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Study on the Thermal Properties of Epoxy Resin Reinforced with Arylidene-based Polybenzoxazine

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Abstract

In this study, a new bis-arylidene derived benzoxazine: 2,6-bis((3-(2-hydroxyethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methylene)cyclohexanone (HEB) was synthesized from its precursor: 2,6-bis(4-hydroxybenzylidene)cyclohexanone (BCH). The BCH was obtained as an aldocondensation product of cyclohexanone and 4-hydroxybenzaldehyde, in an acid catalysed organic medium. Both HEB and BCH were characterised using Fourier Transform Infrared (FTIR), and Nuclear Magnetic Resonance (NMR) spectroscopic techniques to ascertain the structural features of the targeted products. Different weight ratios of HEB (0,10, 20, 30, and 40%) were added into an epoxy resin to form the modified epoxy materials; ME-0%, ME-10%, ME-20%, ME-30%, and ME-40%, respectively. The thermal behaviour of the modified epoxy resins was investigated using thermal gravimetric analysis (TGA). The result obtained showed enhanced thermal properties of the modified epoxy materials over the native epoxy resin. The outcome further showed better performance with higher content of the modifier.

Keywords: Polybenzoxazine, Arylidene, Epoxy resin, Thermal property,

1. INTRODUCTION

Epoxy resin is one of the engineering materials used for many industrial applications that include adhesives, coating, sealant, and other constructions (Tesoro, 1988). This is due to some of the attractive properties of the resin which are appropriate for such applications. The properties of this polymer include good chemical, mechanical, electrical, and thermal behaviour (May, 2018). Nevertheless, the resin suffers some shortcomings such as poor water resistance, notch sensitivity, brittleness, and lack of toughness, hence, needs further upgrade to make it fit and suitable for fabrication of high-performance polymer materials with wider fields of application. One approach that has been established for the enhancement of the properties of the resin include their modification with reinforcements such as polymers (Al Shaabania, 2019; Jiang *et al.*, 2018; Musa *et al.*, 2020), fibres (Lila *et al.*, 2018; Sarikaya *et al.*, 2019), and nanoparticles (An *et al.*, 2019; Arash *et al.*, 2021).

Benzoxazines are an organic compounds synthesized from the reaction of readily available reagents such as phenols, amines, and formaldehyde using both solvent and solventless systems (Holly & Cope, 1944), and they are classified as phenolic resins. Their polymerisation results in the production of high-performance thermosetting materials known as polybenzoxazines. Polybenzoxazines exhibit attractive characteristics worthy of industrial applications such as excellent resistance to moisture, chemicals, and heat. Other properties of the polymer include high strength, good electrical and mechanical behaviour (Ning and Ishida, 1994). They also have low melt viscosity, and their chemical structure allows for their design flexibility (Ishida and Froimowicz, 2017). Polybenzoxazines have been used to modify epoxy resin for some targeted application (Musa *et al.*, 2021), however, the bis-arylidene derivatives of these polymers are yet to be explored and that appears as an interesting research gap in this field of research.

In this work, a new bis-arylidene based benzoxazine monomer: 2,6-bis((3-(2-hydroxyethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methylene) cyclohexanone (HEB) was synthesized from its precursor compound: 2,6-bis(4-hydroxybenzylidene) cyclohexanone (BCH) using an organic solvent system. Both the benzoxazine and its precursors were characterised by Fourier Transform Infrared (FTIR), and Nuclear Magnetic Resonance (NMR) spectroscopic analysis, respectively. Weight ratios of the HEB (0,10, 20, 30, and 40%) were used to modify the epoxy resin. The mixtures were cured appropriately and designated as ME-0%, ME-10%, ME-

20%, ME-30%, and ME-40%, respectively. The curing of the materials was monitored using FTIR and their thermal behaviour was studied by thermal gravimetric analysis (TGA). The surface morphology of the materials was also investigated by scanning electron microscopy (SEM). The results obtained revealed enhanced thermal stability of the modified epoxy resins in comparison to the neat resin and the trend suggests a linear increment in thermal stability with increasing amount of the modifier.

