

Infrared Studies Of Curing Of Araldite DLS 772 / 4 4' DDS And Araldite LY 5052 / 4 4' DDS Epoxy Systems Using Conventional And Microwave Energy.

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ABSTRACT

Comparative studies were carried out on the effects of infrared radiation on the cure of two epoxy resins Araldite DLS 772, Araldite LY 5052 and a hardener, 4 4' Diaminodiphenyl sulfone.

A microwave heated calorimeter and an industrial oven were used to cure the samples at various isothermal conditions and different holding times. A FT-IR spectrometer was used to carry out infrared studies of the cured epoxy samples. The infrared spectra of microwave and conventionally cured samples are similar, indicating a similar reaction pathway. For both epoxy systems, the rate of consumption of epoxy and amine groups was higher during curing under microwave conditions. This is because microwave heating directly heats the polymer molecules as a result of the relaxation of the polarized polymer dipoles along the electric field, allowing more epoxy to be reacted with the amine in the curing reaction.

Keywords: - Infrared, Epoxy, Microwave, Curing

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I. INTRODUCTION

Fourier Transform Infrared Spectroscopy has been widely used to study crosslinked systems. It can provide detailed information on the chemical structure of the molecules. Fourier Transform Infrared spectroscopy also provides a quick and accurate means of determining the extent of conversion. For an epoxy system, the use of Fourier Transform Infrared Spectroscopy has mainly been limited to the investigation of the disappearance of epoxy and amine groups [1-4]. The reason for this limitation is because of several factors such as the complexity of the reactions, the difficulties associated with the characterization of the products during network formation, and the superimposition of the characteristic bands which make peak identification very difficult [1-4].

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. An electromagnetic radiation consists of an electric field whose plane is perpendicular to the plane of a magnetic field. The microwave heating effect originates from the interaction of the electric field component of the microwaves with charged particles in the materials. A current will be induced through the material if the charged particles are able to move through the electric field. If the particles can not move because they are bonded to the material, they will simply rearrange themselves in phase with the electric field. This mechanism is called dielectric polarisation [5].

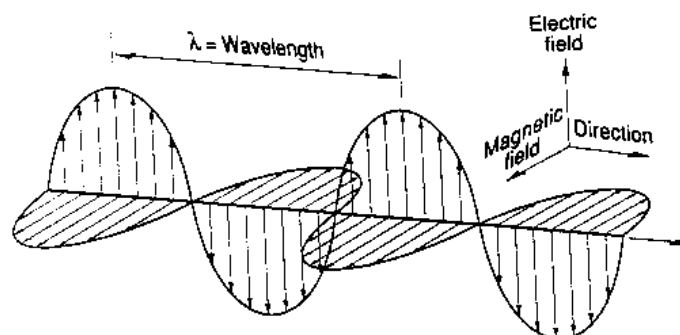
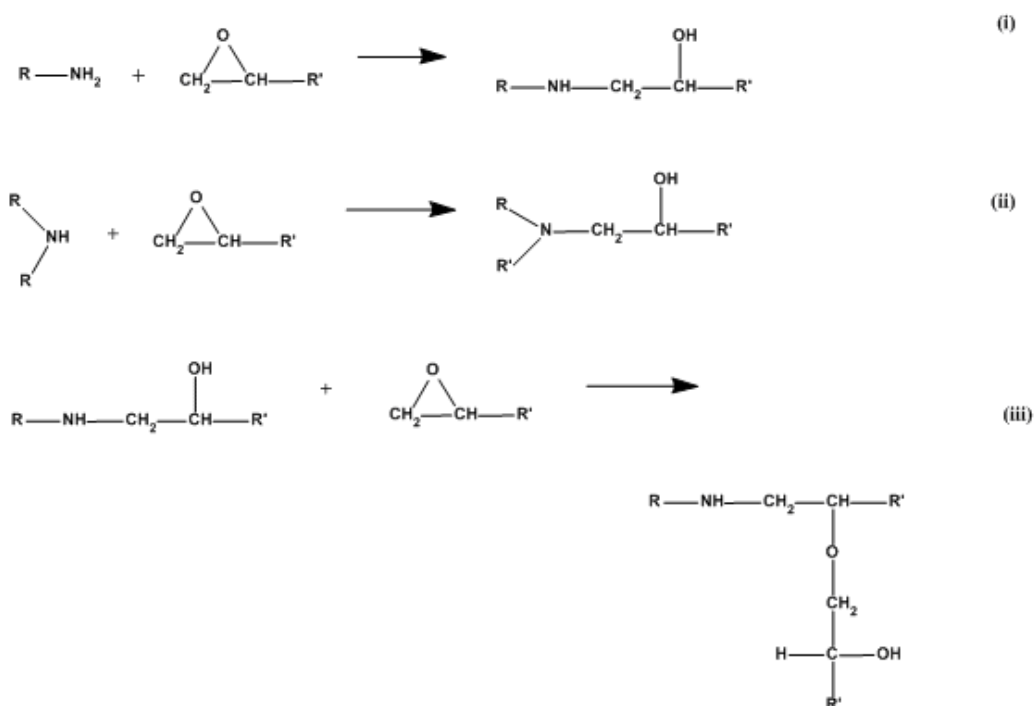


Figure 1 An electromagnetic wave [6].

Microwaves have been found to be a good alternative method for curing thermoset polymers. Compared to conventional heating techniques which are based on conduction of heat through a material, microwave heating is a direct form of heating. Microwaves generate heat within the materials. Microwave radiation enables sample temperatures to be potentially changed or controlled more readily [7]. Any increase or decrease in the microwave input power leads to a corresponding increase or decrease in the temperature of the material undergoing cure. Unlike conventional heating which heats the material being processed, along with the walls of the oven and the air surrounding the process material, microwave heating affects only the material being processed. This makes microwave heating a more energy efficient method of heating materials being processed, and this translates into lower production costs for microwave heating [3]. Microwaves do not have any intrinsic difficulties associated with their use, as a result of this, microwave cured products are applied to many diverse industries [4].

The curing of epoxy resin by amine curing agents is expressed by the formula shown in figure below. The epoxy moieties of the DGEBA can react with either the primary or secondary amine to form an OH in the main chain as in (i) and (ii) which, later on, can react with another epoxide ring to further crosslink the resin. The relative rates of those three reactions are important for the final structure and properties of the cured resin[8].



This article presents the results of the infrared studies on the conventional and microwave cure of Araldite DLS 772 / 4 4' DDS and Araldite LY 5052 / 4 4' DDS epoxy

II. EXPERIMENTAL

2.1 MATERIALS

Araldite DLS 772 and Araldite LY 5052 were the epoxy resin used for this research. It was supplied by Hexcel, UK. Araldite DLS 772 has an epoxy equivalent of 192.33, while Araldite LY 5052 has an epoxy equivalent of 148. The hardener used for this study was 4 4' Diaminodiphenyl sulfone. It was supplied by Sigma-Aldrich.

