



Green Synthesis Of Bio-Based Benzoxazines And Epoxies From Thymol-Citronellal For Low-Toxicity Thermosets

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Abstract

As an alternative to petroleum based raw materials, bio-based bisphenol (TC) was derived from thymol (T) and citronellal (C) emphasizing two principles of green chemistry by employing safer solvents and auxiliaries for synthesis and utilization of renewable feedstocks are justified. The novelty of this work lies in demonstrating the dual utility of this renewable bisphenol (TC) for the first time in the synthesis of two commercially significant thermosets polybenzoxazines and epoxy resins establishing a sustainable possible replacement for conventional petrochemical monomers. Benzoxazines (TC-fa, TC-la and TC-sa) were synthesized using TC with three different primary amines viz. furfurylamine (fa), laurylamine (la) and stearylamine (sa) separately. Also, TC was epoxidized to obtain bio-based epoxy (TC-E). The molecular structure of the targeted benzoxazines and epoxy were confirmed by spectral analysis. TC-fa showed lowest temperature of 205 °C to undergo polymerization. Whereas, poly(TC-sa) was found to possess highest water contact angle of 144° with a corrosion inhibition efficiency of 98.8% which was further supported by DFT studies. On comparing the antimicrobial activity and cytotoxic effects of TC with benzoxazines, TC exhibited greater bacteriostatic property with 30 and 20 mm inhibition zone against *E.coli* and *S.aureus*. Also, TC coated cotton fabric exhibited 99.9% bacterial growth inhibition efficiency. Mild toxicity with IC50 value of 138.81 µg/mL was exhibited by TC when compared to benzoxazine. The epoxidized bisphenol (TC-E) was cured with different curing agents and found the suitable catalyst to cure the epoxy resins at a least temperature of 141 °C. Thermally cured epoxy material was subjected to flexural test which revealed a maximum flexural stress of 0.77 MPa and a modulus of 40.20 MPa.

Keywords Citronellal · Polybenzoxazine · Environmentally benign solvents · Anticorrosion · Hydrophobicity · Antimicrobial activity · Cytotoxicity · DFT

Introduction

Polybenzoxazines are a class of thermosetting polymers that are known for their excellent thermal stability [1], mechanical properties [2], and resistance to chemical degradation [3]. These properties make polybenzoxazines useful in wide range of applications ranging from aerospace [4], coating [5], automotive industries [6] and electronics [7]. Traditionally, polybenzoxazine materials have been synthesized from phenolic compounds, which are derived

from petroleum-based feedstocks [8]. However, in response to increasing environmental concerns and the demand for more sustainable materials, bio-based polybenzoxazines have emerged as an alternative by fulfilling some of the principles of green chemistry [9, 10]. Also, epoxies are a class of thermoset polymers which has high value and demand commercially derived from tradition phenols. Epoxies derived from sustainable resources have gained momentum due to the higher toxic effects exhibited by conventional epoxides derived from petroleum sources [11].

Bio-based polybenzoxazines are synthesized using naturally derived phenols, amines and aldehydes. Some of the reported bio-based phenolic precursors used in the synthesis of polybenzoxazines and epoxies are cardanol [12, 13], eugenol [14, 15], chavicol [16], guaiacol [17, 18], curcumin [19, 20], sesamol [21, 22], thymol [23], resveratrol [24], lignin derivatives [25] and flavone derivatives [26, 27]. By

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replacing the fossil fuel raw materials, bio-based polybenzoxazines and epoxies do not compromise the efficiency of the end product. Several bio-based polybenzoxazines have been explored for various applications where, curcumin based benzoxazines proved to possess good anticorrosion property [28]. Daidzein based polybenzoxazine exhibited excellent antimicrobial and antifungal property [29]. Naringenin [30], and apigenin [31] based polybenzoxazines proved to possess high thermal stability with excellent flame retardance. Cardanol [32] and eugenol [33] derived polybenzoxazines were reported as hydrophobic coating materials. Sesamol based benzoxazines were studied for dielectric properties [34]. Magnolol based benzoxazines were proved to possess low toxicity [35]. Magnolol and eugenol based epoxies have been utilized as strong adhesives showing potent antimicrobial and antioxidant agents [36, 37]. Cardanol derived epoxies exhibited higher thermal stability [38].

