Decomposition And Chemical Analysis Of Cured Epoxy System Using A Microwave Reaction System

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Abstract: - Fully cured epoxy samples of Araldite DLS 772 / 4 4' DDS with an amine to epoxy ratio of 0.8M were dissolved in 4M nitric acid in a microwave reaction system at a temperature of 120^oC for a total of 75 minutes. The dissolved compound was collected and dried. High Performance Liquid Chromatography was used to analyze and separate the components in the compound. Infrared spectroscopy, nuclear magnetic resonance spectroscopy and electrospray ionization mass spectrometry was used to identify the dissolved product. The dissolved product was identified as 1, 3 – di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene**.**

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1 INTRODUCTION

Plastics and polymers are very beneficial to our society. They have played significant roles in the advancements of satellites aircrafts and missiles. As beneficial as these plastics and polymers are, they also cause a lot of environmental problems [1, 2]. They are non-organic substances and hence, various micro-organisms that decay matter cannot act upon the plastics. As a result of this, they very slowly decay in nature. As they slowly decay, they release hydrocarbons which are added to the carbon cycle. They also have long half-lives in landfills. Burning them will also create pollution which releases toxic gases. Chemical recycling of plastics and polymers is being explored as an interesting route for converting plastic wastes back into its original constituents, or into other usable substances[3, 4]. Chemical recycling is a very effective and promising method for plastics. It has advantages for the industry especially in the recycling of thermosetting resins. Amine cured epoxy resins have been successfully dissolved in nitric acid solution. This is because they have a low resistance to nitric acid solution. This successful dissolution has increased the possibility of recycling thermosetting resins [1, 2]. Microwave heating uses the ability of some liquids and solids to convert electromagnetic energy into heat. It is based on the principle that a material can be heated by applying energy to it in the form of high frequency electromagnetic waves.Microwave processing is able to quickly and controllably absorb energy for cooking, dehydration or curing.

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Microwaves offer fast heating rates. Microwave heating is directed at the material, not through the containing vessels. These all result in more homogenous cure, smaller thermal stresses and minimal material degradation. The objectives of this paper is to explore the use of microwave energy as an alternative, faster route to the decomposition of cured epoxy resins, and to identify the decomposed product.

2 EXPERIMENTAL

Fully cured samples of Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 were cut into small rectangular pieces of between 1 – 2 grammes. They were put in reaction vessels 20 ml of 4M HNO_3 was added to each reaction vessel. The vessels were then placed in the microwave reaction system. The samples were heated in the reaction vessels to a temperature of 120^0C and held at this temperature for about 25 minutes. This experiment was repeated three times. It took a total of 75 minutes for the sample to be completely dissolved in the nitric acid.
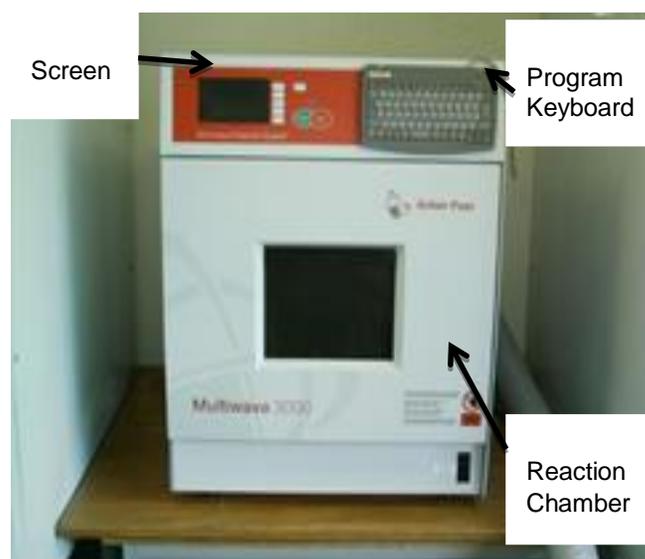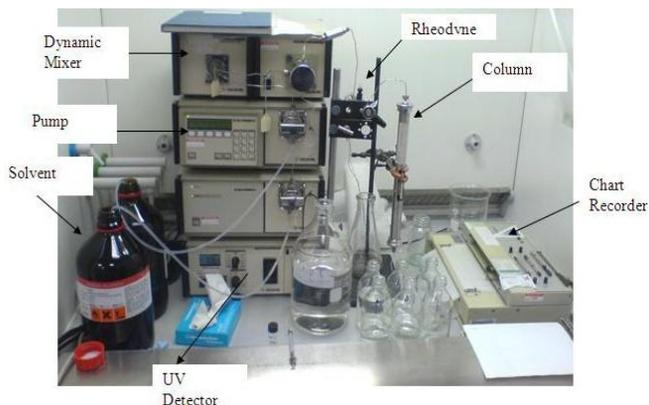

Fig. 1: A microwave reaction system

Fig. 2 Fully cured sample of Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 beforedecomposition in Microwave Reaction System.