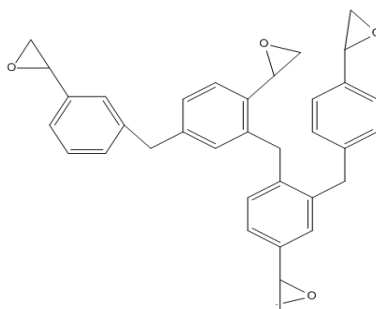


Figure 2 Chemical Structure of Epoxy Phenol Novalac Resin



Figure 3 Chemical structure of 1,4-butanedioldiglycidyl ether

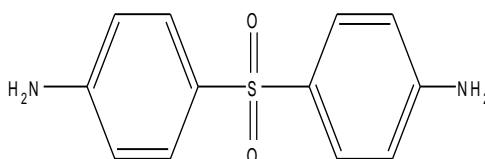


Figure 4 4,4'-diphenyldiaminosulfone [4]

III. CURING PROCEDURE

In order to choose the appropriate stoichiometric amine / epoxy (A/E) ratio value to be used for this research, Araldite LY 5052 / 4,4'-DDS and Araldite DLS 772 / 4,4'-DDS epoxy systems were prepared with amine / epoxy stoichiometric ratios of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2. DSC scans were carried out on these systems. The systems were heated at 10 K min^{-1} from 30 to $350 \text{ }^\circ\text{C}$ in order to cure the sample. It was then cooled back to $0 \text{ }^\circ\text{C}$, and reheated at a heating rate of 10 K min^{-1} in order to determine the glass transition temperature value. The epoxy amine / epoxy ratio with the highest T_g was chosen for this research.

Similar samples of Araldite LY 5052 / 4,4'-DDS and Araldite DLS 772 / 4,4'-DDS epoxy system with amine / epoxy ratios of 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2 were prepared for microwave curing. A heating rate of 10 K min^{-1} was used to cure the sample from 30 to $310 \text{ }^\circ\text{C}$, and allowed to cool. Pieces of the cured samples were extracted from the microwave sample tube, and a DSC scan was carried out on the extracted piece from 30 to $350 \text{ }^\circ\text{C}$ at a heating rate of 10 K min^{-1} in order to determine its glass transition temperature.

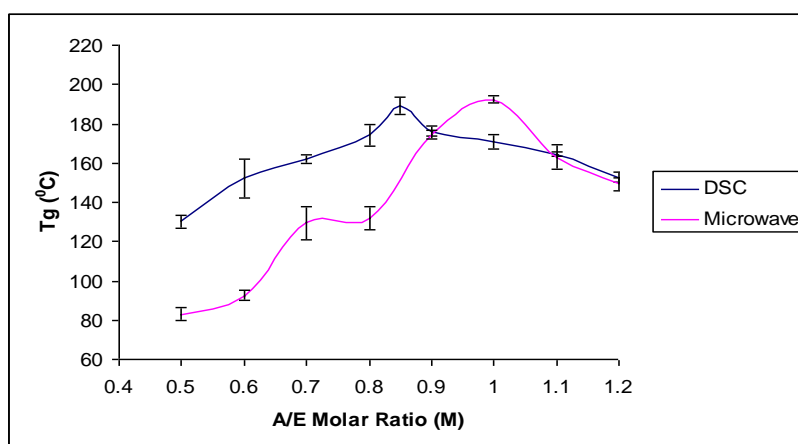


Figure 5 Plot of Glass Transition against Molar ratio for different stoichiometric ratios for both conventional and microwave cured samples of Araldite LY 5052 / 4,4'-DDS epoxy system.

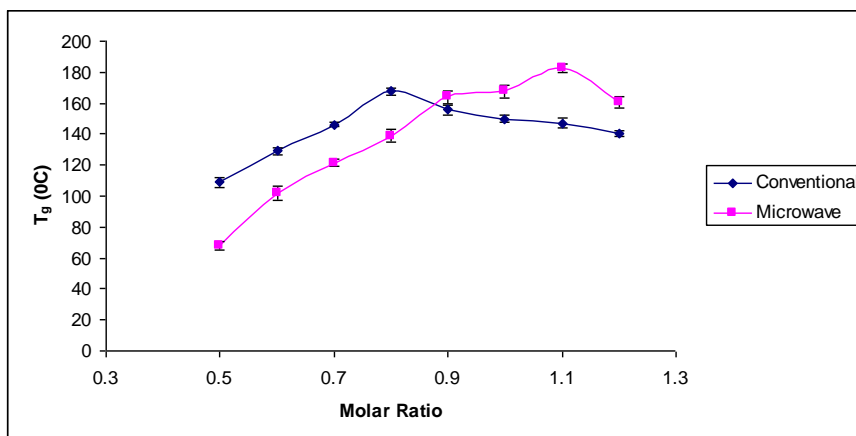


Figure 6 Plot of Glass Transition against Molar ratio for different stoichiometric ratios for both conventional and microwave curing for Araldite DLS 772 / 4 4' DDS epoxy system.

Both plots show a increase in T_g values as the Amine / Epoxy ratio increases up to a maximum, and then the T_g starts to decrease. The highest T_g values of conventional and microwave heated samples occur at different stoichiometric ratios. The highest T_g value of the microwave cured sample occurs at a higher Amine / Epoxy Molar ratio than conventional heating. This is an early indication that the curing mechanisms for conventional and microwave curing are different. For both epoxy systems, the Amine / Epoxy ratio with the highest T_g for both microwave and conventionally cured samples were selected and used for all subsequent experiments in this research. Table 4.5 below show the selected Amine / Epoxy ratio from the conventionally and microwave cured samples which were used this research.

Table 1 Stoichiometric ratios chosen for this research.

Epoxy system	Conventional (amine / epoxy ratio)	Microwave (amine / epoxy ratio)
Araldite LY 5052 / 4 4 DDS	0.85	1.0
Araldite DLS 772 / 4 4 DDS	0.8	1.1

An industrial oven was used for the thermal curing of the Araldite DLS 772 / 4 4' DDS and Araldite LY 5052 / 4 4' DDS epoxy system. Samples weighing between 2-5 mg were placed in aluminium sample pans; and heated in an industrial oven to 30 , 60, 90, 120, 150, 180, 210, 240 degrees. The samples were held at these temperatures for 30 minutes.