All the above studies led the researchers to explore the potential of thymol based polybenzoxazines in various applications. Thymol based benzoxazines containing amines with varying chain length was reported for hydrophobicity and corrosion resistant properties [39]. Thymol derived epoxies were reported with low moisture uptake and good adhesive strength [40, 41]. Our research group has earlier reported fully bio-based benzoxazines from monofunctional thymol for corrosion resistant applications [42]. A wide range benzoxazines were derived from thymol and structurally different amines which proved to exhibit super hydrophobicity and durability [43]. Bifunctional thymol was derived and its polybenzoxazines were assessed for diverse properties including aggregate induced emission [44, 45]. Similarly, trifunctional polybenzoxazines were synthesized and studied for anticorrosion, hydrophobicity and dielectric properties [46].

Collectively, these findings highlight the versatility of thymol-based systems and underscore the growing interest in renewable precursors capable of delivering high-performance thermosets. However, the development of new sustainable aldehydes for bisphenol synthesis remains largely unexplored, leaving a distinct gap in existing bio-based polymer chemistry. Among thermoset polymers, both epoxy and polybenzoxazine hold high commercial value. Thus, this study focuses on synthesizing polybenzoxazines and epoxies from bio-based derivatives by fulfilling two principles of green chemistry which refers to “Safer Solvents and Auxiliaries” and “Use of Renewable Feedstocks” [47]. Despite ongoing research, renewable aldehydes remain largely unexplored. To date, only synthetically derived aldehydes have been utilized as components in the synthesis of new type of bisphenols and benzoxazines.

Addressing this gap, the present work introduces citronellal a renewable aldehyde not previously utilized

in bisphenol synthesis to develop a new type of bisphenol (TC), marking the first report of a citronellal-derived bisphenol in benzoxazine and epoxy resin chemistry. Newly synthesized bio-based bisphenol and sustainable primary amines derived from natural resources were used as raw materials for the synthesis of benzoxazines. In this work, the majority of materials utilized were derived from renewable bio-based sources. Thymol was obtained from thymus species, while citronellal, serving as the aldehyde component, was extracted from lemongrass. Furfurylamine was sourced from corn cobs, laurylamine was derived from lauric acid present in coconut oil, and stearylamine originated from stearic acid found in vegetable fats. The exceptional molecular design versatility of benzoxazine resins facilitated the development of a practical, solvent-free synthetic pathway that aligns with the principles of green chemistry 5 and 7.

Building on the renewable bisphenol platform, the synthesized bifunctional bisphenol (TC) was subsequently converted into both benzoxazines and epoxies through a unified methodology, thereby establishing a dual thermoset development route from a single sustainable precursor. Usage of citronellal in the synthesis of bisphenol is not yet reported to the best of our knowledge. Hence, a bifunctional bisphenol (TC) was synthesized by utilizing thymol and citronellal. Further, the synthesized TC bisphenol was converted to bifunctional benzoxazines and epoxies by a solvent-less approach. The structural elucidation of the synthesized products was confirmed by spectral analysis. The polymerization of benzoxazines and epoxies containing curing agents were assessed by DSC analysis. The thermal stability of the polybenzoxazines and cured epoxy resins was monitored by TGA. Hydrophobicity was studied by measuring water contact angle using water as probe liquid. Anticorrosion properties were studied by measuring electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) parameters on electrochemical work station. Antimicrobial activity was assessed by agar well-diffusion method and cytotoxicity was evaluated through 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) assay.

