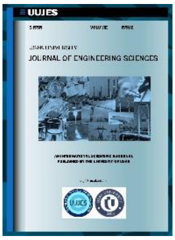

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Research article

RAMAN SPECTROSCOPY AND CURE KINETICS STUDIES OF A DLS 772 AND 4 4'DDS EPOXY SYSTEM DURING THERMAL AND MICROWAVE CURING

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Abstract

This research was carried out in order to further understand the effects of microwave heating on the functional groups and curing of epoxy systems. Raman Spectroscopy was used to record the stokes and the antistokes spectra of Diglydicydyl Ether of Bisphenol A (DGEBA) and 4,4' Diphenyldiaminosulfone (DDS) epoxy system at different temperatures during conventional and microwave cure, and their molecular temperatures were calculated from the data obtained. The temperatures showed that thermal heating does not excite the functional groups of the epoxy resin and the hardener, as their molecular temperature was in the same region as the cure temperature whereas Raman spectroscopy was unable to produce any stokes or antistokes spectra during microwave curing of the epoxy system. The cure kinetics of the DLS 772 / 4, 4' DDS system was also studied by using Differential Scanning Calorimetry (DSC) and a Microwave heated calorimeter. The DSC results showed that microwave curing of the DGEBA / 4, 4' DDS system began at a higher temperature than thermal curing. Higher rates of reaction and activation energies were also observed in the microwave cured samples. The temperature at which fractional conversion began increased with increase in heating rate during microwave curing, but it was independent from heating rate during conventional cure. The rates of reaction also increased with an increase in heating rates for both thermal and microwave cure. These results suggest that, compared to conventional heating, microwave heating is more efficient curing technique which leads to more uniform cure and less internal stresses within the material.

Keywords: *Raman spectroscopy; epoxy; microwave; cure kinetics.*

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1. Introduction

Thermosetting resins usually start out as liquids. They are converted into solids by chemical reaction only. An epoxy is a thermosetting resin when cured becomes irreversibly hard. Epoxy based polymers have good mechanical properties and show chemical resistance to degradation. They are also very adhesive during the crosslinking process. When these properties are put together, combined with the wide range of basic epoxy chemicals from which an epoxy system can be formulated, this make epoxy materials very versatile [1]. There is an increase in the demand for epoxies. This is because, epoxy materials are used as high performance structural adhesive systems in industry especially in aerospace and microelectronics fields.

Thermal curing has some advantages. It increases the rate at which a material cures. It also reduces the time required for the material to cure. Despite these advantages, for thermal curing, there is an optimum temperature when the rate of reaction is at its maximum. Further heating to a higher temperature leads to a degradation of the material rather than an increase in the rate of reaction [2]. Several options to thermal curing, which can accelerate the rate of reaction, reduce the cure time or provide a more energy efficient method for curing have been explored. These other options looked into were using ultraviolet light, electron beams and gamma rays to cure materials. Ultraviolet light has poor ability to penetrate into the material and also has restricted dose rate. This is because that ultraviolet light is used in the curing of materials in limited curcumstances [2]. Gamma rays are usually delivered from naturally radiating sources such as cobalt-60, but there are several environmental and health issues associated with the radiation hazards caused by gamma rays. Due to these problems, they are hardly used. Curing with the electron beam has shown to be an efficient and quick method of curing, but the high cost involved with the operation is a huge disadvantage of this method [2].

Microwaves have been found to be a good alternative as the method for curing thermoset polymers. Microwaves do not have any major difficulties associated with their use, which is why microwave cured products are applied to many different industries [3]. Microwave heating occurs because some solids and liquids are able to convert electromagnetic energy into heat. If energy in the form of high frequency electromagnetic waves is applied to the material, the material can be heated. This is the principle on which microwave heating operates. An electromagnetic radiation consists of an electric field whose plane is perpendicular to the plane of a magnetic field [4]. It is the interaction of charged particles within the material with the electric field component of microwaves which gives rise to the microwave heating effect. If the charged particles can move in the electric field, then a current will be generated. If the particles cannot move since they are bonded to the material, they will simply rearrange themselves in phase with the electric field. This mechanism is known as dielectric polarisation [5]. Microwaves are used for melting, drying, polymerisation, sintering, pasteurising. They are the main carriers of high-speed telegraphic data transmissions between stations on the earth and also between ground-based stations, satellites and space probes [6].

An epoxy system is essentially made up of a resin and a hardener. Sometimes, there is a third component, which is an accelerator, but this is not very common. The resin component is the ‘epoxy’ while the hardener is what chemically reacts with the epoxy. A hardener is often a type of ‘amine’. When the epoxy and the amine are added together and mixed in order, they react chemically and link together irreversibly. When the full reaction is completed, the resulting product becomes rigid plastic polymer material [7].

1.2. Raman spectroscopy

When light, which contains photons, is focused on a sample, the molecules within the sample become excited and they subsequently scatter the light. Most of this light is scattered elastically, and this process is known as Rayleigh scattering. In this type of scattering, the emitted photon (light) has the same wavelength with the absorbing photon [8]. Some of this light is scattered inelastically, however, it is scattered at a different wavelength from that of the absorbing photon. This inelastically scattered light is known as the "Raman scatter", and this can be called the Raman effect. The Raman effect arises from the molecule changing its molecular vibration characteristics [8]. In this process of exchange of energy, a transition of the molecule from one of its energy state to another occurs, and the photon gains or loses energy [9]. The fundamental equation is as follows:

$$h\nu_o + E_1 = h\nu_r + E_2 \tag{1}$$

where h is Planck constant, ν_o is the frequency of the incident light, ν_r is the frequency of scattered light. E_1 and E_2 are the initial and final energies of molecules respectively. The difference in the frequency of the incident light and the scattered light may be positive or negative in sign. Its magnitude is referred to as the Raman frequency [9]. When the energy of the scattered light is less than the energy of the incident light, stokes line is produced, and when the energy of the scattered light is greater than the energy of the incident light, an antistokes line is produced [10]. The magnitude of this excitation of the sample molecule is related to the vibrational energy spacing in the ground electronic state of the molecule and therefore the wavenumber of stokes and antistokes lines are a direct measure of the vibrational energy of the molecule [10].

1.2.1. Stokes and Antistokes lines

A Raman spectrum can be explained as an assembly of spectral lines that are arraigned proportionately to the right and the left of the spectral line of the exciting laser. This is shown in Fig. 1. It is also observed that shifts to the right or left spectral lines are equal and this is due to the fact that phonons with the intrinsic single frequencies are absorbed or excited. Antistokes radiation is characterised by a greater wavenumber than that of the excitation line, while stokes radiation has wavenumbers that are less than those of the excitation laser [11].