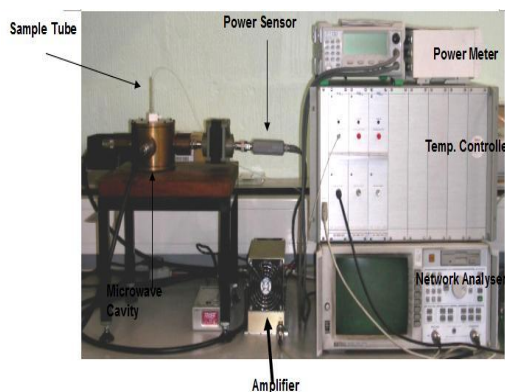


Figure 7 : Microwave Heated Calorimeter used for this research.

A microwave calorimeter shown in figure 7 was used to carry out microwave curing of the samples. The microwave curing was carried out in a cylindrical brass, single mode cavity operating in a TE111 mode which was designed to give maximum field strength at the centre of gravity. A Hewlett-Packard 8720ET was used to generate microwaves at a frequency of 2.45GHz; which were then amplified to a maximum power of 30W with a solid state amplifier. An Anritsu power meter was used to measure the transmitted and reflected powers. The power required for heating the sample was calculated by subtracting the transmitted and reflected powers from the amplifier power. This power is similar to the heat flow to the DSC cell in the sense that there will be a decrease in the microwave power during exothermic reaction, while an endothermic reaction will require an increase in the microwave power.

For microwave curing, epoxy resin samples weighing an average of 0.3g were poured in glass test tubes and placed in the centre of the cavity. A fluoroptic thermometer was inserted in a 1.5 mm diameter glass tube placed in a test tube. Separate samples were heated to 30 , 60, 90, 120, 150, 180, 210, 240 degrees and held at these temperatures for 30 minutes.

RESULTS AND DISCUSSION

3.1 Araldite LY 5052 / 4 4 ' DDS and Araldite DLS 772 / 4 4 epoxy systems.

FT-IR was used to study the changes in the epoxy peaks which occur when the curing reaction took place. The spectrum of an uncured mixture of Araldite LY 5052 / 4 4 'DDS epoxy system with an amine / epoxy ratio of 0.85 is shown in figure 5 below.

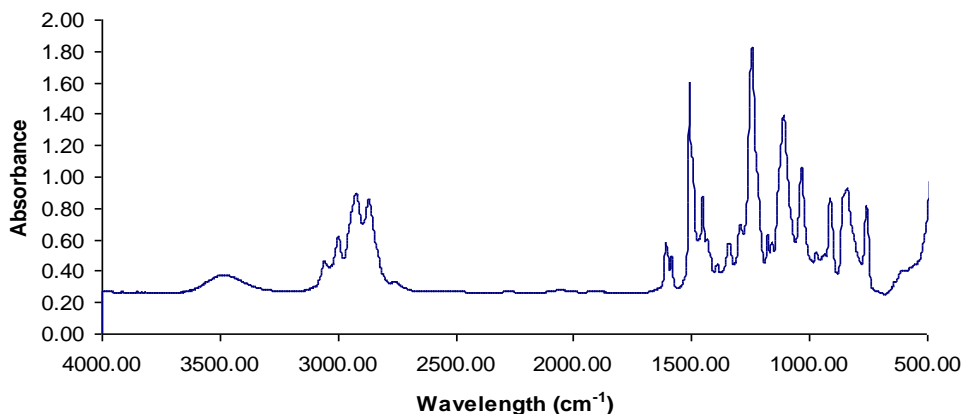


Figure 8 FT-IR Spectra of uncured Araldite LY 5052 / 4 4 ' DDS epoxy system with an amine / epoxy ratio of 0.85.

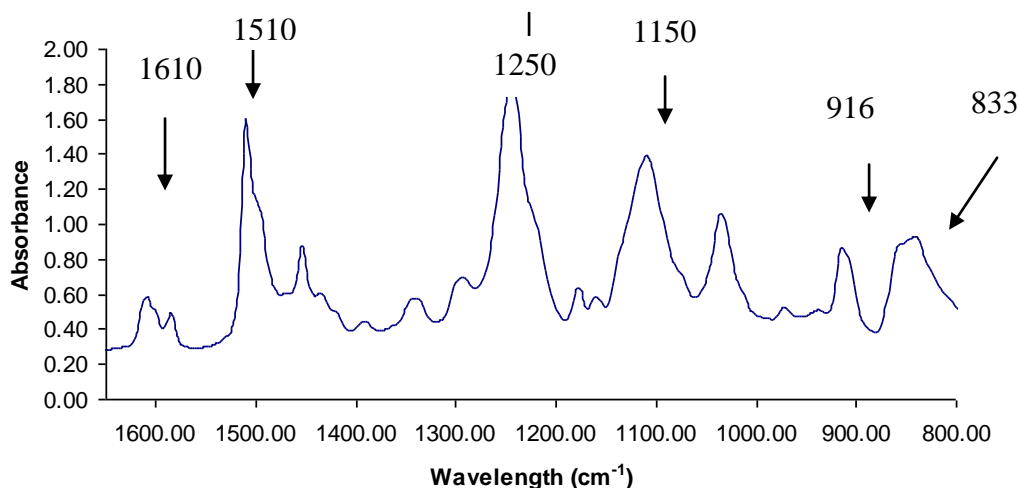


Figure 9 Expanded view of FT-IR Spectra of uncured 0.85M amine / epoxy ratio for Araldite LY 5052 / 4 4 ' DDS epoxy system .

The spectrum in figure 9 shows a noticeable oxirane ring (epoxy) peak at 916 cm^{-1} . This is the asymmetric ring stretching band of the epoxy ring [9-12]. The spectrum also shows the symmetric stretching of the epoxy ring at 1250 cm^{-1} . The bands at 1510 cm^{-1} and 833 cm^{-1} are assigned to the p-phenylene groups [10, 11]. The aliphatic stretching vibration of $-\text{CH}_2-$ groups is shown as a peak at 2920 cm^{-1} [10]. The stretching vibration of the primary amino group ($-\text{NH}_2$) which is from the hardener (4 4 ' DDS) shows an absorption peak at 1610 cm^{-1} [10]. The peaks at 1250 cm^{-1} and 1150 cm^{-1} are the strong asymmetric and symmetric SO_2 stretching [10].

