has been suggested that the hydroxylated chalcone based benzoxazines can be suitably exploited for advanced photo-curable anti-corrosion coatings applications.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability

Data will be made available on request.

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