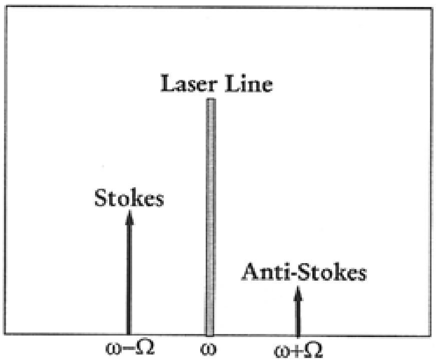

Fig. 1 A schematic drawing of a Raman Spectra [11].

Although the frequency of the Raman scattered light is shifted due to the excitation frequency, the magnitude of this frequency shift does not depend on the excitation frequency [11]. This Raman shift can be said to be an intrinsic property of the sample.

1.2.2. Relationship between Antistokes/Stokes ratio and molecular temperature

The ratio of the intensities of stokes and antistokes spectral lines is a function of compound temperature, and this ratio increases with temperature. Assuming that there is a Boltzman distribution for the levels involved {v=0 and v=1}, the ratio of antistokes and stokes intensities for a particular vibration can be used to evaluate the temperature of a substance [11]. The formula is given below.

$$\frac{I_{as,wv}}{I_{s,wv}} = \frac{(w_L + w_v)^4}{(w_L - w_v)^4} \exp\left(-\frac{hw_v}{KT}\right) \tag{2}$$

1.3 Microwave vs. thermal heating

There has been a lot of research in the past which was aimed that revealing the potential benefits of microwave curing of epoxy resins might have over thermal curing in terms of structure, dielectric properties, and fracture toughness upon modifier addition, percentage cure, mechanical strength, and glass transitions.

Wei et al. [12] observed that there was a higher reaction rate in the curing of a DGEBA / DDS system using microwave cure compared to thermal cure; and ultimately high extent of cure was observed for microwave cure. These two microwave radiation effects were interpreted to mean that microwave radiation may increase the mobility of the reactants after gelation so that more reactants can be consumed to form a more rigid network thereby forming a more rigid network as the extent of cure increases.

Wei et al. [13] suggested that if the reaction pathway is the same, then microwave cure is expected to have faster reaction rate than thermal cure, and then the local temperature will be higher in microwave heating than in thermal heating for the same bulk temperature. Also, the rigidity of the formed network is reduced so that more reactants can be consumed for the same level of molecular mobility. The molecular mobility of the reactants in the network structure can be increased by induced polymer and monomer molecules polarization along the applied electromagnetic field.

Miyovic et al. [14] carried out a study for the cure kinetics of the DGEBA/DDS epoxy resin. Their findings show that samples in thermal field cured slightly faster than samples in microwave field. Also, during the same curing time, there was a higher degree of cure in the thermally cured samples than in the microwave cured samples. Marand et al. [15] used in situ measurements of infrared spectroscopy to compare the reaction mechanism of epoxy resins undergoing both thermal and microwave cure. It was observed that crosslinking rate of microwave cured samples was higher than that of thermally cured samples. This rapid crosslinking created a molecular network which was strong enough to trap the unreacted amine compounds in the resin structure which ultimately causes a lower degree of cure in microwave cured samples.

Hill et al. [16] observed that the reaction rates of primary amine and the secondary amine were the same for both the thermal and the microwave cure process. There was no kinetic evidence for any specific effects of microwave radiation on either the primary or the secondary amine reaction.

Navabpour et al. [17] used dynamic and isothermal curing methods to study the cure kinetics of commercial epoxy resin system, RTM6, using a microwave heated calorimeter and a conventional differential scanning calorimeter. The resins cured isothermally using microwave heating were found to have larger values of preexponential factor and higher values of activation energy then those of resins cured using thermal heating. It was observed that the reaction orders were similar for both microwave and thermal heating. This suggested that the mechanisms of curing were similar. Wallace et al. [18] cured PR500 epoxy resin using conventional oven and commercial microwave oven. Modulated Differential Scanning Calorimetry MDSC, Infrared Spectroscopy, Dynamic Thermal Analysis, and solid-state NMR spectroscopy were used to compare the cured resins. Their investigations showed that in microwave-cured samples, the epoxy-amine reaction is more dominant than the other possible curing reactions, including the epoxy-hydroxyl reaction. At the same degree of cure, Infrared spectroscopy revealed that the intensities of hydroxyl and amine bands were more in the thermally cured sample. This indicated that during microwave cure, the amine-epoxy reaction was more dominant under these conditions. –CH_2OH group is formed in the epoxy-hydroxyl reaction.

This study was undertaken to understand the effects of microwave heating on functional groups of DLS 772 / 4 4’ DDS epoxy system during curing, and further to obtain the cure kinetics of a microwave cured epoxy system and a conventionally cured epoxy system.

2. Materials and method

2.1. Materials

Two epoxy resins and three hardeners were initially selected for this research; through them, one hardener and one epoxy were used. The selection was made based on the ability of Raman spectroscopy to record stokes and anti-stokes spectra for at least one functional group of one epoxy and hardener. Thus, temperature of the functional group was determined. The starting materials and functional groups to be identified are listed in Table 1.

Table 1 Materials used and the functional groups to be identified.

Material	Functional group to be identified
DGEBA	Epoxy group
DER 332	Epoxy group
DICY	C=N
3 3 Diphenyldiaminosulfone	Amine, Aromatic, Sulfone
4 4 Diphenyldiaminosulfone	Amine, Aromatic, Sulfone

A 633 nm laser was first used to take the spectra of materials, but an antistokes band could not be obtained for any of materials with the 633nm laser. As a result, a 785 nm laser was used and both stokes and antistokes bands of functional groups of two epoxies and a hardener were recorded by the laser. It was decided that DGEBA and 4 4’ DDS should be used for the research.

After an epoxy and a hardener were picked, Raman spectroscopy was used to take stokes and antistokes spectra of each material at room temperature. Wavenumbers and intensities of the stokes and antistokes peaks for each functional group were also recorded and Equation (2) was used to calculate the molecular temperature of each of these peaks.

Each material was then heated from room temperature at a rate of 20 ^{o}C/min up to 1750 ^{o}C using a thermal hot stage. Heating was held to provide constant temperature at 500 ^{o}C, 750 ^{o}C, 1000 ^{o}C, 1250 ^{o}C, 1500 ^{o}C, and 1750 ^{o}C for 10 minutes. The spectra (stokes and antistokes) of each material were taken along with the corresponding wavenumbers and intensities; and the molecular temperatures of these peaks were calculated at the temperatures mentioned above. Each of these materials were also heated in the microwave, and the same procedure used for thermal heating was also employed for microwave heating. The spectra were taken again at 500 ^{o}C, 750 ^{o}C, 1000 ^{o}C, 1250 ^{o}C, 1500 ^{o}C, and 1750 ^{o}C after the material had been held isothermally for 10 minutes at each temperature indicated above. Equation (2) was also used to calculate the molecular temperature at the different temperatures where the spectra of the materials were taken. During the microwave heating, the spectra of the materials were taken "in situ", while the material was being heated in the microwave. For this purpose, an optic fibre was employed. The use of the optic fibre was to transmit laser from the Raman microscope onto the material in the microwave and to record the spectra while the material was being heated.