2. MATERIALS AND METHODS

2.1 Materials

4-hydroxybenzaldehyde (98%), cyclohexanone (≥ 99%), paraformaldehyde (96%), ethanolamine (≥ 98%), absolute ethanol, epoxy (Epikote-1001 x-75 % (2642)), anhydrous magnesium sulphate, ethanol (96%), methanol (98%), sodium hydroxide, sulphuric acid (98%), dioxane (≥ 99%). The reagents and solvents were purchased from Sigma Aldrich and used as supplied.

2.2 Methods

2.2.1 Synthesis of 2,6-bis(4-hydroxybenzylidene) cyclohexanone-(BCH)

Cyclohexanone (2.454 g, 0.0250 mol) and 4-hydroxybenzaldehyde (6.106 g, 0.0500 mol) were dissolved in 30 mL of methanol and kept on an ice bath with continuous stirring until the well-cooled mixture dissolved completely. Then, the concentrated sulphuric acid (3 mL) was added in drops with the stirring condition maintained for 5 min. The stirred mixture was kept at room temperature for 13 hr. The solid precipitate formed was filtered and rinsed with water before further purification by recrystalizing from ethanol. Yield: 90%; melting point (m.p) > 255°C.

2.2.2 Synthesis of 2,6-bis((3-(2-hydroxyethyl)-3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl)methylene) cyclohexanone-(HEB)

To a 100 mL round-bottom flask containing 40 mL of dioxane and equipped with a magnetic stirrer, BCH (2.208 g, 0.00721 mol), ethanolamine (0.894 g, 0.0144 mol), and paraformaldehyde (0.865 g, 0.0288) were added. The mixture was heated gently until it reaches 90°C, and then maintained at this temperature for 14 hr. The product formed was concentrated using rotary evaporator and redissolved in chloroform before washing with 1N sodium hydroxide solution, and water, respectively. Magnesium sulphate was used to dry the organic phase before concentrating the mixture using rotary evaporator to give a reddish solid product. Yield: 55%

2.2.3 Formation of pure epoxy resin

The pure epoxy resin was prepared by dissolving 50% weight percent of the epoxy and 50% weight percent of the hardener in a little quantity of chloroform sufficient to dissolve the mixture as reported in our previous work (Musa *et al.*, 2020). The mixture was sonicated for 20 minutes before pouring into a petri dish and left at room temperature for 24 hr to evaporate the solvent. Then the pure epoxy film formed was removed and left in a desiccator for continuous drying before usage.

2.2.4 Fabrication of modified epoxy resin

The same procedure as adopted for the preparation of the pure epoxy resin was employed for this fabrication, however, varying weight ratios (0, 10, 20, 30, and 40%) of HEB were added to the equal volume of the epoxy and its hardener before ultrasonication for 2 hr. The resulting mixture was poured into a petri dish and left at ambient temperature for 24 hr. The materials formed were labelled: ME-0, ME-10, ME-20, ME-30, and ME-40 and post cured step-wisely at 160, 180, 200, and 220°C, respectively. The modified final products obtained were then removed from the petri dishes individually and characterized accordingly.

2.3 Characterization techniques

2.3.1 FTIR analysis

The FTIR spectral analysis was performed on a Thermo Scientific Nicolet iS50 FT-IR spectrometer using a KBr pellet from 450 cm^{-1} to 4500 cm^{-1}. A minimum of 32 scans were collected for each sample at a resolution of ±4 cm^{-1} after loading the samples.

2.3.2 NMR measurement

The NMR spectra (^{1}H and ^{13}C) of BCH and HEB were measured using a 400 MHz NMR spectrophotometer (Bruker).

2.3.3 SEM investigation

The surface morphology of the modified epoxy resin was examined using a field emission scanning electron microscope (FESEM) (JEOL JSM 7600-F) at an acceleration voltage of 2.00 kV, with the samples coated with gold before analysis.