Fig. 3 Product obtained after decomposition of fully cured samples of Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 after decomposition at 120^{0}C for a total of 75 minutes in Microwave Reaction System.

2.2 ANALYTICAL METHODS

The compounds which made up the decomposed epoxy system were determined. High Performance Liquid Chromatography HPLC was used to separate the peaks. Infrared Spectroscopy, Nuclear Magnetic Resonance Spectrometry and Mass Spectrometry were used to identify the decomposed compound.


Fig 4. A Gilson Pump Controlled HPLC system.

3. RESULTS AND DISCUSSION

Figs. 2 and 3 show the fully cured samples of Araldite DLS 772 / 4 4' DDS with amine / epoxy ratio of 0.8 at 180^{0}C for 240 minutes before and after decomposition in the microwave reaction system. 10 micro-liters of 10mg / mol. concentration of the decomposed product was injected through the HPLC analytical system to test for purity and the constituents in the product. The analytical results for the dissolved epoxy systems are shown in the fig 5.
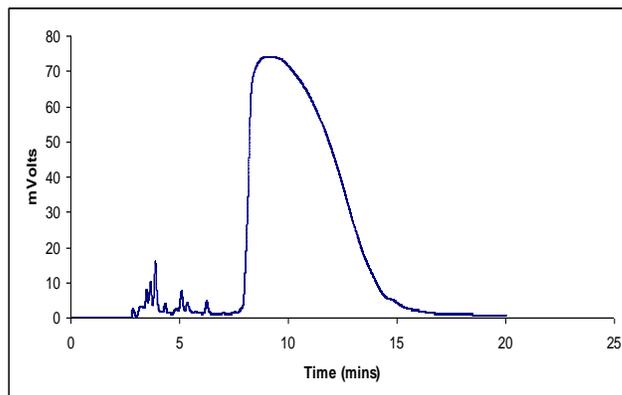
Fig. 5. HPLC trace results of decomposed product offully cured Araldite DLS 772 / 4 4'DDS epoxy system with an amine / epoxy ratio of 0.8 passed through a silica column using 50:50 Hexane / Ethyl acetate as solvents and detected at 254 nm.

Fig. 5 above shows a broad peak. This broad peak suggests that a range of similar compounds were probably eluted. The broadness of the peak also occurs when the compound is strongly absorbed on the silica column. This is usually the case when the compound is Polar. Some of the end groups of the compound stuck longer to the silica as it was being forced through the pump. Polar compounds attach themselves chemically to the silica column. In order to collect and analyse the major peak, a much stronger concentration of about 100 mg / mol. was prepared. 100 micro-litres were injected into the pump controlled HPLC system. The chart recorder was used to monitor the elution of the sample to be collected. The collected sample was rerun by analytical HPLC to confirm the purity of the collected peak.The results of the rerun analytical HPLC test for purity for each epoxy system are shown in the fig. 6 below.
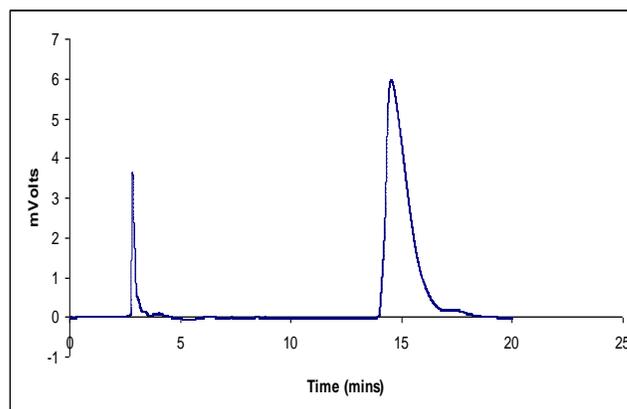
Fig. 6 Analytical HPLC trace results of collected isolated compound of decomposed cured Araldite DLS 772 / 4 4'DDS epoxy system with an amine / epoxy ratio of 0.8.