An epoxy system was then formulated using DLS 772 and 44 DDS using a mass ratio of 1:20. Raman Spectroscopy was also used to obtain the 'stokes and antistokes spectra of each sample, along with their wavenumbers and intensities the molecular temperature of each of these peaks were calculated at the above indicated temperatures using Equation (2). The prepared epoxy system was also put in the microwave heated calorimeter, and the procedure used as with the thermal heating was also repeated for the microwave cure, and with the help of the optic fibre, Raman Spectroscopy was used to record both the stokes and the antistokes spectra of the epoxy system.

Fig. 2 shows the set up for the microwave curing of the resin system. This set up consists of the microwave cavity, the network analyser, the flouroptic thermometer, the amplifier, power controller and the computer. The peak frequency used for the microwave heating was 2.482Ghz.

The microwave frequency and source power adjusted by a GPIB interface between the network analyser and a computer. The output from the amplifier (Fig. 3) was fed to a microwave cavity by a directional coupler. The directional coupler also allowed the reflected signal from the cavity to be monitored. The transmitted and reflected powers were measured by a power sensor connected to a power meter. The powers were recorded by the computer via a GPIB interface. The sample temperature was measured using a fluoroptic fibre sensor and thermometer. The thermometer was connected to a PID temperature controller, which was programmed to give the desired heating rate.

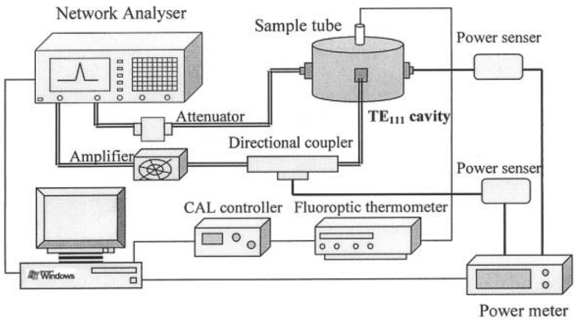

Fig. 2 Schematic diagram of a microwave heated calorimeter.

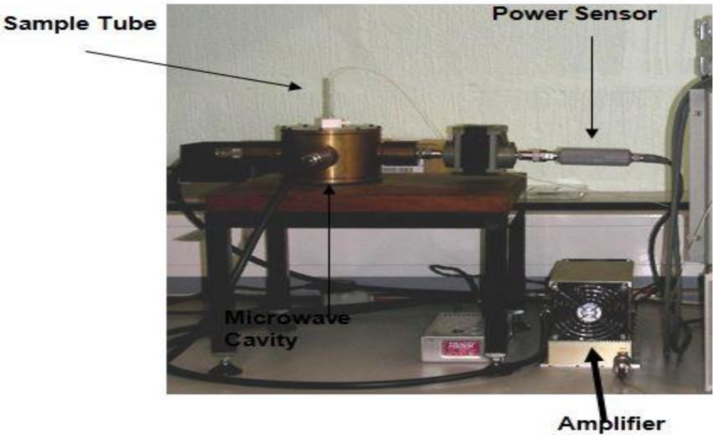

Fig. 3 A microwave calorimeter.

2.2. Degree of conversion (α) and reaction rate ($d\alpha/dt$)

Epoxy resin curing is an exothermic reaction. For exothermic reaction, we assume that:

i. The number of double bonds which has reacted in the system during curing is proportional to the exothermic heat which is generated during curing.
ii. When all the bonds, which can react, have reacted, it is said that maximum cure is attained.
iii. The rate of heat generated is proportional to the rate of reaction.

It is possible to determine the degree of conversion α, and the reaction rate $d\alpha/dt$ at time t [19]. This can be determined by the following expressions.

$$\alpha = \frac{\Delta H_t}{\Delta H_R} \tag{3}$$

$$\frac{d\alpha}{dt} = \frac{(dH/dt)_t}{\Delta H_R} \tag{4}$$

where $(dH/dt)_t$ is the rate of heat generation and is directly relevant with the calorimetric signal at time t; ΔH_R is the total reaction heat associated with the complete conversion of all reactive groups; and ΔH_t is the heat released until time t. This can be obtained directly by integrating the calorimetric signal dH/dt until the time t [19].

In order to calculate the reaction rate and the degree of conversion, it is important for us to understand how the calorimetric signal changes according to temperature or time. This depends on whether the experiment is dynamic or isothermal. It is also essential to quantify the reaction heat perfectly [19].

2.3. Kissinger’s Method

Kissinger’s method is a method for estimating the activation energy of polymers [20]. It relates the activation energy with the exothermic peak temperature of the reaction and uses an nth-order equation to describe curing kinetics. An nth – order equation used to express the equation for dynamic curing is described as given in Equation (5).

$$r = \frac{d\alpha}{dt} = \Phi \frac{d\alpha}{dT} = A\exp\left(\frac{-E_a}{RT}\right)(1-\alpha)^n \tag{5}$$

Here *r* is the reaction rate. Since the maximum rate occurs when *dr*/*dt* = 0, differentiating Equation (5) with respect to time and equating the resulting expression with zero gives:

$$\Phi \frac{E_a}{RT_P{}^2} = An(1-\alpha_P)^{n-1} \exp\left(\frac{-E_a}{RT_p}\right) \tag{6}$$

If Equation (6) is rearranged, and natural logarithms are taken, following expression is obtained.

$$-\ln\left(\frac{\Phi}{T_P{}^2}\right) = \ln\left(\frac{E_a}{RAn}\right) - (n-1)\ln(1-\alpha_P) + \frac{E_a}{RT_P} \tag{7}$$

The activation energy is found from the slope of the straight line of $-\ln(\Phi/T_P{}^2)$ plotted against $1/T_p$.

3. Results and discussion

The spectra of these materials revealed both the stokes and the antistokes band for the peaks corresponding to their respective functional groups in the region of 300cm^{-1} to 1500cm^{-1}. The individual materials were then heated at 2 K/min from room temperature to 175^{0}C, and both the stokes and the antistokes spectra of each material were taken at 25 degrees intervals, after being held isothermally for 10 minutes. The spectra of the materials are shown in figures.

3.1. 4 4 DDS

The spectra of 4, 4′ DDS were first taken in the region of 200 to 3500cm^{-1}. It was observed that antistokes spectra could be recorded for 4 4' DDS from 1600 cm^{-1}. Consequently, the spectra were taken in the region of 300 to 1500cm^{-1} and the stokes and antistokes could be recorded for the amine, sulfone and aromatic bands in the hardener. Some of the stotes and anti-stokes spectra are shown in Figs. 4 to 7.

The stokes spectra of the 4 4 DDS at room temperature showed a very well prominent sulfone peak. The amine and the aromatic peaks are not as prominent as the sulfone bands, but they are well defined. The antistokes spectra of the 4 4 DDS was not easily obtained as the stokes spectra. The peaks are weak and not as easily observed as the stokes spectra. Heating the material did not show any visible change in the stokes spectra as anticipated. However, the antistokes spectra became more intense as the temperature increased and the material could be more easily identified as the temperature increased.