Experimental Section

Chemicals and Reagents

Thymol (99%) and furfurylamine (99%) were procured from Sisco Research Laboratories (SRL), Mumbai, India. Laurylamine (98%), stearylamine (98%) and epichlorohydrin (99%) were obtained from Tokyo Chemical Industry (TCI), Chennai, India. Citronellal (96%) and paraformaldehyde were secured from Sigma-Aldrich, Mumbai, India. Solvents

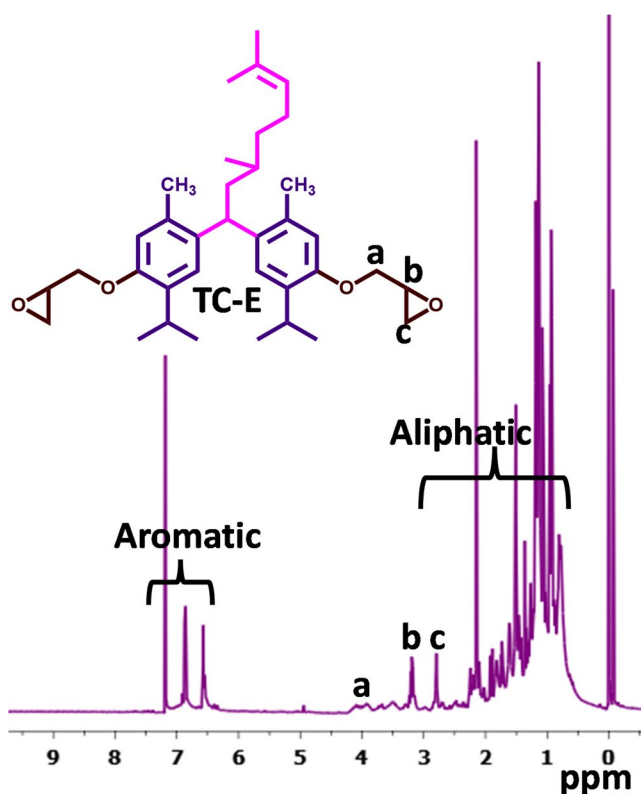


Fig. 15 $^1\text{H-NMR}$ spectrum of bio-based TC-E epoxy

Thermogravimetric Analysis of Cured TC-E with Different Curing Agents

The thermal stability of the cured epoxy resins with various curing agents were assessed by TGA under nitrogen atmosphere (Fig. 18). Table 6, presents the initial degradation ($T_{5\%}$ and $T_{10\%}$), maximum degradation temperature along with the char yield of the cured epoxy resins. It is evident that all the cured epoxy resins possess excellent initial thermal stability where the 5% degradation takes place around 300 °C. The char yield of cured epoxies was recorded at 800 °C and TC-E-at showed highest char yield of 22%. This could be attributed to the increased cross-linking density due to additional allyl crosslinking [72]. Whereas, adenine containing epoxy resins possess char yield almost equal (21%) to TC-E-at due to its rich aromaticity and nitrogen abundance which resists degradation under high temperature.

TC-E-ip has found to possess least thermal stability with a char yield of 8% at 800 °C which is due to its aliphatic nature which under goes fragmentation readily at high temperature [60]. TC-E-dt and TC-E-im also exhibit poor thermal stability when compared to adenine and allyl-thiourea containing epoxies. Thus, this study reveals that the bio-based TC derived epoxies when cured with different catalysts show lower thermal stability when compared to the bifunctional and trifunctional epoxies derived from