The figure above shows two peaks. The first peak is the solvent front. It usually comes out about two minutes after the sample is injected in the HPLC instrument machine using 50: 50 hexane/ethyl acetate solvent mixtures. This solvent front is probably ethyl acetate. It absorbs at about the same UV at 254 nm. The second peak also shows that isolated compound seem to consist of a range of similar compounds in the solvent collected from the HPLC pump system. A rotary evaporator was used to dry the collected compound, leaving the just the residue.

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infra red spectra were taken of the residue samples. The spectra of the samples are shown in figs. 8 and 9 below.
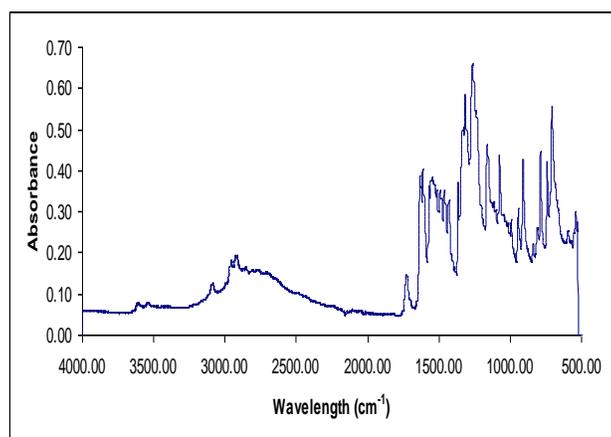

Fig 7 Infrared spectra of dried isolated compound collected from the decomposed product of cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8
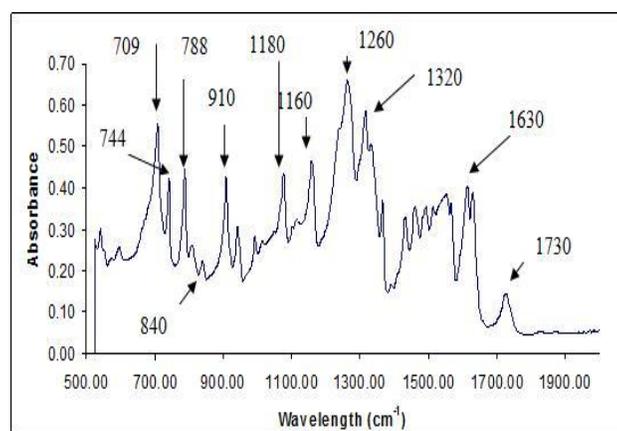

Fig.8 Expanded view of Infrared spectra of dried isolated compound collected from the decomposed product of cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

Fig. 8 above shows the infrared spectra for the isolated compound of the dissolved microwave cured Araldite DLS 772 / 4 4 DDS. The peaks at 709 cm^{-1} and 788 cm^{-1} correspond to the mono-substituted benzene and meta-disubstituted benzene bands respectively. The peak at 1430 cm^{-1} is the aromatic C=C bond [5-7]. The absorption peaks at 1020 cm^{-1} and 1080 cm^{-1} correspond to the aliphatic amine band. The aromatic ethers C-O bond is represented by the absorption

peak at 1260cm^{-1}, while there is also an aromatic nitro bond N-O at 1320 cm^{-1}[8, 9]. A tertiary alcohol which is represented in the band 1160 cm^{-1}. The absorption peak at 1730 cm^{-1} signifies an ester or a carboxylic acid C=O bond [5, 6]. The FT-IR spectrum reveals that the compound contains some benzene rings, aromatics, amine and an ester or carboxylic acid.

3.2 NUCLEAR MAGNETIC RESONANCE

[1] H-NMR and ^{13}C-NMR spectroscopy were used to determine the chemical structure of the unknown compound. The ^{1}H-NMR and ^{13}C-NMR spectroscopy measurements are described in section 3.19. The ^{1}H nucleus is the most commonly observed nucleus in NMR spectroscopy. This is because hydrogen is found throughout most organic molecules. The proton has high intrinsic sensitivity [10, 11]. It is also almost 100% abundant in nature. These factors make it a favorable nucleus to observe. The proton spectrum contains a wealth of chemical shifts and coupling information. This is a starting point for most structure determinations [12]. The ^{1}H-NMR spectra of the unknown compound is shown in figure 9 below:

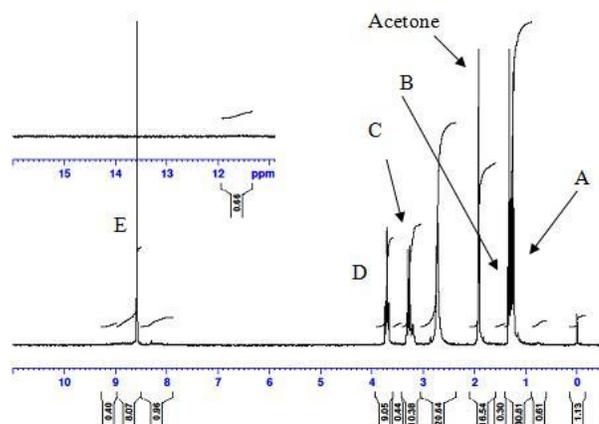**Fig 9 ^{1}H-NMR spectra of dried isolated compound collected from the decomposed product of cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.**

The ^{1}H-NMR spectrum of the unknown compound is shown in fig. 9. The compound was dissolved in dueterated acetone before the NMR analysis. The dueterated acetone solvent gave rise to a peak at 2.09 parts per million (ppm). Two triplet absorbances at areas of 1.38 and 1.45 ppm were attributed to the methyl groupspresent in the compound[5, 11, 13].Two quartet absorbances at areas of 3.40 and 3.85 ppm due to the presence of methylene groups in the compound which are separately connected with nitrogen and oxygen[5, 14]. There is a quartet as aresult of spin-spin splitting which creates one more peak than the number of hydrogens adjacent to it. The quartet means that they are next to 3 hydrogens or a terminal CH_3 group. One methylene quartet is attached to a nitrogen atom, while the other methylene quartet at 3.85ppm is directly bonded to the strongly deshielding O_2 or a carbonyl atom[15]. The more electronegative an atom is, the more electron time it will draw away from the nucleus. This will make the atom more deshielded, making the chemical shift move further downfield [11, 16].There is a single sharp peak at 8.71 ppm. This peak is generated from the resonance of the aromatic protons. The presence of this single peak is an indication that the aromatic

ring is symmetric. Another reason for this single peak is because the proton is next to no other hydrogen. Due to an absence of other hydrogens, the local magnetic field induced by the nucleus of other protons will not cause a multiplet of peaks. Rather, there is just a single peak [5, 11].The downfield shift of the aromatic peak is as a result of the nitration of the aromatic ring during the decomposition of the cured resin causes a downward shift in the aromatic peak. Nitrogen, being an electronegative atom, withdraws electron density. This consequently reduces the magnitude of the local magnetic field. The nitrogen atom desheilds the aromatic proton from the applied magnetic field. As a result of this, the aromatic proton experiences a slightly weaker magnetic field and resonance occurs at a higher ppm [15].

3.3 ^{13}C-NMR AND DISTORTION ENHANCEMENT BY POLARIZATION TRANSFER (DEPT)

^{13}C-NMR and DEPT were used to obtain more information about the backbone structure of the unknown compound. The ^{13}C-NMR spectrum of the compound is shown in figure 10. The ^{13}C-NMR spectrum is usually recorded with broadband decoupling of all protons. This removes multiplicity in carbon resonances. As a result, the doublet, triplet and quartet patterns which are indicative of CH, CH$_2$ and CH$_3$ groups are not seen, and each carbon resonance appears as a singlet, increasing sensitivity[17, 18]. Each peak identifies a carbon atom in a different environment within the molecule. There are different ranges of chemical shifts for different carbon environments.
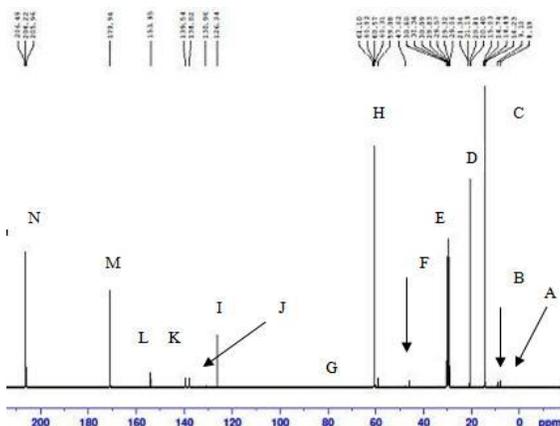