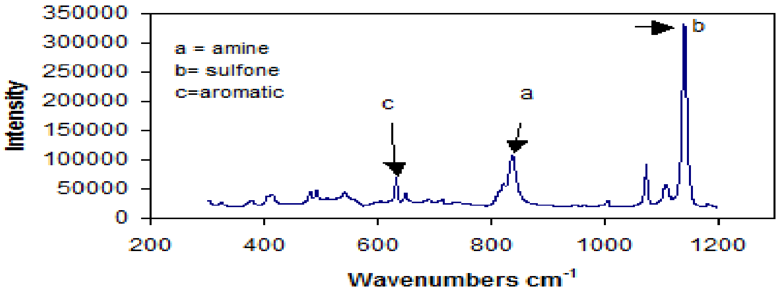

Fig. 4 Stokes spectra of 4, 4' DDS at 25^0C.

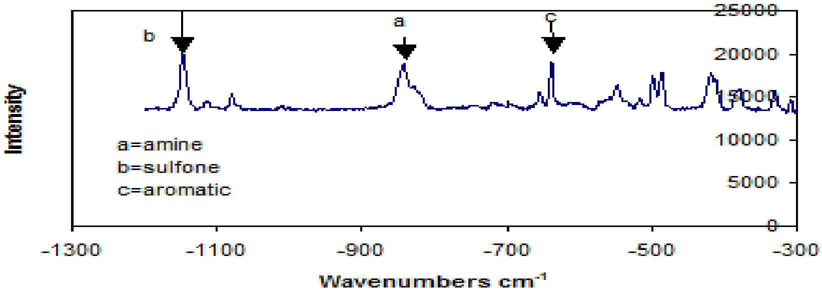

Fig. 5 Antistokes spectra of 4, 4' DDS at 25^0C.

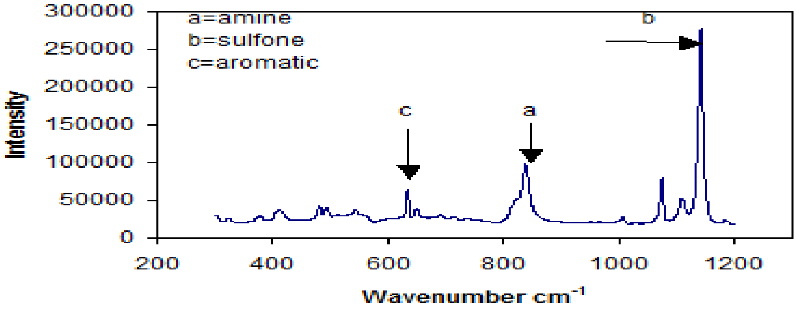

Fig. 6 Stokes spectra of 4, 4' DDS at 75^0C.

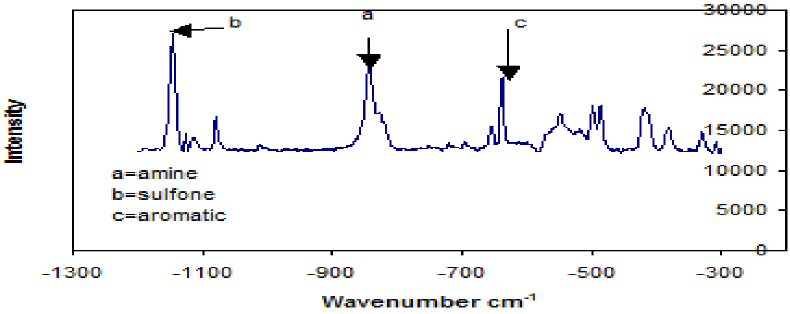

Fig. 7 Antistokes spectra of 4, 4' DDS at 75^0C.

3.2. DLS 772

The spectra of DLS 772 were taken in the region of 200 to 3500cm^{-1}. Like the 4, 4' DDS, no antistokes spectra could be recorded for the hardener from 1600 cm^{-1}. Hence, the spectra were taken in the region of 500 to 1500cm^{-1} and the stokes and antistokes could be recorded for the epoxy and phenyl bands in the epoxy resin. Some of these spectra are shown in Figs. 8 and 9.

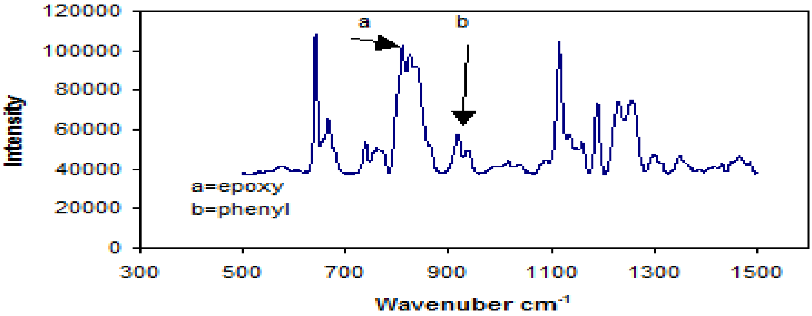

Fig. 8 Stokes spectra of DLS 772 at 75^{0}C.

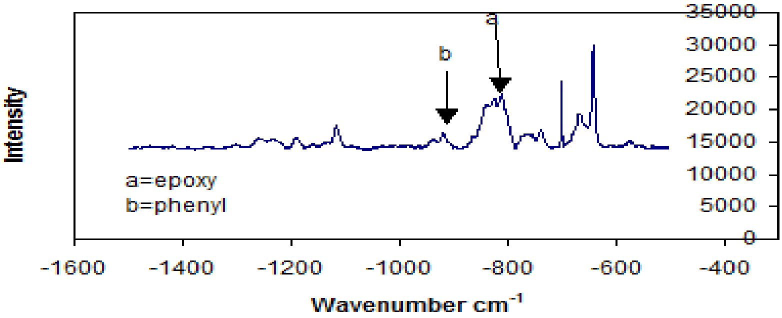

Fig. 9 Antistokes spectra of DLS 772 at 75^{0}C.

The stokes spectra of the DLS 772 showed a lot of peaks. Among these peaks, the epoxy peak was very strong and easily identified. The phenyl group on the other hand, was not as prominent as the epoxy peak, but could be identified. The antistokes spectra of the DLS 772 showed the epoxy and the phenyl peaks. These peaks were weaker than the stokes spectra. There was no visible change in the stokes spectra as the temperature increased. Unlike the 4 4 DDS, the antistokes spectra did not seem to be more intense as the temperature increased.

3.3. DLS 772 / 4 4 DDS Epoxy system

A spectra of the epoxy system consisting of DLS 772 and 44' DDS was taken in the region from 300cm^{-1} to 1500cm^{-1}. Phenyl band for the epoxy resin is seen in the spectra. The Sulfone and the Aromatic bands from the hardener can also be observed from the spectra. The Epoxy band and the amine band appear in a single band in the spectra. The reason for this could be that there is very little difference in the wavenumbers of the epoxy and the phenyl bands. The spectra of the resin taken at room temperature and at selected temperatures are shown in Figs. 10 and 11.