2.3.4 TGA studies

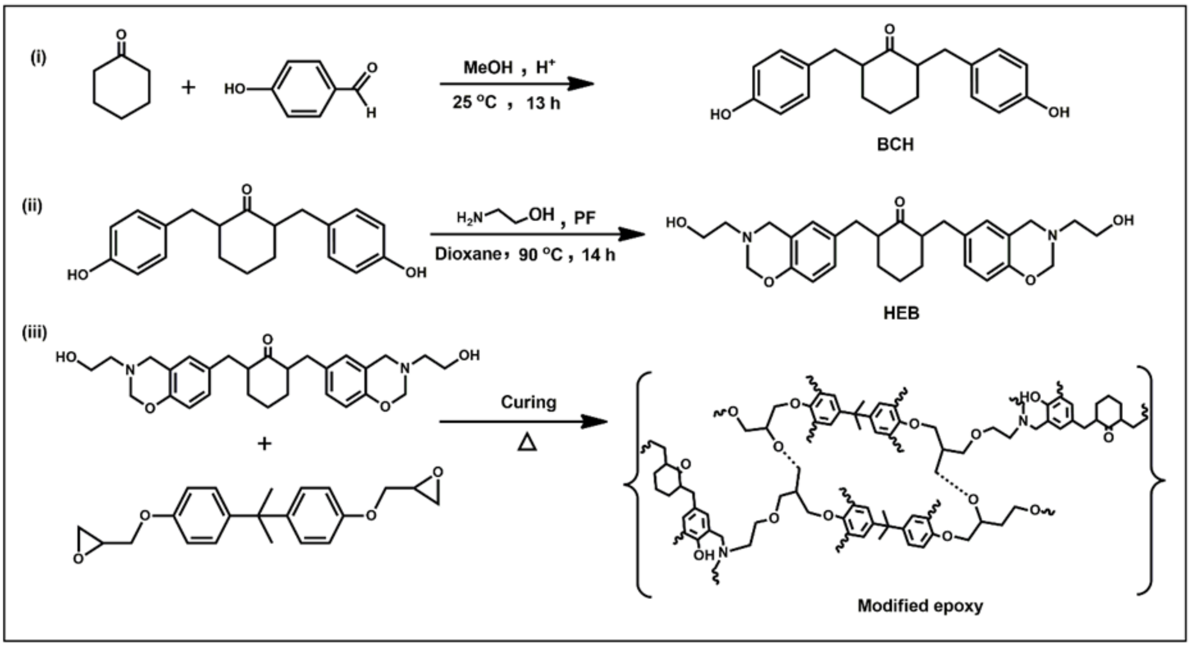
The TGA plots were collected on a (TA 2000) thermal analyzer instrument ata heating rate of 10 °C per minute under nitrogen atmosphere.

3. RESULTS AND DISCUSSION

3.1 Synthesis and spectral analysis of BCH and HEB

A new benzoxazine monomer: 2,6-bis((3-(2-hydroxyethyl) -3,4-dihydro-2H-benzo[e][1,3]oxazin-6-yl) methylene)cyclohexanone-abbreviated as HEB, containing both oxazine and arylidene structures was conceptualized and synthesized accordingly. The synthesis was performed in two stages, and the steps involved are summarized in **Scheme 1(i)**. In the first stage, a precursor compound: 2,6-bis(4-hydroxybenzylidene) cyclohexanone (BCH) was prepared via the aldol condensation reaction of 4-hydroxybenzaldehyde and cyclopentanone in an acidic medium (Figure 1a) (Kannapan and Jonathan, 2013).

The IR spectrum (Figure 1A) reveals a strong band at 3257 and 2933 cm^{-1} attributed to the hydroxyl (-OH), and alkenyl proton (=C-H) groups of the BCH structure. And the bands of the carbonyl functional group and the carbon-carbon bonds of the aromatic rings of the same compound appeared at 1648, and 1582 cm^{-1}, respectively (Faizan and Ahmad, 2018). In the ^{1}H-NMR spectrum (Figure 2C), the peak at 7.55 can be associated with the vibration frequency of the alkenyl protons (=CH-C) (Borgati *et al.*, 2019). While the phenolic hydroxyl proton (Ar-OH) of the BCH structure appeared at 9.97 ppm (Charisiadis *et al.*, 2014). The aliphatic protons of the cyclohexanone ring (=C-CH2-C - and -C-CH2-C-) displayed their signals at 2.85, and 1.71 ppm, respectively (Chutayothin and Ishida, 2009). The carbon NMR of BCH was also studied to further confirm the structure of the starting material (Figure 2D).