Fig. 10 ^{13}C-NMR spectra of dried isolated compound collected from the decomposed product of microwave cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

Each chemically distinct carbon atom gave rise to a single peak in its normal ^{13}C NMR spectrum. The peaks at 47.6 and 60 ppm arose as a result of different carbons singly bonded to an oxygen atom. The external magnetic field experienced by the carbon nuclei is affected by the electronegativity of the atoms attached to them. The effect of this is that the chemical shift of the carbon increases if an atom like oxygen is attached to it [16, 19]. This is because the electronegative oxygen pulls electrons away from the carbon nucleus thereby leaving it more exposed to any external magnetic field. This means that a smaller external magnetic field will be needed to bring the nucleus into the resonance condition than if it was attached to less electronegative atoms [19, 20]. The peak at 170 ppm is a carbonyl resonance which is due to a carbon in a carbon – oxygen double bond in an acid or ester. The peaks at 126.3, 130.9, 139.5, and 153 ppm are typical for carbons in an aromatic benzene ring [5, 17, 21]. The triplet peak around 30 and 206 ppm are as a result of the carbon atoms present in the solvent.

3.4   DISTORTION ENHANCEMENT POLARIZATION TRANSFER

There are four possible types of carbon atoms. They are methyl (CH$_3$), methylene (CH$_2$), methane (CH) and quaternary carbon (C) [15]. The carbon type depends on the number of hydrogens directly attached to a particular carbon atom. The ^{13}C NMR does not dive any information as to the types of carbon present in the spectrum [15]. Distortion Enhancement by Polarization Transfer (DEPT) is used to differentiate the carbon types. In DEPT with θ = 90^0 spectrum, only CH carbons appear as positive signals. In DEPT with θ = 135^0 spectrum, CH and CH$_3$ carbons produce positive peaks while CH$_2$ carbons produce negative peaks. Quaternary carbons do not appear in the DEPT spectra. Any extra peaks found in the normal ^{13}C spectrum are due to quaternary carbons. The DEPT with θ = 90^0 and DEPT with θ = 135^0 spectrum of the unknown compound are shown in figures 12 and 13 below
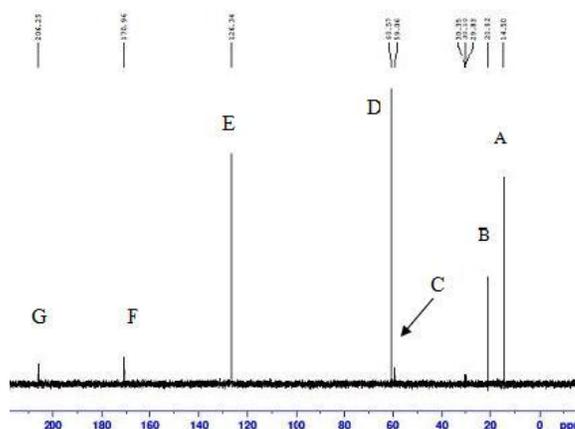

Fig. 11 DEPT with θ = 90° spectra of dried isolated compound collected from the decomposed product of microwave cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.
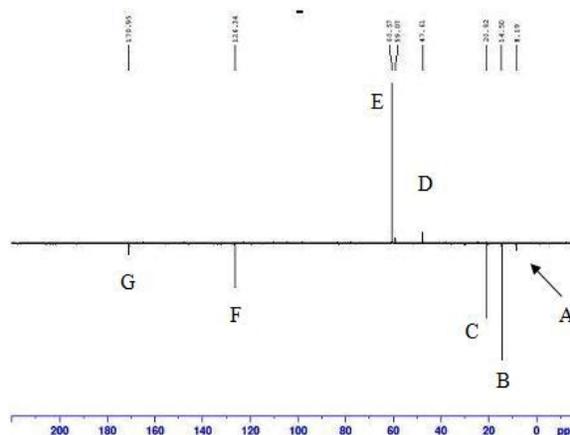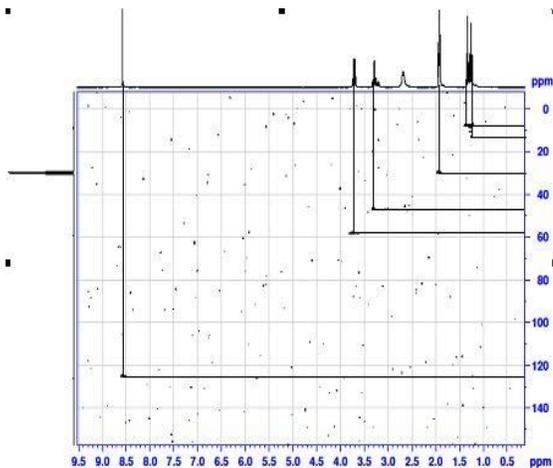