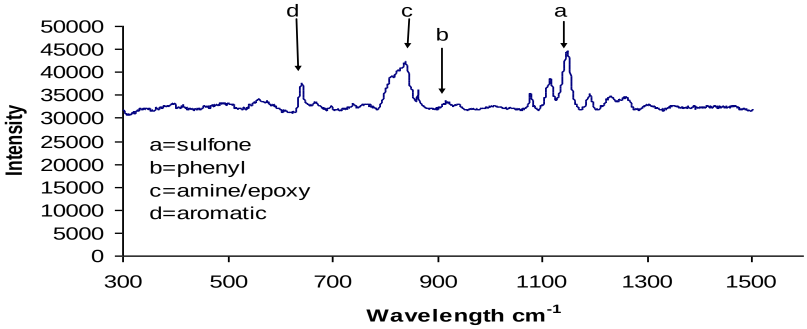

Fig. 10 Stokes spectra of DLS 772 / 4, 4' DDS resin at 100^{0}C.

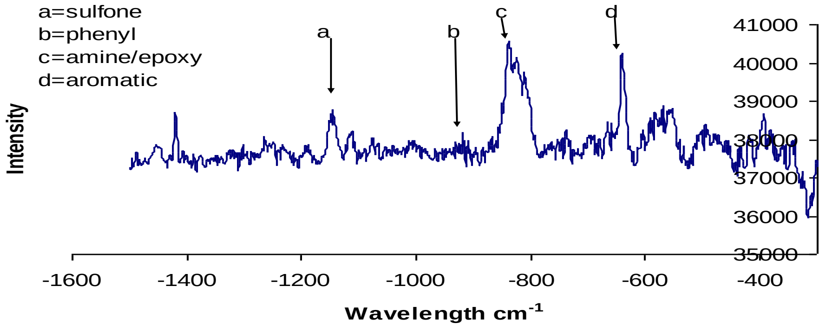

Fig. 11 Antistokes spectra of DLS 772 / 4, 4' DDS resin at 100^{0}C.

Like the 4 4 DDS, there was no visible change in the stokes spectra of the DLS 772 / 4 4 DDS as the material was heated. But the antistokes spectra seemed to be more intense as the resin was heated. With the exception of the phenyl group, all the other bands could be identified quite easily.

3.4. Microwave heating

An optic fibre was used to transmit light and laser radiation onto the sample in the microwave cavity. The optic fibre was also used to obtain the spectra of the material as it was heated in the cavity. All attempts to obtain a spectra for the 4 4 DDS, DLS 772 and the DLS 772 / 4 4 DDS materials ailed as no peak could be picked from any spectra.

3.5. Temperature determination from the Stokes and Antistokes values

Using Equation (2), along with the wavenumbers, wavelengths and the intensities of the stokes and the antistokes bands of each material and the resin comprising of both materials, the molecular temperature of each material was calculated. The results are shown in the Table 2.

It is seen from Tables 2 to 4 that for 4, 4' DDS , DLS 772 and the DLS 772 / 4 4 DDS epoxy system, the molecular temperature of the functional groups are in the same region as the temperature at which the material was heated. It can then be said that since the temperature of the functional groups are within the same region as that of the temperature at which they were heated, thermal heating does not excite the functional groups of the 4, 4' DDS, DLS 772, and the DLS 772 / 4, 4' DDS epoxy system.

Table 2 Temperature determination from stokes and antistokes values for 4 4' DDS.

Tempera-ture	Functional group	Stokes Wavenumb. cm^{-1}	Antistokes Wavenumb. cm^{-1}	Stokes Intensity	Antistokes Intensity	Raman Temperature ^{0}C
25^{0}C	Aromatic	637	638	46619	5555	27
25^{0}C	N-H	837	840	78174	4097	29
25^{0}C	S=O	1142	1147	308368	6548	28
50^{0}C	Aromatic	634	635	34056	1429	54
50^{0}C	N-H	836	840	53661	4899	58
50^{0}C	S=O	1141	1146	229100	8413	56
75^{0}C	Aromatic	633	638	40390	8265	78
75^{0}C	N-H	837	840	71843	7989	80
75^{0}C	S=O	1141	1146	256471	14493	79
100^{0}C	Aromatic	633	637	43075	3979	103
100^{0}C	N-H	832	836	48943	8336	105
100^{0}C	S=O	1138	1143	249378	20701	106
125^{0}C	Aromatic	633	638	38991	10716	125
125^{0}C	N-H	832	836	37053	8461	125
125^{0}C	S=O	1138	1143	182711	19798	124
150^{0}C	Aromatic	633	637	41458	13207	156
150^{0}C	N-H	832	836	41459	10800	158
150^{0}C	S=O	1138	1143	240145	28664	157
175^{0}C	Aromatic	633	638	33276	13207	177
175^{0}C	N-H	832	836	49838	10800	177
175^{0}C	S=O	1138	1142	209140	28664	175

Table 3 Temperature determination from stokes and antistokes values for DLS 772.

Tempera-ture	Functional group	Stokes Wavenumb. cm^{-1}	Antistokes Wavenumb. cm^{-1}	Stokes Intensity	Antistokes Intensity	Raman Temperature ^{0}C
25^{0}C	Epoxy	827	826	46035	3449	27
25^{0}C	Phenyl	919	919	11925	652	29
50^{0}C	Epoxy	824	825	51432	5402	52
50^{0}C	Phenyl	917	917	16598	988	53
75^{0}C	Epoxy	824	824	54531	7209	78
75^{0}C	Phenyl	919	924	20042	900	77
100^{0}C	Epoxy	823	833	72600	8529	109
100^{0}C	Phenyl	919	918	14697	2124	105
125^{0}C	Epoxy	821	821	72660	13980	128
125^{0}C	Phenyl	917	918	14697	2559	128
150^{0}C	Epoxy	820	820	66711	16082	155
150^{0}C	Phenyl	917	917	12252	1632	158
175^{0}C	Epoxy	819	819	44920	10313	177
175^{0}C	Phenyl	936	917	2287	1796	178

Table 4 Temperature determination from stokes and antistokes values for DLS 72 / 4 4' DDS.