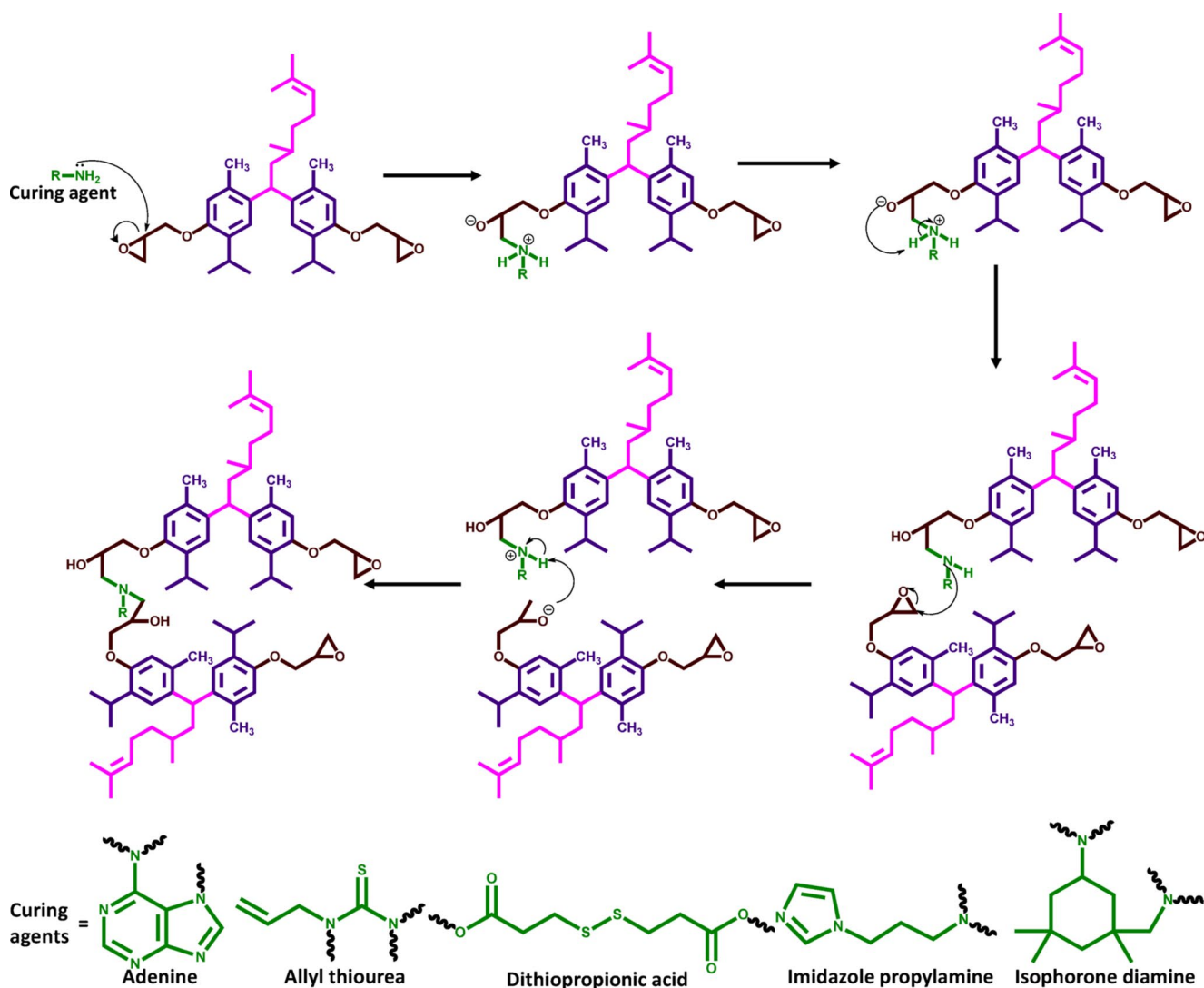
thymol. The HRI index has been calculated which is given in Table 6. The HRI of all the cured epoxies with curatives are found to be high indicating that they have the ability to resist the heat flow. Therefore, the stability of cured epoxies over the temperature is fair with lower char production.