Scheme 1: Synthesis of: (i) BCH, (ii) HEB, and (iii) fabrication of modified epoxy

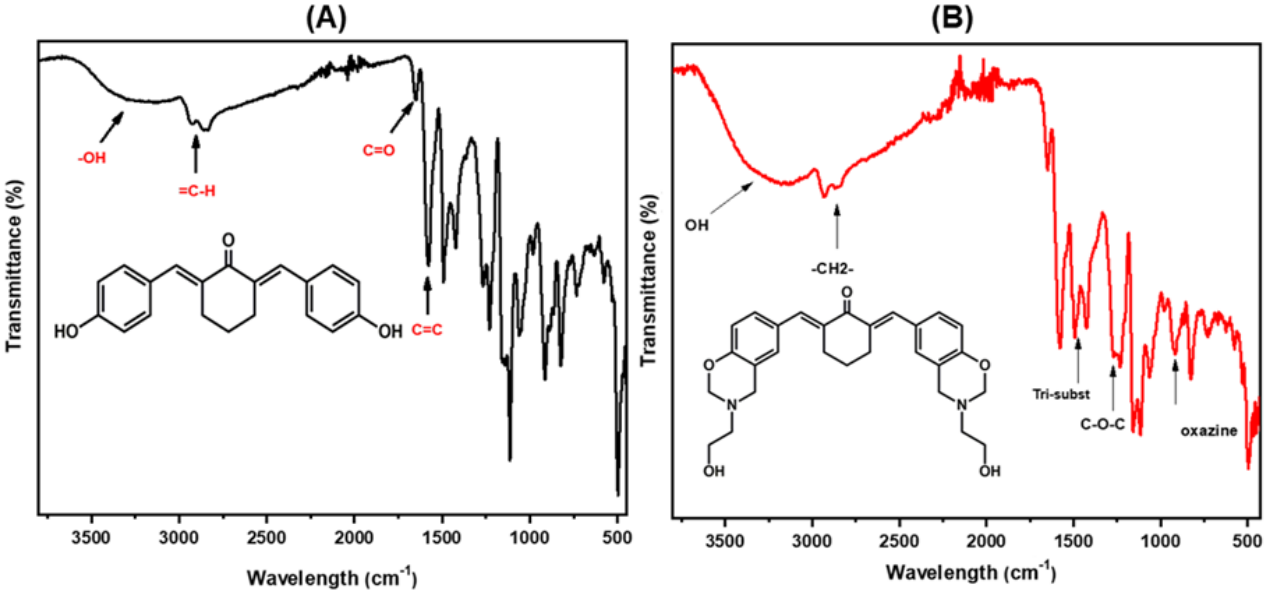


Figure 1: The FTIR spectra of: (A) BCH and (B) HEB

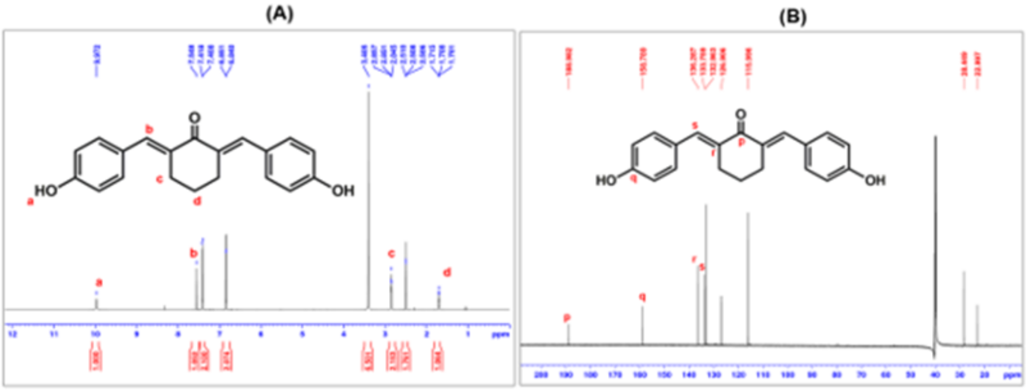


Figure 2: The ^{1}H-NMR (A), and ^{13}H-NMR (B), spectra of BCH

The signal of carbonyl carbon vibration displayed at 188.98 ppm, while the carbon centre exocyclic to the cyclohexanone ring showed at 136.28 ppm along with the other alkenyl carbon at 133.76, and the phenolic carbon appeared at 158.79 ppm. The second stage involves the synthesis of the target benzoxazine compound HEB from the condensation reaction (mannich) of BCH with paraformaldehyde and ethanolamine (Scheme 1(ii**)**) (Kannapan and Jonathan, 2013).

