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Studies on thermal, optical, anti-microbial and corrosion resistant properties of diarylidene cycloalkanones-based benzoxazines

Subasri Appasamy[1] · Balaji Krishnasamy[1] · Sowbakya Palani[1] · V. Kavimani[2]

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Abstract
Two series of photosensitive diarylidene cycloalkanones-based benzoxazines were synthesized using vanillylamine (va), tyramine (ty) and aminophenol (ap) with bis-hydroxyl derivative of divanillidene cyclopentanone (DVCP) / cyclohexanone (DVCH) through Mannich condensation. The structure of the synthesized benzoxazines were confirmed from ATR-FTIR and ^{1}H-NMR spectral analyses. Curing behavior and thermal stability were studied using DSC and TGA, respectively. DVCP-ap/DVCH-ap-based benzoxazines exhibited the lowest curing temperature of 211 °C and 202 °C, respectively, than rest of the benzoxazines. Among the synthesized polybenzoxazines DVCP-ap/DVCH-ap exhibited higher char yield value of 55% and 57%. The α, β-unsaturated moiety present in the divanillidene cyclopentanone/cyclohexanone undergone 2π + 2π cycloaddition reaction to form cyclobutane on irradiation under UV light of 365 nm and leads to form a cross-linked network structure. Also, aggregation-induced emission has been explored by adding water fractions to the benzoxazine solvent mixture. Poly(DVCP-ty) exhibited the highest water contact angle value of 146° and possess an excellent corrosion protection efficiency of above 98% toward mild steel surfaces.

Keywords Diarylidene cycloalkanones-based benzoxazines · Photosensitive behavior · Aggregated induced emission · Thermal stability · Antimicrobial behavior · Corrosion resistance

✉ Balaji Krishnasamy
balaji.psgtech@yahoo.co.in

[1] Department of Chemistry, PSG Institute of Technology and Applied Research, Neelambur, Coimbatore 641062, India

[2] Department of Mechanical Engineering, Centre for Material Science, Karpagam Academy of Higher Education, Coimbatore 641021, India

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Introduction

Scientists and researchers worldwide are continually trying to develop new precursor materials for advanced polymeric materials with a view to utilize them for high-performance industrial and engineering applications [1–4]. Among the materials used for high-performance applications, polymeric materials play a significant role as coatings, adhesives, sealants, encapsulants, matrices, elastomers, plastics, and composites [5–7]. In this context, polybenzoxazines, a new type of phenolic thermoset resins, have been developed which possess low water absorption, high glass transition temperature (T_g), superior mechanical and thermal properties, near-zero volumetric shrinkage, and excellent electrical properties [8–11]. These attributes arise from the intra- and intermolecular hydrogen bonding exist within the cross-linked network structure of polybenzoxazines [12–14]. The flexible design of benzoxazine monomers with various functional groups in the phenol or amine structure enhances their versatility in organic coatings with enhanced thermal stability [15, 16]. Due to their high-performance characteristics and cost-competitive nature, polybenzoxazines are considered as potential polymeric substitute materials to replace several conventional resins such as phenolics, epoxies, and cyanate esters in the wide range of applications. Also, in order to broadening the utilization and scope of the benzoxazines has been explored in the field of CO_2 capture, metal-ion adsorption, UV light shielding and anti-corrosion coatings [17–24].

A new class of photocross-linkable main-chain polymers containing photo-active bisbenzylidene cycloalkanone groups, a stilbenoid class of organic molecules, have been proposed [25, 26]. These polymers exhibit both mesogenic and photo-active properties. The presence of bisbenzylidene unit imparts high thermal stability, which can be further enhanced through thermal or optical crosslinking [27, 28]. The photo-reactivity of these polymers can be controlled by modifying the structure through the appropriate selection of cycloalkanone. Polymers having conjugated benzylidene group influence both charge mobility and thermal and photo stability favorable for potential applications in photo recorders, photocurable coatings, energy exchange materials, and printing plates [29, 30]. Photopolymerization serves as the basis for numerous conventional applications, including coatings, adhesives, inks, printing plates, optical waveguides, and microelectronics. The bisbenzylidene cycloalkanones being an optically active compounds, find application in the field of fluorescent sensors, photoresist technology, optical data recording and UV shield materials [29, 31].

The present study focuses on the development of two series of di-chalcone-based benzoxazines using vanillylamine, tyramine and aminophenol with paraformaldehyde through Mannich reaction. The molecular structure, curing temperature, thermal stability and hydrophobic behavior of the synthesized benzoxazines were characterized using appropriate analytical techniques. Anti-bacterial activity of the synthesized benzoxazines were studied against two different bacteria. Optical properties were studied using UV–Vis spectrophotometer and aggregation-induced emission was ascertained using fluorescence spectrophotometer.

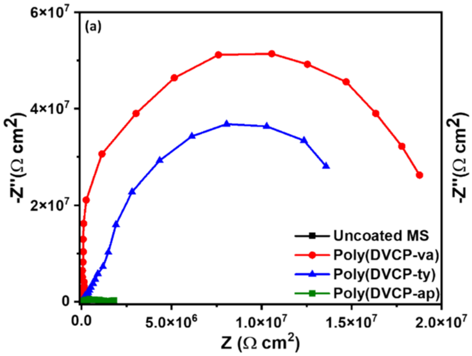

Fig. 16 Nyquist plots of bare MS **a** DVCP and **b** DVCP-based polybenzoxazines

the semi-circle, poly(DVCP-va/DVCH-va) possess the largest diameter than that of other samples including uncoated MS specimen.

Conclusion

The diarylidene cycloalkanones (DVCP/DVCH) based hydroxyl terminated benzoxazines were synthesized using three different amines with paraformaldehyde through Mannich condensation. Benzoxazine samples were characterized using different analytical techniques and methods. Among the diarylidene cycloalkanones-based benzoxazines studied for anti-microbial behavior, DVCP-ap exhibited good inhibition of 22 mm against two different bacteria than that of others indicting its suitability for anti-fouling corrosion applications. The results obtained from different studies infer that all the benzoxazines exhibited higher values of char yield, LOI and heat resistant index, good aggregated induced emission (AIE) characteristics, good microbial resistance, excellent hydrophobic behavior with water contact values above 140° and possess an excellent corrosion protection efficiency of above 98% toward mild steel surfaces. Overall the outlook of diarylidene cycloalkanones (DVCP/DVCH)-based benzoxazines developed in the present work can be suitably exploited in anti-microbial coating, photoresist and photocurable coatings, and flame retardant applications.

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Data availability Data will be made available on request.

Declarations

Conflict of interest The authors declare no conflict of interest.

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