Figures 10 to 13 show the overlaid FT-IR spectra of Araldite LY 5052 / 4 4 ' DDS and Araldite DLS 772 / 4 4 ' DDS epoxy systems after conventional and microwave heating at $180\text{ }^\circ\text{C}$ for 240 minutes

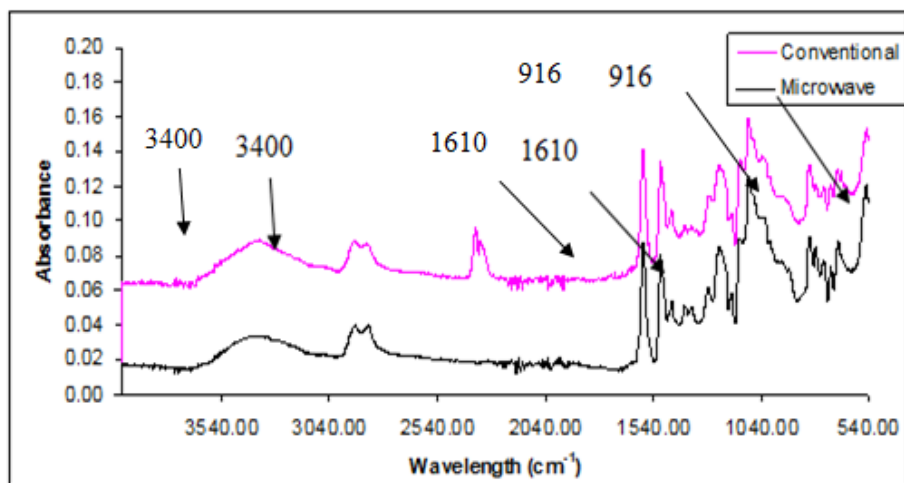


Figure 10 Overlaid FT-IR Spectra of Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85 after conventional and microwave heating at 180°C for 240 minutes.

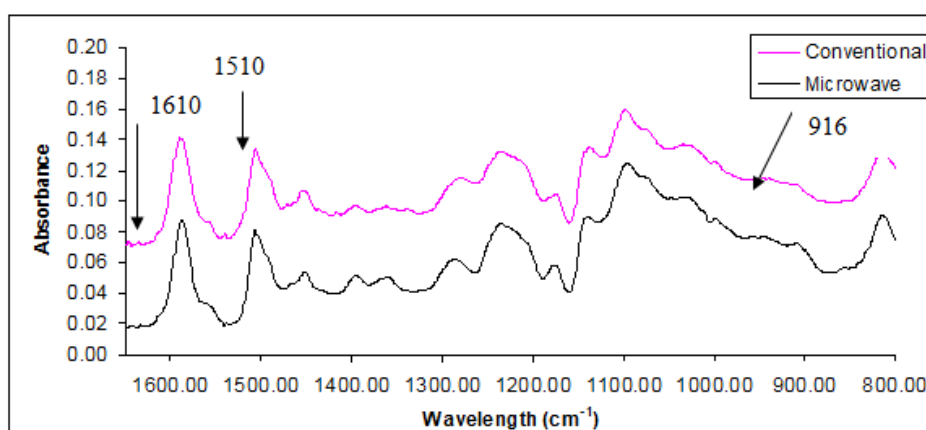


Figure 11 Expanded view of Overlaid FT-IR Spectra of Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85 after conventional and microwave heating at 180 °C for 240 minutes

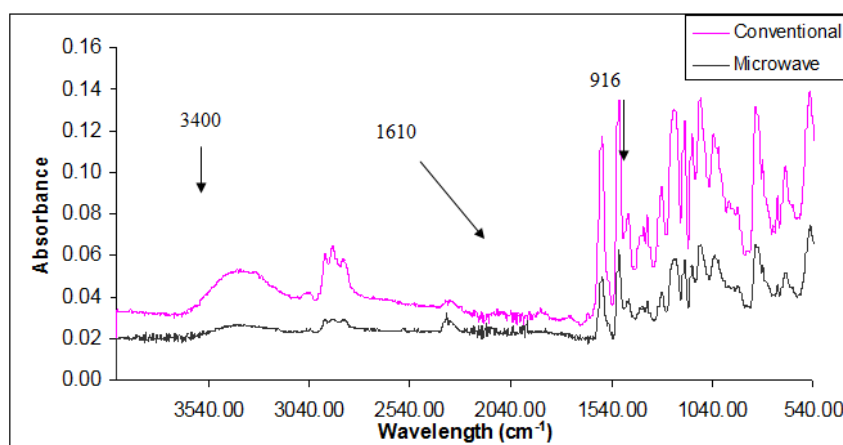


Figure 12 Overlaid FT-IR Spectra of Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 after conventional and microwave heating at 180 °C for 240 minutes.

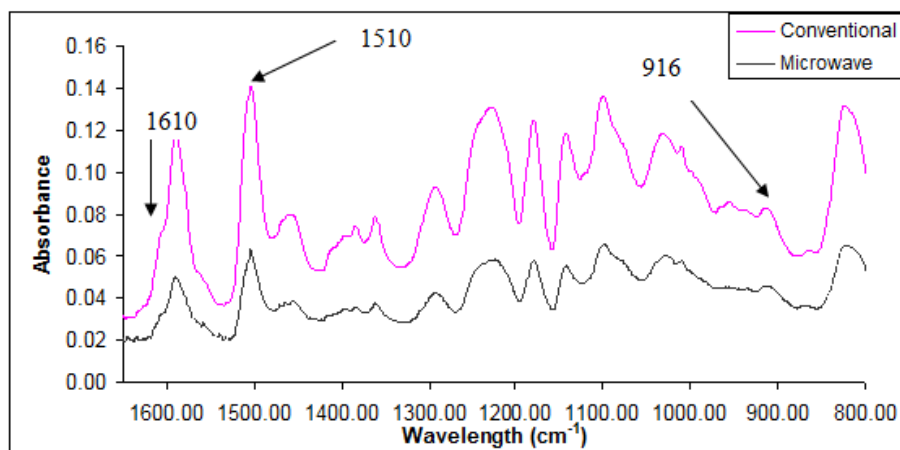


Figure 13 Expanded view of Overlaid FT-IR Spectra of Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 after conventional and microwave heating at 180 °C for 240 minutes.

For both epoxy systems, the infrared spectra of the specimens after they had been cured at 180°C for 240 minutes were noticeably different from the spectra of the uncured specimen. The prominent features that occurred during polymerization were the decreasing and almost complete disappearance of the epoxy ring at 915 cm^{-1} and 862 cm^{-1} [9, 12]. The N-H stretch band at 1610 cm^{-1} also decreased in size. The decrease in the epoxy and the amine bands is an indication of the consumption of the epoxy and the amine bands during the reaction. The curing reaction occurs by the reaction of the end epoxy groups with the hardener. The epoxy rings open out and the molecules become linked in a three dimensional network. New absorptions were formed around 3400 cm^{-1} . This was as a result of the formation of the secondary amine and the hydroxyl groups during cure. The bands at 833 and 1510 cm^{-1} were unaffected during cure and thus remained constant [9, 11, 12]. The almost complete disappearance of the epoxy and the amine peaks at the end of the spectra showed that most of the epoxy and the amine group reacted during the curing process. These occurrences indicated that a crosslinked network was formed.