The spectral analysis of the product formed was used to ascertain structural features of HEB. The FTIR spectrum of HEB showed the presence of the unique functional groups of HEB (Figure 1B). The aliphatic hydroxyl group (-OH), and the alkane protons ($-CH_2-$) of HEB appeared at 3300, and 2853 cm^{-1}, respectively (Zhuang *et al.*, 2020). The vibration frequency of oxazine ring appeared at 912 cm^{-1} whereas that of C-O-C asymmetric stretch showed at 1233 (Han *et al.*, 2017). The trisubstituted benzene ring band displayed at 1476 cm^{-1}.

Additionally, the NMR analysis further compliments the results of the FTIR spectrum where the proton NMR (Figure 3) revealed the presence of vibration frequencies at 3.99 and 4.87 ppm associated with the protons of Ar-C**H**$_2$-N and O-CH$_2$-N of the oxazine ring (Ning & Ishida, 1994). The aliphatic protons (N-**CH$_2$**-C, and O-C**H$_2$**-C), attached to the oxazine ring appeared at 2.83, and 1.69 ppm, respectively. The methylol proton (C-O**H**) displayed a vibration frequency at 4.43 ppm (Gilbert *et al.*, 2018). The carbon NMR spectrum (Figure 4) also showed some charac-

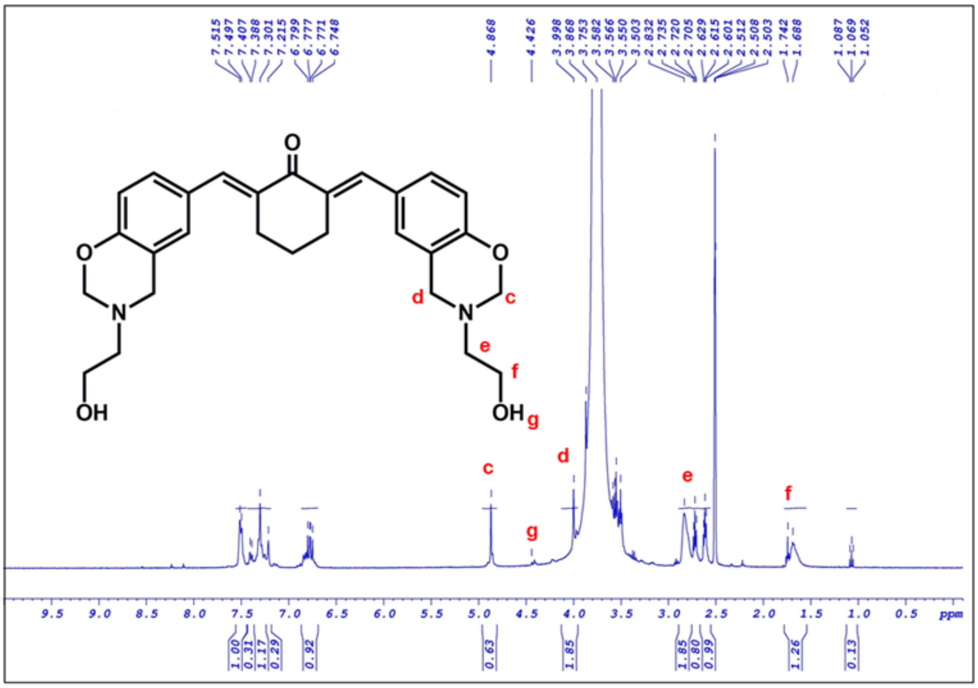


Figure 3: The ^{1}H-NMR of HEB

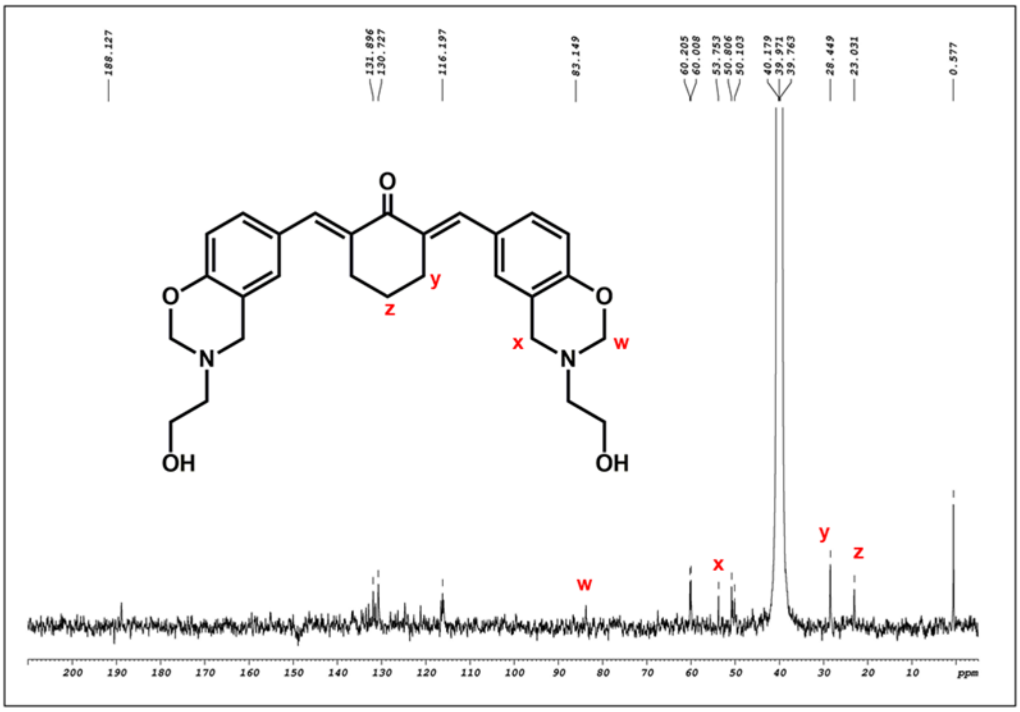


Figure 4: The ^{13}H-NMR of HEB

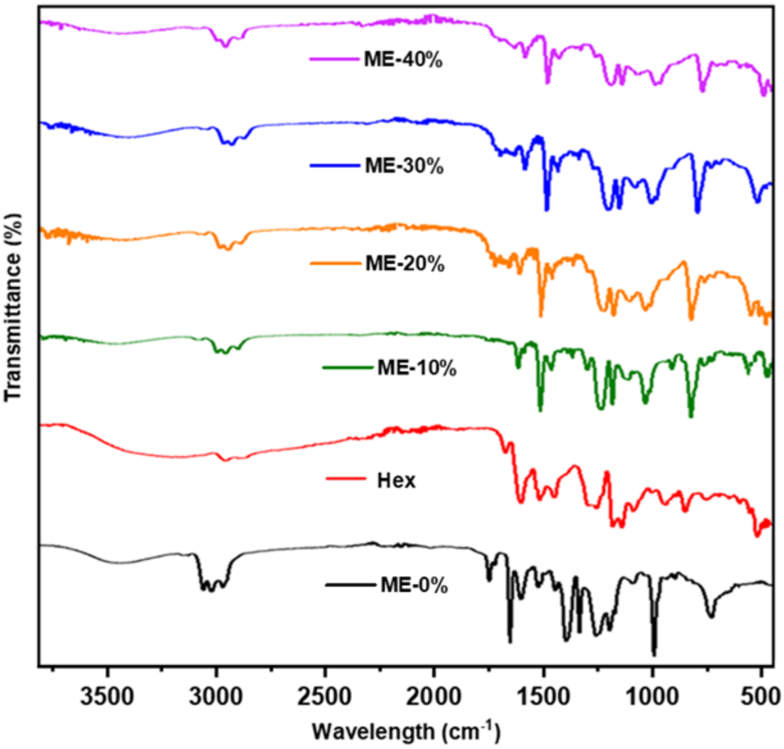


Figure 5: The FTIR characterization of ME-40, ME-30, ME-20, and ME-10, ME-0%, respectively

teristic peaks ascribable to the oxazine ring carbons of the HEB structure. The frequency of the carbon centre of Ar-CH$_2$-N appeared 53.75 ppm, while that of O-CH$_2$-N appeared at 83.15 ppm. The peaks at 28.45 and 23.03 are the frequencies of the aliphatic carbons of the cyclohexanone ring (=C-**C**H$_2$-C- and -C-**C**H2-C-), respectively.

