





Studies on catalyst assisted low-temperature curing of benzoxazines

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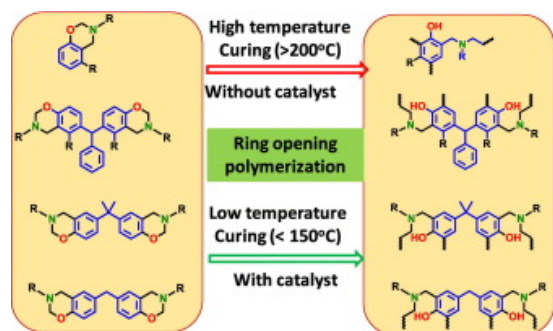
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Highlights

- Cardanol-furfurylamine and card-bisphenol-furfurylamine benzoxazines were synthesized.
- Catalytic effect of acid and dimethyl catalysts with benzoxazines were studied.
- The curing temperatures were found at low temperature.
- The gallic acid catalyst was found to be the better catalyst and reduces the curing temperature to 130°C

Abstract

The present study addresses an increasing interest in achieving low-temperature curing of benzoxazines by utilizing chemical substances with acid moieties of varying functionalities as curing catalysts. Specifically, cardanol-furfurylamine (1), card-bisphenol-furfurylamine (2), bisphenol-A-aniline (3) and bisphenol-F-aniline (4) based benzoxazines were chosen for curing studies. The selected catalysts were systematically applied into benzoxazines and its curing behavior was studied with minimum amount of 5wt%. Catalysts, including those with carboxyl and *N,N*-dimethyl functionalities, were evaluated based on their performance, with a focus on their substituent effect on curing behavior. The results contribute to the identification of catalysts with optimal potential for achieving the efficient low-temperature curing of benzoxazines with an objective of utilizing them for wide area of applications. Among the catalysts studied, gallic acid was found to be the better catalyst and reduces the curing temperature to 130°C. The conversion graph for both bisphenol-A-aniline benzoxazine (3) in the absence of catalysts and bisphenol-A-aniline benzoxazine in the presence of catalysts (3s) have been studied by DSC analysis. The activation energy (E_a) has been calculated using Kissinger-Ozawa method through DSC analysis. Data resulted from different catalysts used for curing of benzoxazines, it was inferred that the pK_a values of the catalysts also play a crucial role in the polymerization of benzoxazines. Further, the study aims to meet the growing demand for efficient and economically viable low-temperature curing processes for benzoxazines.



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Introduction

Benzoxazine monomers typically are made from phenols, primary amines and formaldehyde through Mannich condensation reaction [[1], [2], [3]]. Thus so called benzoxazines are a class of materials that have gained significant attention in recent years due to their unique combination of properties, including high thermal stability, low shrinkage and excellent mechanical strength [[2], [3], [4], [5], [6], [7]]. However, the high temperature required for the ring-opening polymerization is one of the main shortcomings, since the curing of benzoxazines involves the ring-opening polymerization of the oxazine group and the high temperature may destroy the inner hydrogen-bonding interactions and result in degradation of the polymer, which limits their applicability in certain areas especially, when used with low melting substrates for bonding or sealing [[8], [9], [10], [11]]. Hence, a low curing temperature is highly warranted and attempts to reduce the curing temperature have been carried out, with different degree of success [12,13]. To overcome this challenge, low temperature curing benzoxazines have emerged as a solution by adopting various methods, such as catalyst addition, functional molecule design, and zwitterion intermediate stabilization, have been attempted to reduce polymerization temperature [[14], [15], [16], [17]]. Moreover, the presence of a catalysts / hardeners / curing agents / initiators / accelerators influences the reaction rate and reduces the curing time and temperature. The concept of reducing curing temperature of benzoxazines using appropriate chemical substances are considered as cutting-edge route to pave an avenue to reduce energy and alleviates short-comings prevailing in the field of processing and fabrication of benzoxazines for industrial applications [18].

For instance, the use of varying nature of catalysts can reduce the curing temperature of benzoxazines through different mechanisms. This type of reaction involves typically by incorporating the catalysts directly into benzoxazines, which help to activate the oxazine ring and facilitate the polymerization reaction relatively at lower temperature. One of the key factors that influence the curing temperature of benzoxazines is the catalyst used in the curing process for facile fabrication. Lewis acids, Bronsted acids, organometallic catalysts, organic catalysts and photocatalysts, etc., viz., aluminum chloride, boron trifluoride, phosphoric acid, sulfuric acid, titanium tetra(2-ethylhexanoate), zinc acetylacetonate, trimethylamine, 1-methylimidazole and camphorquinone are widely used as catalysts/ accelerators to promote the curing of benzoxazines at lower temperatures [[19], [20], [21], [22], [23], [24], [25], [26]].

The second most extensively considered route to solve this problem is the addition of chemical substances having phenolic moiety as initiators or catalysts directly into benzoxazine monomers or precursors. As it proceeds with the cationic ring-opening polymerization mechanism, the reported initiators or catalysts mainly include phenolic moieties such, methoxy phenol, hydroquinone, resorcinol, 2-methylresorcinol, pyrogallol, 2-naphthol, 2,7-dihydroxy naphthalene, 1,1-bi-2-naphthol, naphthoxazines and thiophenols [[27], [28], [29], [30]]. These chemical compounds facilitate the process of ring-opening polymerization of benzoxazine and involves in the reduction of polymerization temperature according to their nature and concentration.

Though numerous studies have been reported, still the curing of benzoxazine at lower temperatures with minimum weight percentage of cost effective catalysts is in its early stage. To this end, a need exists for better understanding of benzoxazine curing at lower temperatures with different acid catalysts containing both phenolic and acid moieties having varying