Fig. 12 DEPT with θ = 135^0 spectra of dried isolated compound collected from the decomposed product of microwave cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

The DEPT with θ = 90⁰ spectra in figure 11 identifies CH resonances at 170.9, 126.3, 60.57, 20.82 and 14.5 ppm. The DEPT with θ = 135⁰ spectra in figure 12 identifies the CH_2 resonance as negative peaks at 126.3, 20.8, and 14.5 ppm. Since the DEPT with θ = 135⁰ spectra shows both CH_3 and CHs as positive peaks, the peaks at 47.6 and 8.19 ppm can be quickly identified as CH_3 resonances by comparing it to figure 11 which only shows CHs as positive peaks. The absence of the peaks 153 and 139 ppm in the DEPT spectra indicates that they are quaternary carbons. The peaks 29-31 ppm and 206 ppm arise from the carbon atoms present in the solvent (acetone) used for the NMR analysis.

3.5   HETERONUCLEAR MULTIPLE-QUANTUM CORRELATION

In Heteronuclear Multiple-Quantum Correlation experiment, two different types of nuclei (^{1}H and ^{13}C) are correlated into a 2-dimensional experiment by the evolution and transfer of single quantum coherence [22, 23]. It offers a means of identifying 1-bond H-C activities within a molecule. One dimension represents the ^{1}H chemical shift, while the other represents the ^{13}C chemical shift. Cross peaks indicate a one-bond ^{1}H-^{13}C connectivity. The HSQC technique relies on magnetization transfer from the proton to its directly attached atom, and back on to the proton. As a result of this magnetization transfer, no responses are expected for non-protonated carbons, or for protons bound to other heteroatoms [22-24].

Fig. 13 HSQC spectra of dried isolated compound collected from the decomposed product of microwave cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

Fig. 13 shows the HSQC spectra for the unknown compound. Here the ^{1}H protons from the ^{1}H-NMR spectra are related to the carbon atoms from the ^{13}C-NMR spectra. From the figure above, the aromaticproton indicated at peak 8.7 ppm is directly bonded to the aromatic carbon atom at about 126 ppm. The signals at 3.85 ppm which are characteristic for the methylene protons attached to O_2 is directly bonded to the carbon atoms of the methylene group at 60 ppm in the ^{13}C-NMR spectra. The methylene quartet at 3.4 ppm is bonded to the carbon atoms of methylene at 47 ppm. The signals appearing at 1.38 and 1.45 ppm which indicate methyl groups are bonded to the carbon atoms of the methyl groups at 9.1 ppm and 11 ppm. From the above ^{1}H-NMR, ^{13}C-NMR, DEPT

with θ = 90⁰, DEPT with θ = 135⁰ and the infrared spectra of the isolated compound, it is observed that there are two ethyl ester groups and an amine bound to the benzene ring. The analysis suggests the unknown compound is identified as 1, 3– di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene. Its chemical structure is shown in the fig. 14 below.
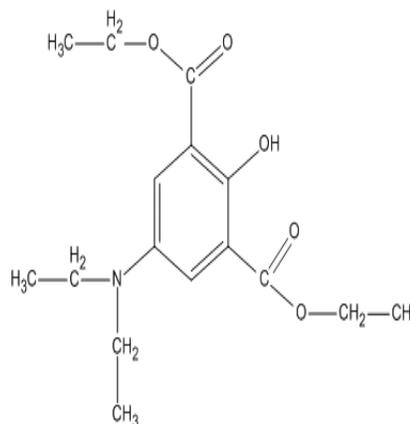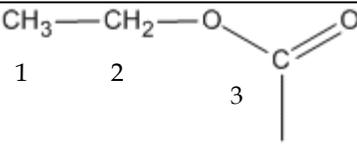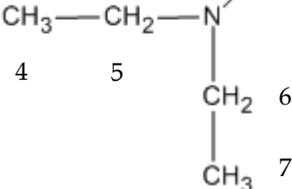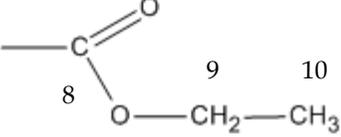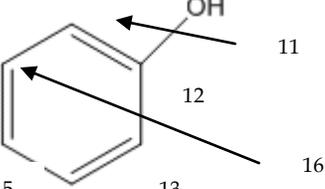

Fig. 14 Structure of 1, 3 – di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene.