Mechanical Performance Evaluation

Mechanical study was conducted using a universal testing machine (Instron 8801) equipped with a 1 kN load cell and a three-point bending fixture for flexural measurements. Among the evaluated epoxy systems, TC-E-ip, which possesses a relatively low curing temperature, was selected as a representative specimen for flexural testing to understand its deformation behavior under moderate processing conditions. The cured plates were prepared under controlled conditions and subsequently cut into standard flexural test strips following ASTM D790, with specimen dimensions of 80 × 10 × 4 mm [73]. After specimen preparation, mechanical characterization of the TC-E-ip system was conducted to assess its structural performance (Table 7). The flexural test results revealed a maximum flexural stress of 0.77 MPa and a modulus of 40.20 MPa, indicating that the material exhibits low rigidity and can undergo significant deformation under bending loads. The 0.2% offset yield strain (0.22%) further supported the compliant mechanical response of the specimen. The smooth stress–strain progression and the absence of brittle fracture features suggest that the cured network behaves as a flexible polymeric matrix rather than a rigid thermoset. Consistent with this behavior, hardness testing produced a value of 20 HD, confirming the high molecular mobility of the TC-E-ip system. Overall, these mechanical results indicate that TC-E-ip is more suitable for flexible, impact-absorbing, or soft-interface applications than for high-load structural environments.

Conclusion

Fully bio-based bisphenol was successfully synthesized from thymol and citronellal. The bisphenol was further utilized as phenolic precursors to develop bifunctional benzoxazines and epoxides by adopting the green chemistry principle 5 and 7. The confirmation of the molecular structure of the synthesized compounds are well supported by various spectral analyses. It was evident that TC-fa was found to possess least polymerization temperature of 205 °C due to the active furan moiety which involves in crosslinking along with the oxazine ring. Whereas, the thermal stability of all the synthesized polybenzoxazines showed good initial ($T_{5\%}$) and maximum (T_{max}) thermal stability but very less char yield value. This behavior is



Scheme 6 Plausible curing mechanism of bio-based epoxy TC using different curing agents

likely inherent to the structural characteristics of citronellal and thymol, which limit the development of thermally robust aromatic char. While these materials may be suitable for applications requiring high thermal onset stability, their low char yield may restrict their use in fields demanding excellent flame retardancy. Further structural modification such as introducing aromatic comonomers or reinforcing fillers may be necessary to enhance char formation in future formulations. All the polybenzoxazines from the current study were found to exhibit excellent hydrophobicity where a maximum water contact angle of 144° was recorded for poly(TC-sa). Poly(TC-sa) also showed greater resistance to corrosion with a corrosion inhibition efficiency of 98.8%. Interestingly, the antimicrobial activity and cytotoxicity of synthesized TC bisphenol was found to be greater than its respective benzoxazines. In case of epoxidized TC bisphenol, a lowest

curing temperature of 141°C was recorded when isophorone diamine was used though these results may vary with different curing agents or processing conditions and require further validation. Mechanical studies suggested that TC-E-ip is better suited for soft, flexible or impact-absorbing applications rather than high-load structural uses. Overall, this work demonstrates the feasibility rather than the full maturity of replacing certain petroleum-derived precursors with renewable alternatives in low toxicity thermoset synthesis. This work highlights the feasibility of designing and synthesizing high-performance materials under environmentally responsible conditions by leveraging renewable bio-based feedstocks and adhering, wherever practically achievable.