Several samples of Araldite LY 5052 / 4 4' DDS and Araldite DLS 772 / 4 4' DDS were cured using both a DSC and a microwave heated cavity at 180 °C. At intervals of 30 minutes up to 240 minutes, a specimen was removed. The reaction was quickly stopped by dipping it into liquid nitrogen for about ten minutes. An infrared spectrum was then taken.

The overlaid spectra for both the conventionally cured and microwave cured samples of both epoxy systems at different times at 180°C are shown in figures 14 to 19.

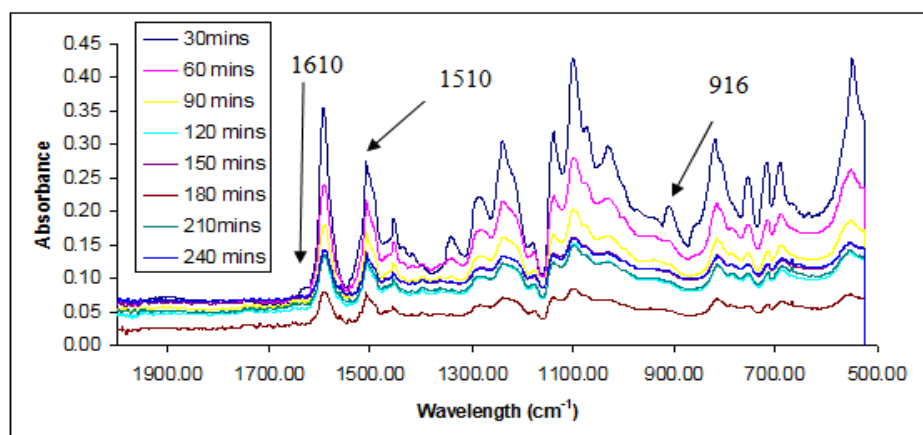


Figure 14 Overlaid spectra for conventionally cured Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85

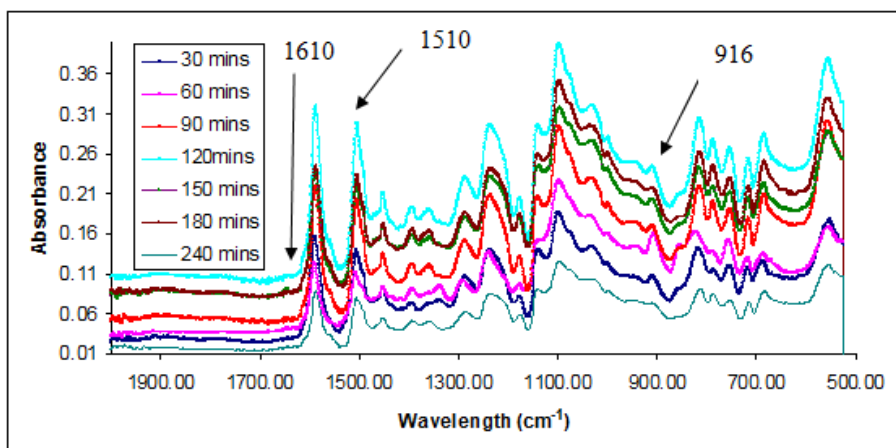


Figure 15 Overlaid spectra for microwave cured Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85

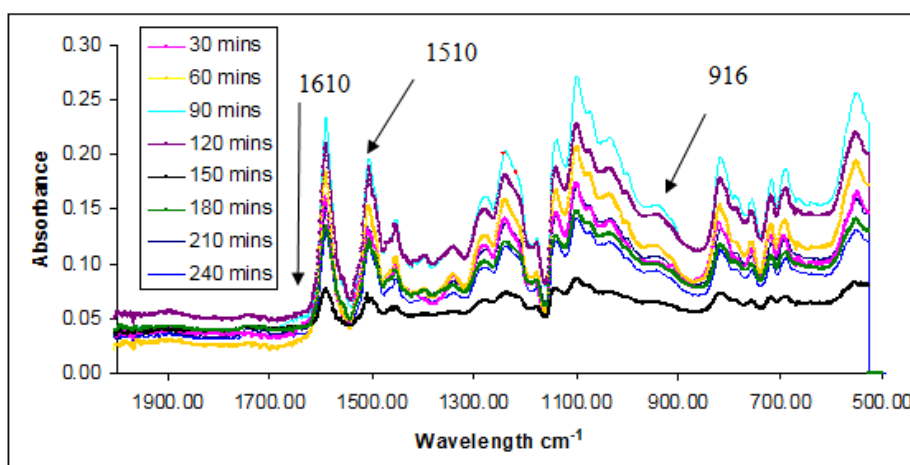


Figure 16 Overlaid spectra for conventionally cured Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0

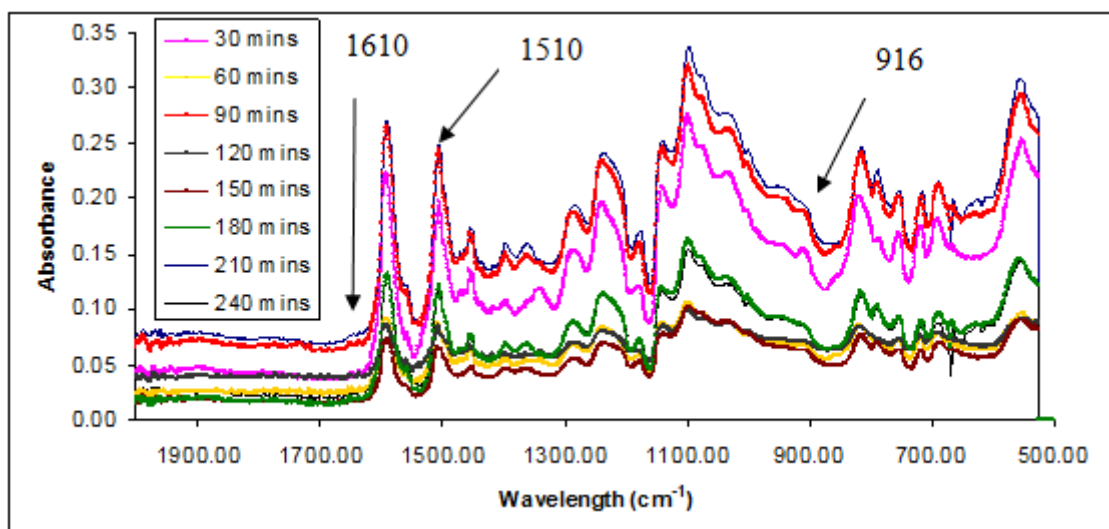


Figure 17 Overlaid spectra for microwave cured Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0