3.2 Characterization of the Modified Epoxy

The structural characterisation of the modified epoxy samples was performed by FTIR analyses of the products formed and the results obtained are depicted in (Figure 5). Benzoxazine is an example of the monomers that polymerise under thermal agitation. Here, the strained, six-membered oxazine ring cleaves, and the cation formed attacks the phenolic ring of another monomer and the reaction progresses in that pattern leading to the form the polybenzoxazine chain. In the process, phenolic hydroxyl groups are generated. The phenolic hydroxyl groups along with the end chain methyol groups of the polybenzoxazine can interact by hydrogen bonding with the strained, polar, and highly reactive epoxy group of the matrix, during the curing process. This can lead to the formation of a well cured polybenzoxazine modified epoxy material. The formation of the phenolic hydroxyl groups can be evidenced from the reduction of the intensity of the vibration due to tri-substituted benzene ring of the benzoxazine at 1490 cm^{-1}, due to the formation of a tetra-substituted benzene ring at 1478 cm^{-1} (Shukla *et al.*, 2016). However, the new phenolic hydroxyl groups generated are involved in hydrogen bond with similar generated hydroxyl groups in the reaction system.

That also can be seen from the reduction in the intensity of the overall hydroxyl bands around 3300 cm^{-1}. The formation of the polybenzoxazine chains can further be confirmed by the disappearance of the vibration frequency due to oxazine ring at 912 cm^{-1}.

3.3 Surface morphology of the modified epoxy materials

The surface properties of the modified-epoxy materials were investigated for some representative specimens: ME-0%, ME-10%, ME-20%, and ME-30%, respectively (Figure 6). The image of the native epoxy shows a smooth resinous surface that is characteristic of a pure epoxy resin (Cao *et al.*, 2017). However, the smoothness is gradually faded with the individual incorporation of 10, 20, and 30% of the polybenzoxazine into the epoxy. The SEM micrographs serve as evidence for the successful incorporation of the modifier into the epoxy resin matrix due to roughness of the surfaces of the materials formed suggesting compatibility of the components that were mixed since no visible fractures are formed (Mimura *et al.*, 2000).