Temperature	Functional Group	Stokes Wavenumb. cm^{-1}	Antistokes Wavenumb. cm^{-1}	Stokes Intensity	Antistokes Intensity	Raman Temperature ^{0}C
25^{0}C	Aromatic	640	640	8942	1701	28
25^{0}C	Epoxy / N-H	830	829	15809	1788	27
25^{0}C	Phenyl	921	923	2910	374	29
25^{0}C	S = O	1146	1147	16933	489	28
50^{0}C	Aromatic	640	640	5051	1982	54
50^{0}C	Epoxy / N-H	830	829	8878	1994	55
50^{0}C	Phenyl	919	925	1288	590	56
50^{0}C	S = O	1146	1146	11078	915	53
75^{0}C	Aromatic	642	644	4989	2108	77
75^{0}C	Epoxy / N-H	831	825	8997	2178	77
75^{0}C	Phenyl	919	916	1545	678	79
75^{0}C	S = O	1144	1150	11679	946	74
100^{0}C	Aromatic	641	640	4913	2451	104
100^{0}C	Epoxy / N-H	829	818	9179	1965	105
100^{0}C	Phenyl	928	928	1058	701	105
100^{0}C	S = O	1147	1146	11391	972	103
125^{0}C	Aromatic	646	649	2463	3445	128
125^{0}C	Epoxy / N-H	828	826	4142	2414	129
125^{0}C	Phenyl	917	917	311	137	129
125^{0}C	S = O	1146	1146	5645	1097	127
150^{0}C	Aromatic	641	641	2420	3753	155
150^{0}C	Epoxy / N-H	822	826	3340	1453	154
150^{0}C	Phenyl	919	921	222	784	157
150^{0}C	S = O	1145	1146	6778	2979	153
175^{0}C	Aromatic	641	640	2698	2836	178
175^{0}C	Epoxy / N-H	819	823	2819	1525	182
175^{0}C	Phenyl	933	912	285	228	178
175^{0}C	S = O	1145	1146	7016	2536	174

3.6. Cure kinetics

A freshly prepared DLS 772 / 4 4 DDS epoxy system was subjected to a DSC run at a heating rate of 10 K/min from 40^{0}C to 350^{0}C. The data is shown in Fig. 12.

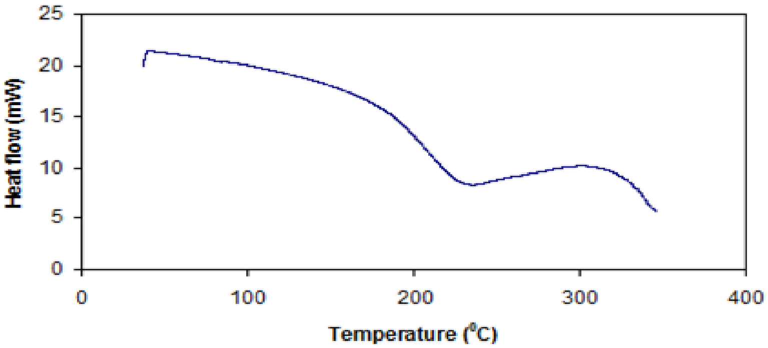

Fig. 12 DSC plot of a fresh DLS 772 / 4 4 DDS system at 10 K/min.

The plot in Fig. 12 shows a cure reaction beginning at about 170⁰C, and coming to an end at about 325⁰C. This is the region at which the material cures. To further determine the cure kinetics of the epoxy resin, a freshly prepared resin was subjected to a DSC run from 40⁰C to 325⁰C at heating rates of 5 K/min, 8 K/min and 10 K/min. The DSC data of the epoxy system at different heating rates are shown in Fig. 13.

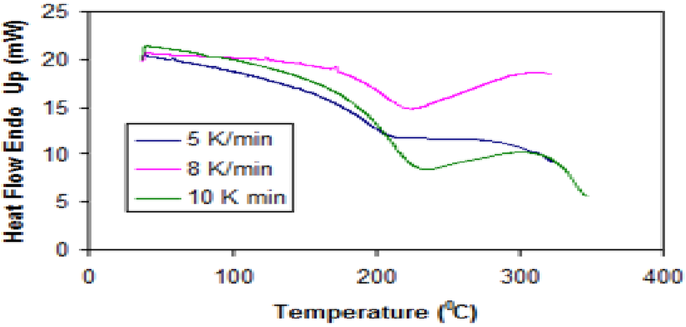

Fig. 13 Dynamic DSC thermograms of DLS 772 / 4 4 DDS obtained from conventional DSC at different heating rates.

From Fig. 13, we can observe an exothermic peak for each heating rate. The temperature, at which the exothermic peak occurred, depended on the heating rate. The exothermic peak moved to slightly lower temperature at slower heating rates. This is because thermal lag is reduced at lower heating rates and because of this, the material starts to react at an apparently lower temperature [15].

The data obtained from the DSC thermogram were used to calculate the reaction rate ($d\alpha/dt$), and the fractional conversion, α of the epoxy system at different heating rates. Before the calculation, all the thermograms were standardized for the purpose of comparison by dividing the calorimetric signal by the weight of the sample.

The temperature dependence of the reaction rates and the fractional conversion at different heating rates for conventional and microwave cured samples are shown in Figs. 14 and 15.

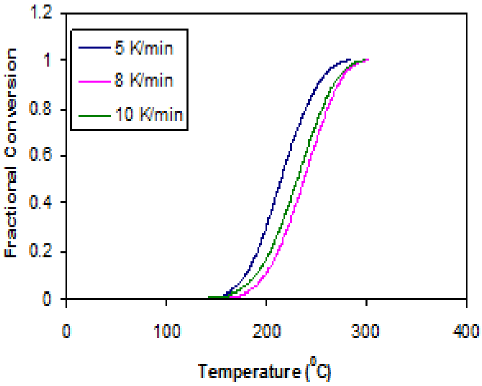

Fig. 14 Fractional conversion for dynamic cure of DLS 772 / 4, 4' DDS at different heating rates using conventional heating.

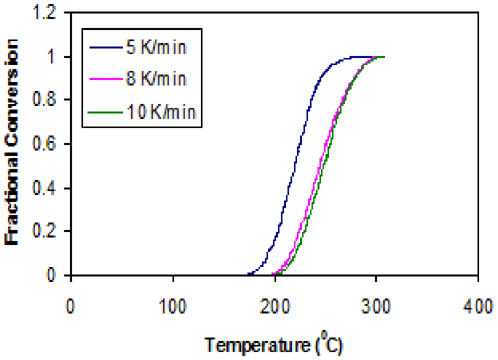

Fig. 15 Fractional conversion for dynamic cure of DLS 772 / 4, 4' DDS at different heating rates using microwave heating.

We observe from Figs. 14 and 15 that, during microwave curing, the temperature at which the fractional conversion began, increased with an increase in the heating rate; but for thermal cure, the temperature at which fractional reaction began was independent of the heating rate. The rates of reaction of the samples in both the thermal field and microwave field shown in Figs. 16 and 17 increase with an increase in heating rate.

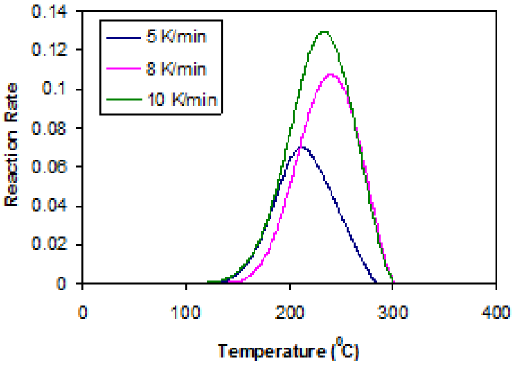

Fig. 16 Reaction rates for dynamic cure of DLS 772 / 4, 4' DDS at different heating rates using conventional heating.