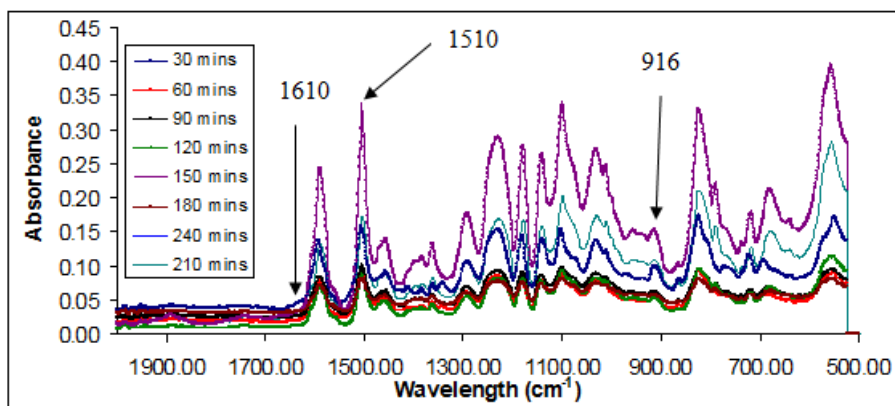


Figure 18 Overlaid spectra for conventional cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

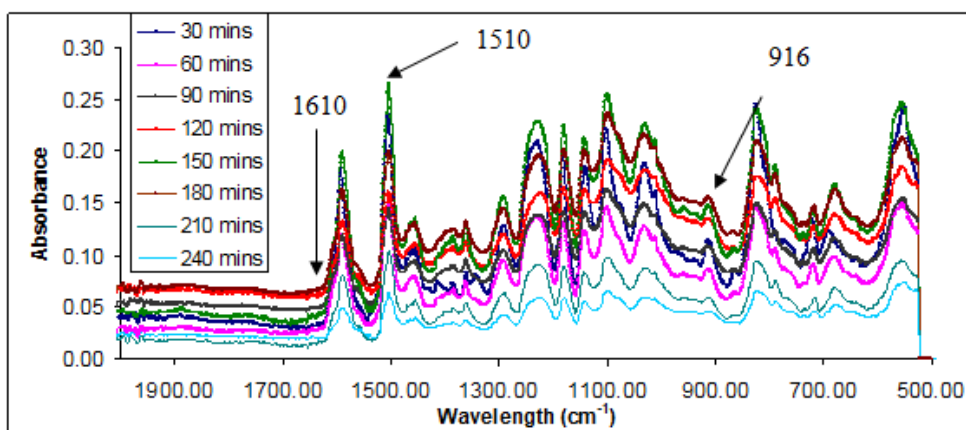


Figure 19 Overlaid spectra for microwave cured Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8.

The epoxide bands can be used to estimate the degrees of polymerization. The rate of polymerization can be estimated by following the loss of epoxide as the isothermal cure time increases. In order to estimate the changes in the epoxide concentrations during polymerization, the absorbance at 916 cm^{-1} is divided by the absorbance at 1510 cm^{-1} which was used as an internal standard [1, 13, 14]. The infrared spectra data used was in absorbance because as stated in Beer's Law, the absorbance is linearly proportional to concentration [15].

A comparison of polymerization rates is shown in figure 20 for conventional and microwave curing of Araldite LY 5052 / 4 4 DDS different times at an isothermal temperature of 180 °C.

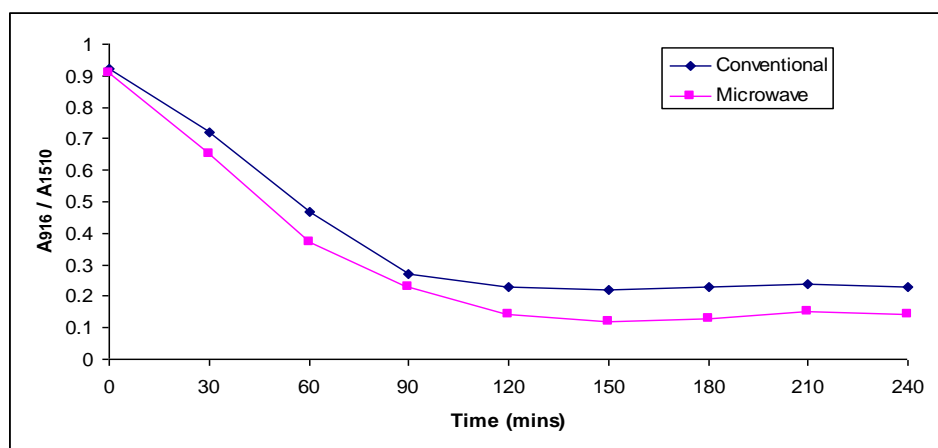


Figure 20 Epoxide absorbance normalised against the absorbance for phenyl for Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85 at different times at 180 °C during conventional and microwave heating.

It can be observed that there was an increase in the consumption of epoxide as the reaction time proceeded. Also, the rate of consumption of the epoxide was much faster in the microwave curing than in conventional curing at each measured time. Overall, there was a higher consumption of epoxy in the microwave curing than in the conventional curing. This enhancement in polymerization in the microwave region is very much anticipated because microwave heating directly heats the polymer molecules as a result of the relaxation of the polarized polymer dipoles along the electric field [9]. This allows more epoxy to be reacted with the amine in the curing reaction.

Epoxide absorbance ratios for Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0 and Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 epoxy systems are shown figures 21 – 24. The results all show that a higher rate of epoxy was consumed in microwave heating than in conventional heating, and a higher rate of polymerization for microwave. As explained, this is because of the ability of microwave energy to selectively heat the localised hotspot in a molecule unlike the conventional heating which requires the entire material to be heated first.