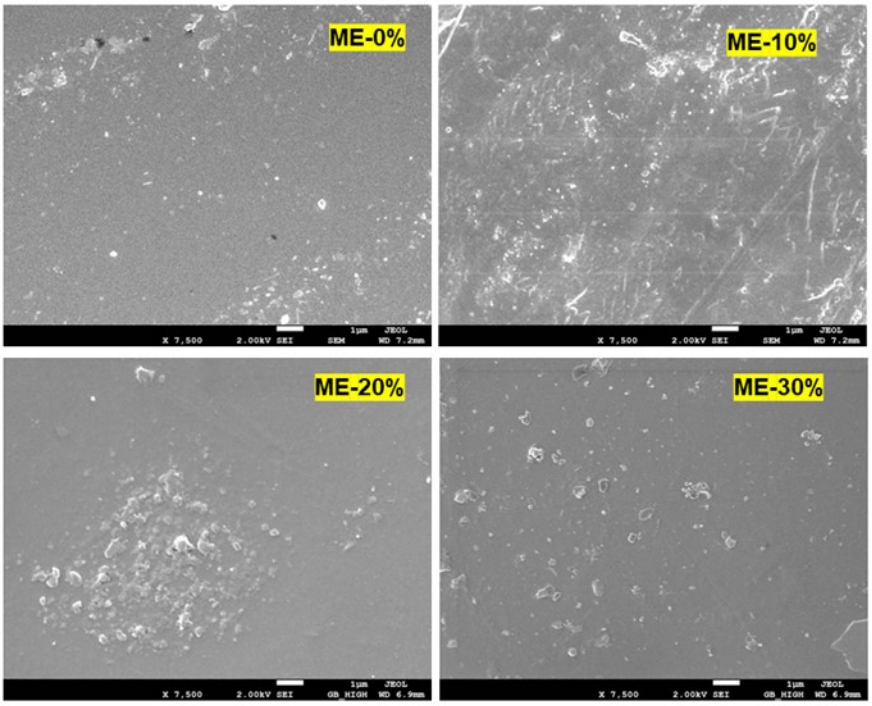


Figure 6: The SEM micrographs of ME-0, ME-10, ME-20, and ME-30%

3.4 Thermal behaviour of the modified epoxy material

The thermal properties of the modified-epoxy resins: ME-10, ME-20, ME-30, and ME-40%, with that of the pure resin (ME-0%) was studied by TGA technique under nitrogen atmosphere at a heating rate of 10 °C/min, and the individual thermographs obtained are presented in (Figure 7). The results are interpreted in terms of some parameters which include initial degradation temperature (IDT), maximum degradation temperature (T_{max}), and the weight loss at temperatures of 10, 20, and 50%, (T_{10}, T_{20}, and T_{50}, respectively), Table 1. The shape of thermographs of the neat epoxy and the modified resins showed some semblance hence suggesting similar degradation mechanism. However, that of the pure epoxy is characterised by an initial loss in small molecules such as water, solvents between 99 and 186°C. From the plots, the IDT, T_{max}, T_{10}, T_{20}, and T_{50} for all the modified resin materials are higher than that of the pure epoxy resin, and that indicates a better thermal stability of the formers. Also, as the amount of the polybenzoxazine modifier is increased in the epoxy matrix (from ME-10 to ME-40%), all the parameters showed linear increment in their values. That may be associated with the formation of more hydrogen bonds between the methyol groups of the polybenzoxazin and the epoxide ring of the resin. Since stronger hydrogen bond leads to higher cross-link density, hence, a well cured product may be obtained in that way (Deshpande *et al.*, 2019), and that can be correlated with the results of the morphological analysis (3.3).

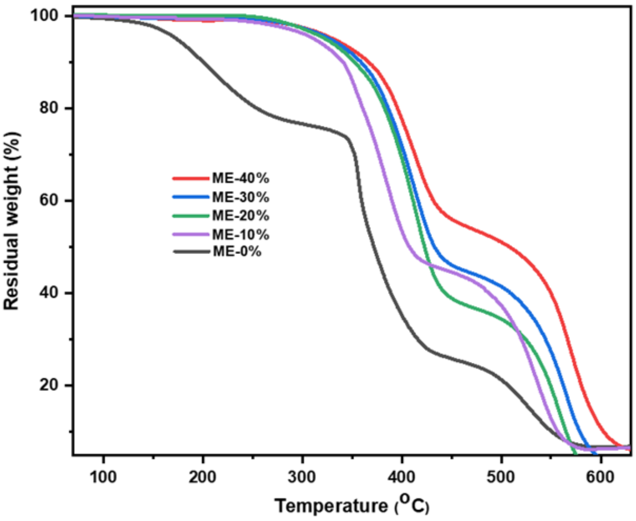


Figure 7: The TGA plots for ME-0, ME-10, ME-20, ME-30%, respectively

The results obtained are also comparable to those of our previously published work (Musa *et al.*, 2021), and additionally, the effect of the arylidene structure in the polymer used can be seen clearly. Being a thermally curable moiety, the arylidene moiety enhanced the thermal stability of the modified-epoxy materials prepared (Lin *et al.*, 2017).

Table 1: The thermal parameters of ME-0, ME-10, ME-20, ME-30, and ME-40%

		Degradation Temperature (°C)*			
Sample	**IDT (°C)***	**$T_{10\%}$**	**$T_{20\%}$**	**$T_{50\%}$**	**T_{max} (°C)***
ME-0%	122	201	253	372	544
ME-10%	259	340	361	407	554
ME-20%	270	352	382	422	566
ME-30%	270	358	386	432	578
ME-40%	288	367	396	508	602

*The values were determined by TGA at a heating rate of 10 °C/min

4.0 CONCLUSION

Epoxy resin is an industrial raw material with a good thermal stability. Enhancement of its thermal property can expand the areas of its applications. A new class of benzoxazine monomer that contains an arylidene structure was designed and synthesized according to established methodologies. The arylidene and benzoxazine structures are thermally curable units that can burst the thermal properties of any polymer matrix they are incorporated into. Hence, the benzoxazine was employed as a modifier to improve the thermal characteristic of the epoxy resin. Different weight ratios of the benzoxazine were mixed with epoxy resin and cured appropriately to form the targeted materials. The outcome of the investigation indicated the formation of the modified-epoxy material with a better thermal property in comparison to similar materials.

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