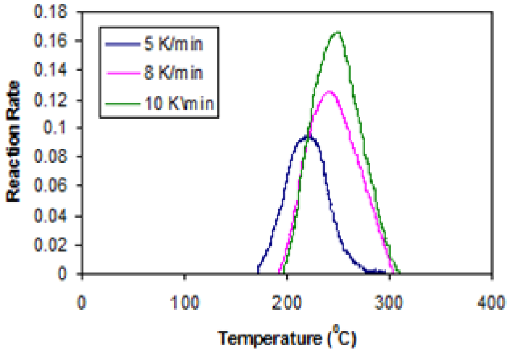

Fig. 17 Reaction rates for dynamic cure of DLS 772 / 4, 4' DDS at different heating rates using microwave heating.

Maximum rates of reaction were observed in a fractional conversion of 0.45 – 0.55 for all the heating rates used in both Figs. 18 and 19. After these points, the reaction rate started to decrease which could be attributed to the increase in the viscosity of the reaction medium as the curing material gelled. At this stage, the molecular mobility was significantly reduced, the material became diffusion controlled, and eventually stopped [15].

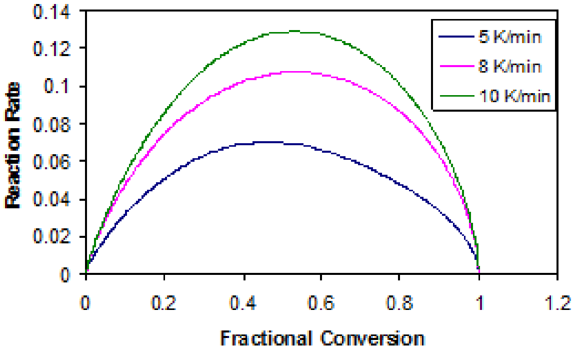

Fig. 18 Reaction rates against Fractional conversion for the curing reaction of DLS 772 / 4, 4' DDS system at different heating rates using conventional heating.

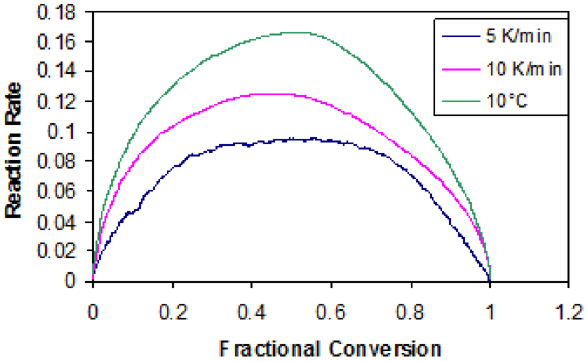

Fig. 19 Reaction rates against Fractional conversion for the curing reaction of DLS 772 / 4, 4' DDS system at different heating rates using microwave heating.

The temperature dependence of the reaction rate for curing DLS 772 / 4, 4' DDS epoxy system is considered for each heating rate as shown in Figs. 20 to 22. For each heating rate, we can observe that the maximum rate of reaction is higher in the microwave field than in the thermal field. Also, all the reactions began at a lower temperature in the thermal heating. It is also observed that, for each heating rate, the reaction occurs over a shorter temperature range for the samples cured with microwave heating.

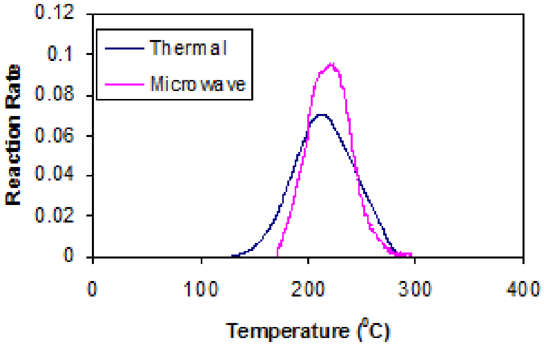

Fig. 20 Temperature dependence of Reaction rate for curing of DLS 772 / 4, 4' DDS system at 5 K/min.

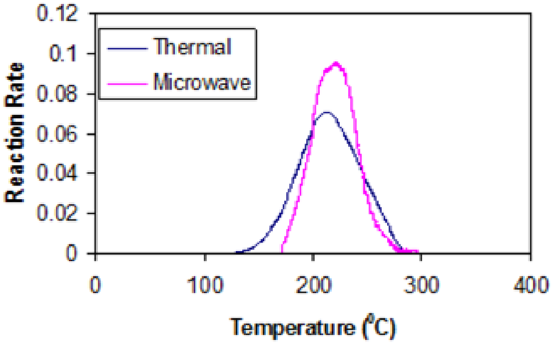

Fig. 21 Temperature dependence of Reaction rate for curing of DLS 772 / 4, 4' DDS system at 8 K/min.

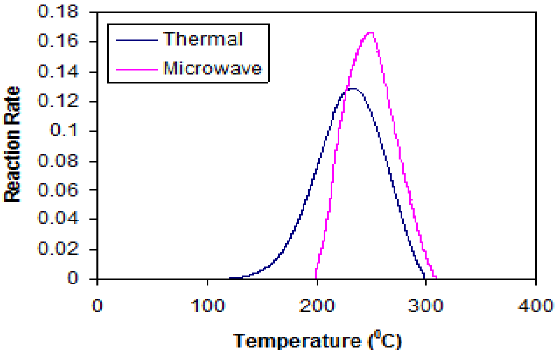

Fig. 22 Temperature dependence of Reaction rate for curing of DLS 772 / 4, 4' DDS system at 10 K/min.

Figs. 23 to 25 show the temperature dependence of the fractional conversion for the epoxy system at each heating rate.

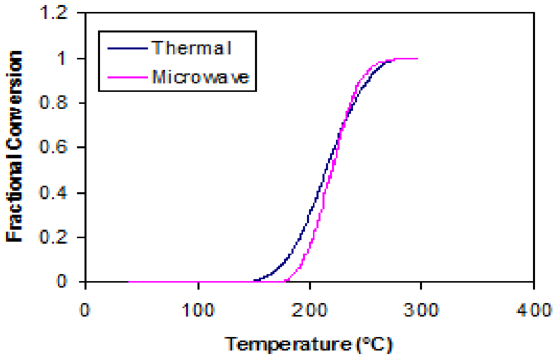

Fig. 23 Temperature dependence of Fractional conversion for curing of DLS 772 / 4, 4' DDS system at 5 K/min.