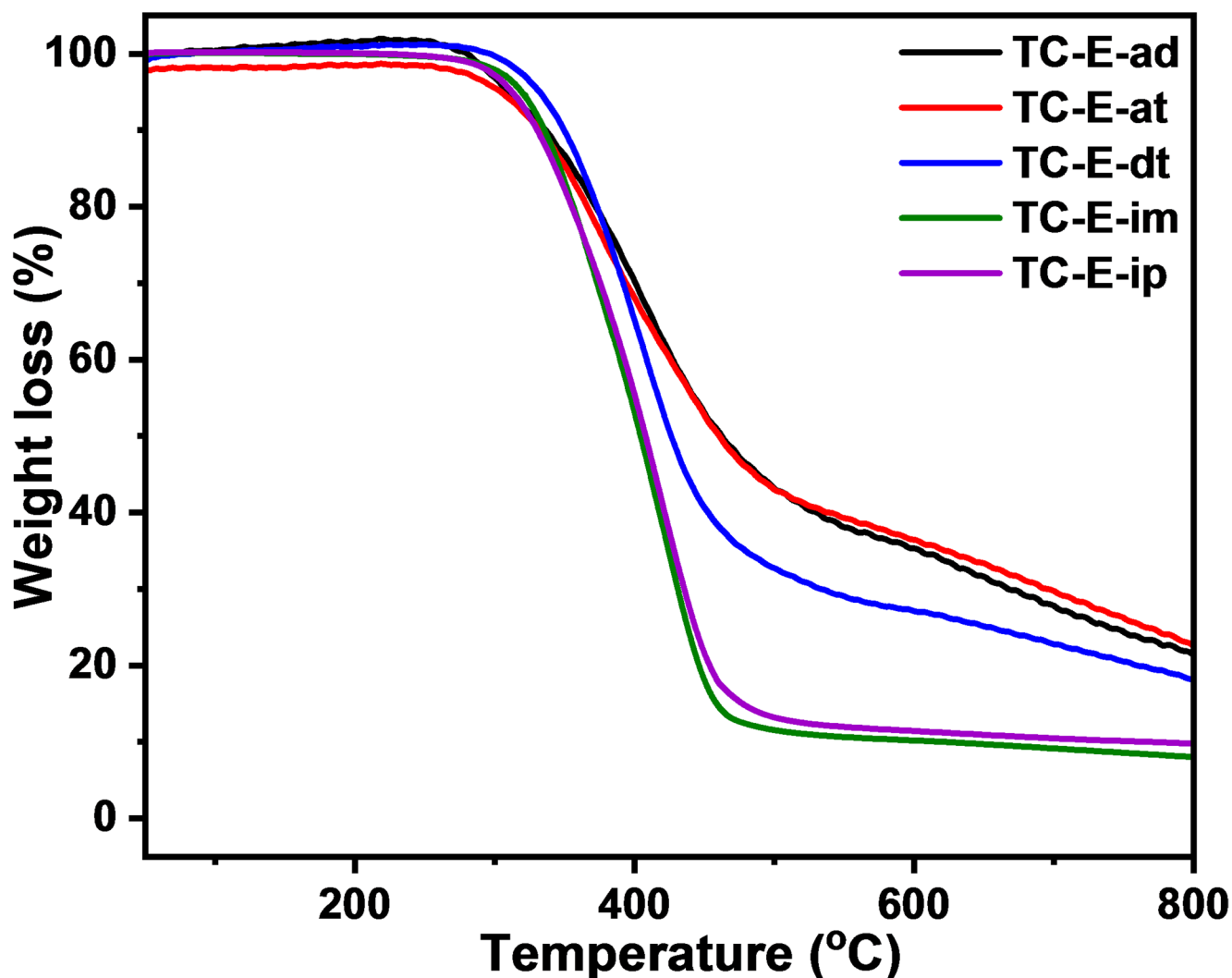


Fig. 18 TGA of cured TC-E with different curing agents

Table 6 Thermal stability of cured TC-E with different catalysts

Sample code	T _{5%} (°C)	T _{10%} (°C)	T _{30%} (°C)	T _{max} (°C)	Char yield (%) at 800 °C	HRI
TC-E-ad	304	337	402	414	21	178
TC-E-at	298	333	395	410	22	174
TC-E-dt	330	350	390	405	18	180
TC-E-im	317	335	373	396	09	172
TC-E-ip	309	330	376	392	08	171

Table 7 Mechanical properties of cured TC-E-ip

Property	Value
Maximum Flexural Stress	0.77 MPa
Flexural Modulus	40.20 MPa
Maximum Force	0.00–0.01 kN
Flexure Strain at Yield (0.2% Offset)	0.22%
Flexure Stress at Yield (0.2% Offset)	–0.01 MPa
Hardness	20 HD

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Data Availability Data will be made available on request.

Declarations

Competing interests The authors declare no competing interests.

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