The assignment of the peaks of the ^{1}H-NMR spectrum of 1, 3 – di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene from figure 10 is tabulated in table 1 below.

TABLE I ASSIGNMENT OF PEAKS OF THE ^{1}H-NMR SPECTRUM OF 1, 3 – DI (ETHYL ESTER)-5-(DIETHYL AMINO)-2-HYDROXYBENZENE

Peak	Chemical Shift, ppm	Assignment
A	1.38 Methyl CH$_3$	CH$_3$—CH$_2$—N (diethyl amino)
B	1.45 Methyl CH$_3$	CH$_3$—CH$_2$—O—C=O (ethyl ester)
C	3.41 Methylene CH$_2$	CH$_3$—CH$_2$—N (diethyl amino)
D	3.85 Methylene CH$_2$	CH$_3$—CH$_2$—O—C=O (ethyl ester)
E	8.71 Benzene	H—benzene ring—H

Assignment	Peak	Chemical shift (ppm)
CH_3—CH_2—O—C(=O)— (1, 2, 3)	C1	9.1
	C2	59.0
	C3	170.9
CH_3—CH_2—N, CH_2, CH_3 (4, 5, 6, 7)	C4	11.5
	C5	47.6
	C6	47.6
	C7	11.5
C(=O)—O—CH_2—CH_3 (8, 9, 10)	C8	170.9
	C9	47.6
	C10	9.1
benzene ring with OH (11, 12, 13, 14, 15, 16)	C11	126.3
	C12	153.9
	C13	126.3
	C14	138.0
	C15	139.5
	C16	138.0

3.4 ELECTROSPRAY IONIZATION MASS SPECTROSCOPY

Electrospray Ionization was used to confirm the molecular weight of the compound which was identified as 1, 3 – di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene. The electrospray ionization spectrum is shown in fig. 15. A base peak of 332 is identified.
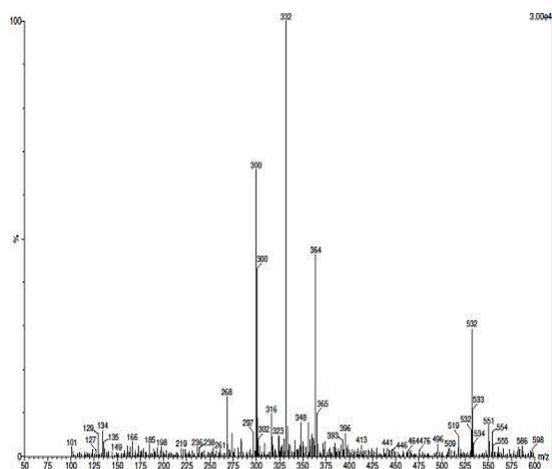

Fig. 15 Electrospray ionization spectra of 1, 3–di(ethyl ester)-5-(diethyl amino)-2-hydroxybenzene.

The molecular formula of 1, 3–di (ethyl ester)-5-(diethyl amino)-2-hydroxybenzene is $C_{16}H_{23}O_5N$. This gives a molecular mass of 309 g mol^{-1}. There is a presence of sodium ion in the electrospray chamber. This sodium ion adds a unit mass of 23 to the molecular ion of the compound. Adding 23 to the molecular mass of 1, 3–di (ethyl ester)-5-(diethyl amino)-2-hydroxybenzene gives us 332. This value corresponds to the molecular ion peak at m/z 332 which also corresponds to the base peak of the electrospray ionization spectra in figure 15. The electrospray ionization mass spectra confirms the molecular mass of 1, 3–di (ethyl ester)-5-(diethyl amino)-2-hydroxybenzene.

4 CONCLUSION

Fully cured samples of Araldite DLS 772 / 4 4' DDS were successfully decomposed by a microwave reaction system. The chemical structure of the decomposed product was determined to be 1, 3–di (ethyl ester)-5-(diethyl amino)-2-hydroxybenzene.

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