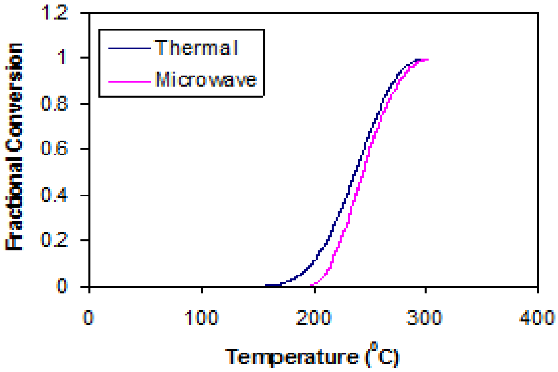

Fig. 24 Temperature dependence of Fractional Conversion for curing of DLS 772 / 4, 4' DDS system at 8 K/min.

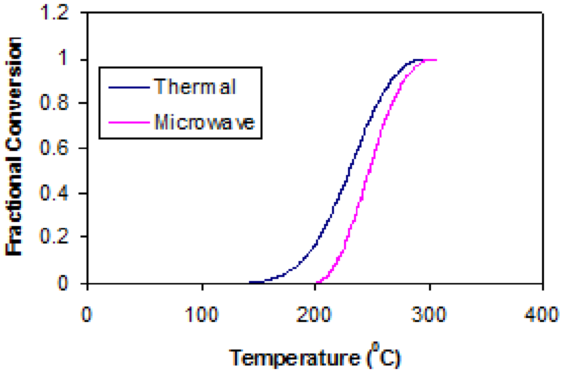

Fig. 25 Temperature dependence of Fractional conversion for curing of DLS 772 / 4, 4' DDS system at 10 K/min.

Table 5 Temperatures of conversion for Thermal cured DLS 772 / 4, 4' DDS epoxy system.

Rate per minute (K/min)	Temperature of maximum conversion (^{0}C)	Temperature at reaction start (^{0}C)	Temperature at maximum reaction (^{0}C)	Temperature at end of reaction (^{0}C)
5	283	134	217	288
8	301	148	245	306
10	298	125	237	302

Table 6 Temperatures of conversion for Microwave cured DLS 772 / 4, 4' DDS system.

Rate per minute (K/min)	Temperature of maximum conversion (^{0}C)	Temperature at reaction start (^{0}C)	Temperature at maximum reaction (^{0}C)	Temperature at end of reaction (^{0}C)
5	295	173	227	283
8	309	194	245	309
10	309	198	253	313

From Tables 5 and 6, the reactions begin at a lower temperature in the thermal field than in the microwave field, and the reactions ended roughly at the same temperatures in both fields. Thus, it can be said that the reactions in the DLS 772 / 4, 4' DDS epoxy system takes place over a shorter temperature range in the microwave field. These differences can be attributed to a better efficiency in the transfer of energy during microwave curing. Unlike thermal heating which involves energy transfer from the surface of the material into the material through conduction or convection, in microwave heating, the electromagnetic field interacts with the molecules leading to a direct delivery of energy to the material. This interaction causes heat to be generated internally throughout the volume of material [4]. The relaxation of dipole polarization along the electromagnetic field enables the polymer molecules to be heated in the microwave field. The cure reaction is enhanced in microwave heating because the reactive polar molecules selectively absorb the microwaves. However in thermal heating, the reaction can only take place after the entire molecules have been heated [15,21]. The higher fractional conversion for the microwave cured samples can be due to an increase in the reactant mobility after gelation. This is the result of the induced polarization of polymer and monomer molecules along the applied electromagnetic field allowing more reactants consumed to form a more rigid network.

3.7.Kissinger Method

Fig. 26 shows the example of the plots of $-\ln(\Phi/T_P^2)$ against T_P^{-1} for the DLS 772 / 4 4' DDS epoxy system cured using DSC and microwave calorimeter. The values of the pre-exponential factor and activation energy are summarised in Table 7. Obtained regression coefficients were between $0.90 < r < 1.00$. The activation energies of the microwave cured samples were also found to be higher than those of the thermal cured samples.

The activation energies of conventionally and microwave cured samples of the DLS 772 / 4 4' epoxy system fall within the range of activation energies of chemical reactions (30 to 100 Kj mol^{-1}) [15].

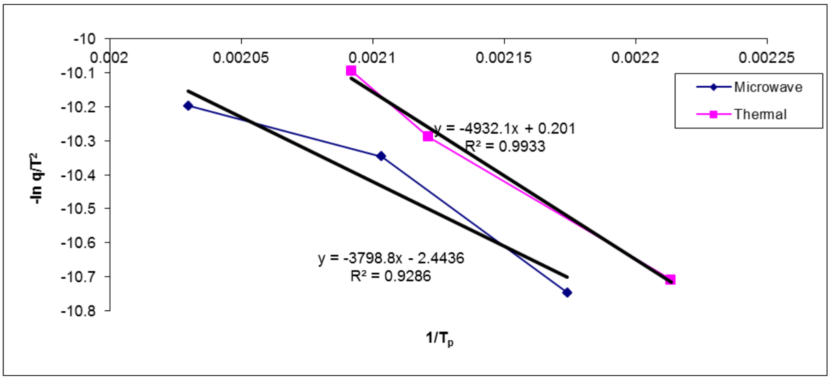

Fig. 26 Plot of $-\ln(\Phi/T_P^2)$ against T_P^{-1} for thermal and microwave curing of DLS 772 / 4 4' DDS epoxy system.

Table 7 Values of pre-exponential factor and activation energy and for DLS 772 / 4 4' DDS epoxy systems using conventional and microwave heating.

Sample	Thermal Heating		Microwave Heating	
	A′ (s^{-1})	E_a (KJ mol^{-1})	A′ (s^{-1})	E_a (KJ mol^{-1})
DLS 772 / 4 4' DDS epoxy system	5.42	53.9	9.56	83.6

4. Conclusion

The results of the experiments show the stokes and the antistokes spectra of DLS 772, 4, 4' DDS and an epoxy system of DLS 772 / and 4 4' DDS at different temperatures during conventional and microwave curing. The molecular temperatures calculated from their corresponding wavenumbers and intensities of specific functional groups were in the same region as their heating temperature. Therefore, conventional heating does not excite the functional groups of each of the material and the epoxy system. Raman Spectroscopy was unable to obtain the stokes or antistokes spectra of DLS 772, 4, 4'DDS and an epoxy system of DLS 772 / and 4 4' DDS during microwave heating. Hence, it is impossible to say that microwave heating excites the functional groups of the above named materials; because a stokes and antistokes spectra could not be recorded. The cure kinetics of the DLS 772 / 4, 4' DDS system was also studied by the use of Differential Scanning Calorimetry (DSC) and a Microwave heated calorimeter. The curing reactions for the microwave cured samples began at a higher temperature than thermal curing. The reactions also took place over a shorter temperature range. Higher rates of reaction and activation energies were also observed in the microwave cured samples. Furthermore, the temperature at which fractional conversion began increased with increase in heating rate during microwave curing, but it was independent from heating rate during conventional cure. The rates of reaction also increased with an increase in heating rates for both thermal and microwave cure. These results suggest that compared to conventional heating, microwave heating is more efficient curing technique which leads to more uniform cure and less internal stresses within the material.

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