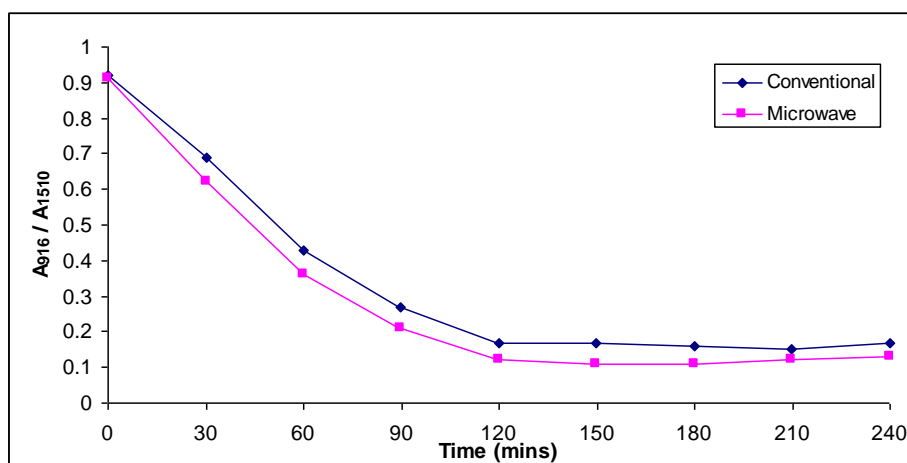


Figure 21 Epoxide absorbance normalised against the absorbance for phenyl for Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0 at different times at 180 °C during conventional and microwave heating.

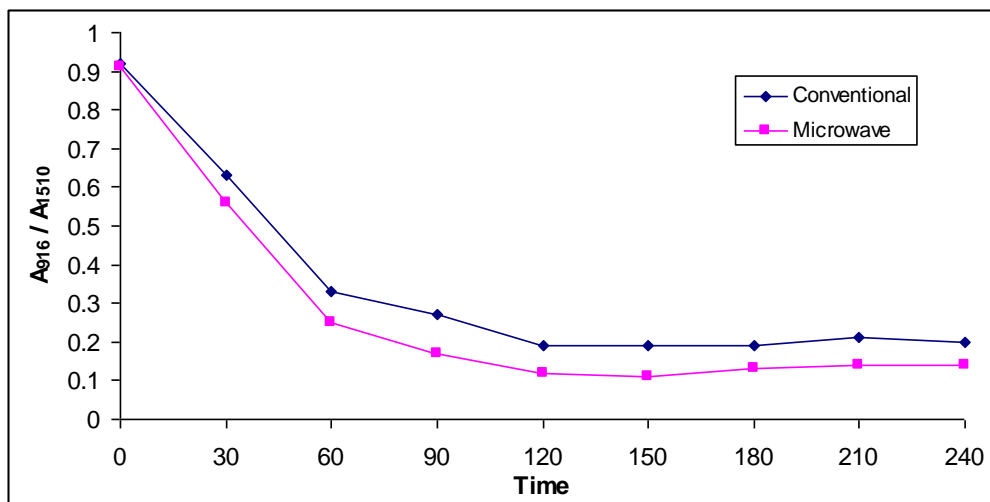


Figure 22 Epoxide absorbance normalised against the absorbance for phenyl for Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 at different times at 180 °C during conventional and microwave heating.

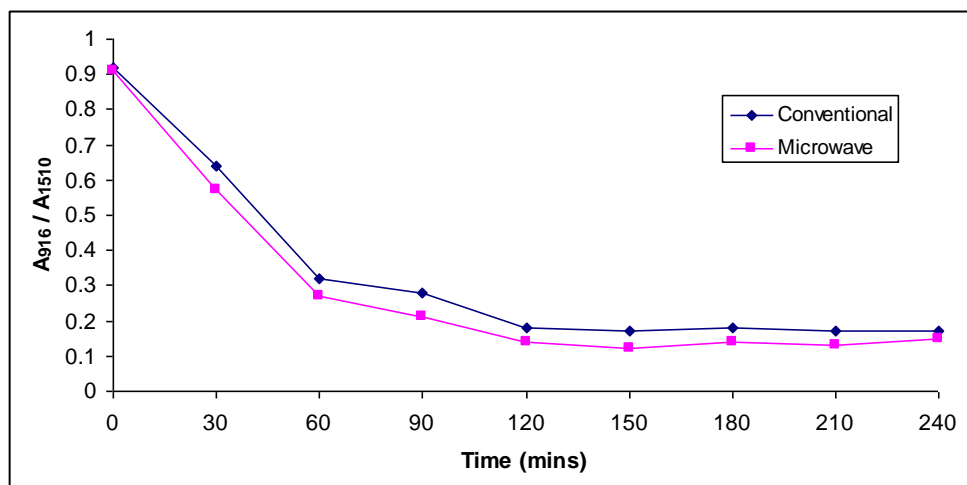


Figure 23 Epoxide absorbance normalised against the absorbance for phenyl for Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 1.1 at different times at 180 °C during conventional and microwave heating.

The amine bands were used to estimate the degrees of polymerization. The loss of the amine band during curing can also be used to follow the rate of polymerization as the isothermal cure time increases. In order to estimate the changes in the amine concentrations during polymerization, the absorbance at 1610 cm^{-1} is divided by the internal standard, which is the absorbance at 1510 cm^{-1} [1, 13, 14].

A comparison of polymerization rates using the amine band is shown in figure 24 for conventional and microwave curing of Araldite LY 5052 / 4 4 DDS an amine / epoxy ratio of 0.85 at different times at an isothermal temperature of 180 °C.

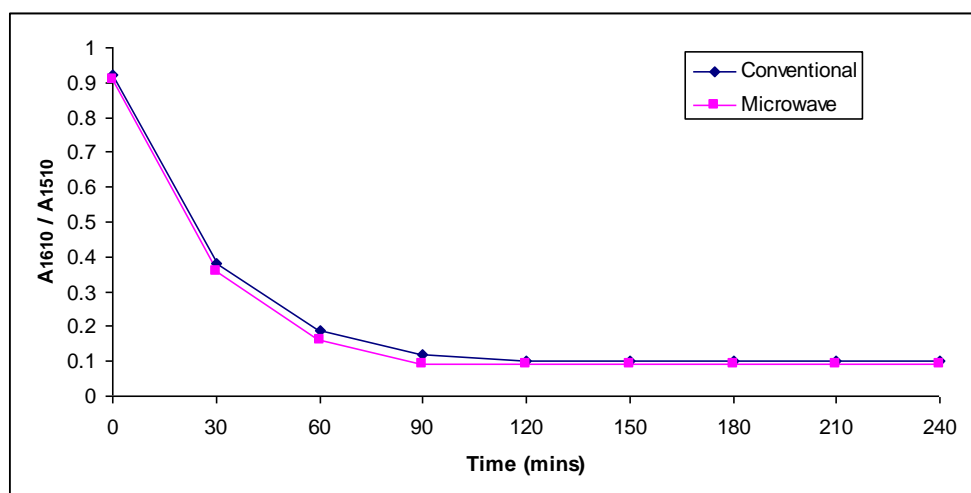


Figure 24 Amine absorbance normalised against the absorbance for phenyl for Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 0.85 at different times at 180 °C during conventional and microwave heating.

It can be observed from figure 24 that the rate of consumption of the amine was much faster in the microwave curing than in conventional curing at each measured time. A higher consumption of amine in the microwave curing than in the conventional curing was observed. This enhancement in polymerization in the microwave region is very much anticipated because microwave heating directly heats the polymer molecules as a result of the relaxation of the polarized polymer dipoles along the electric field [16], allowing more amine to be consumed during the curing reaction.

The amine absorbance ratios Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0 and Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8 are shown in figures 25 to 27 . As with the figures 21 to 24, the results all show that a higher rate of amine was consumed in microwave heating than in conventional heating, and a higher rate of polymerization for microwave. This is because of the ability of microwave energy to selectively heat the localised hotspot in a molecule unlike the conventional heating which requires the entire material to be heated first.

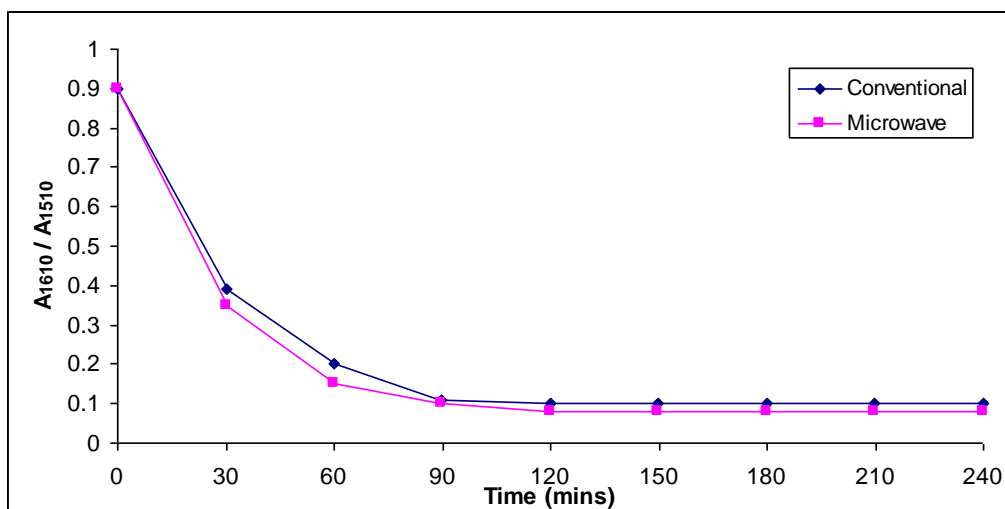


Figure 25 Amine absorbance normalised against the absorbance for phenyl for Araldite LY 5052 / 4 4' DDS with an amine / epoxy ratio of 1.0 at different times at 180 °C during conventional and microwave heating.

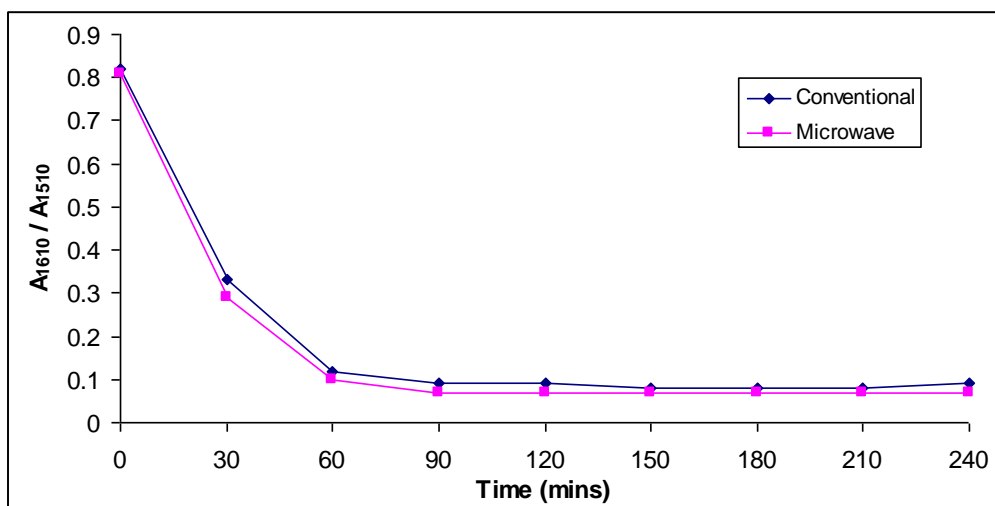


Figure 26 Amine absorbance normalised against the absorbance for phenyl for Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 0.8 at different times at 180 °C during conventional and microwave heating.

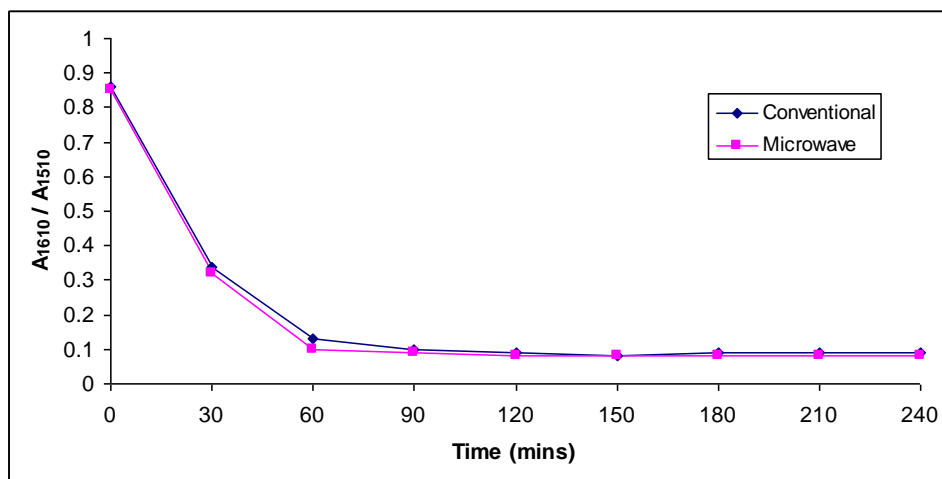


Figure 27 Amine absorbance normalised against the absorbance for phenyl for Araldite DLS 772 / 4 4' DDS with an amine / epoxy ratio of 1.1 at different times at 180 °C during conventional and microwave heating.

CONCLUSION

The similarity of the infrared spectra for both microwave and conventional curing of both epoxy systems is an indication that the curing reactions follows the same reaction pathway. For both Araldite LY 5052 / 4 4' DDS and Araldite DLS 772 / 4 4' DDS epoxy systems, the rate of consumption of the epoxy and amine groups was higher during the microwave curing reactions. This is because microwave heating directly heats the polymer molecules which leads to the relaxation of the polarized polymer dipoles along the electric field, allowing more epoxy and amine to be consumed during the curing reaction.

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