Effect Of Curing Method On Physical And Mechanical Properties Of Araldite DLS 772 / 4 4 DDS Epoxy System

Babatunde Bolasodun, Alan Nesbitt, Arthur Wilkinson, Richard Day

Abstract: - Samples of an epoxy resin system, based on Araldite DLS 772 and 4 4' DDS (a hardener) with an amine / epoxy ratio of 0.8 were cured using conventional and microwave heating. The cured samples were cut into the required dimensions using ASTM standards, and then subjected to Density, Dynamic Mechanical Thermal Analysis and Flexural tests. It was observed that the microwave cured samples had a higher glass transition temperature (T_g), a higher flexural strength, higher cross-link density (v) and lower molecular weight between cross-links than the conventionally cured samples. The results showed that the microwave cured samples had a more compact network structure, and suggest a better stiffness and strength in the microwave cured samples. This improved stiffness is ascribed to a better molecular alignment and a greater homogeneity which is found in the microwave cured samples.

Keywords: - curing, epoxy, glass transition, microwave

1 INTRODUCTION

Microwaves have been found to be a good alternative method for curing thermo set 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 [1]. 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 cocosts 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]. During the curing of thermoset polymers, low molecular weight liquid monomers are transformed into a three-dimensional thermoset network by the means of chemical reactions.

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Hence, the structure of the network formed is affected by the way the resin reacts during polymerization[2]. The way the resin reacts during polymerization also influences the physical and the mechanical properties of the polymer produced. The mechanical behaviour of the polymer materials in particular is important for the practical applications of these materials. The mechanical properties usually dictates when a given polymer material can be used for a particular purpose. Thus, the study these mechanical properties are vital so as to predict the performance of the polymer[3]. Different network structures are anticipated for samples cured using conventional and microwave heating. This is because conventional and microwave samples are heated in different ways[4]. This article presents the results of density, dynamic mechanical thermal analysis and flexural tests on cured samples of Araldite DLS 772 / 4 4' DDS epoxy system using conventional and microwave heating.

2 EXPERIMENTAL

Araldite DLS 772 was the epoxy resin used for this research. It was supplied by Hexcel, UK. Araldite DLS 772 has an epoxy equivalent of 192.33. The hardener used for this study was 4 4' Diaminodiphenylsulfone. It was supplied by Sigma-Aldrich, UK. Samples were prepared and poured into a PTFE mould with dimensions 120mm length x 30mm breath x and 5mm height. The mould was placed inside an oven and was heated at a rate of 2 K min^{-1} to 180^0C and was held at this temperature for 240 minutes. Microwave curing of the epoxy system was performed in a cylindrical brass, single mode cavity having a radius of 46.9mm, and a length of 265.0mm.The cavity was at a frequency of 2.45 GHz in the resonant TM_{010} mode. As shown in the figure 1 below, this cavity is designed to have its maximum electric field strength along the centre of the cavity axis. Fig. 2 shows the schematic diagram of the microwave heating system.

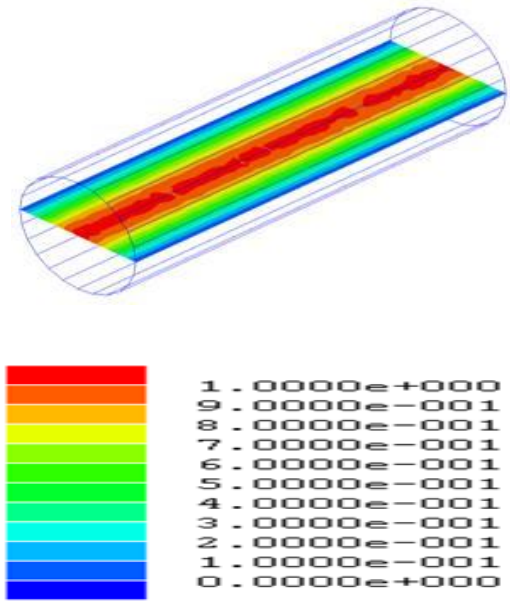


Fig. 1 Simulated electromagnetic field patterns at 2.45GHz for TM010 mode microwave cavity with the presence of sample generated using Ansoft HFSS v8.5 simulation software. The colour scale shows the relative field strength generated inside the cavity [5]

The microwaves are generated by a network analyzer (Hewlett Packard 8714ET). A solid state amplifier (Microwave Amplifier Limited) was used to amplify the generated microwaves. This Amplifier has a maximum output of 200W. A GPIB interface between the network analyzer and the computer was used to adjust the source power and the microwave frequency. The sample temperature was monitored using an Opsensfluoroptic thermometer which was inserted through a small hole drilled at the top of the cavity. A small glass tube was used to protect the tip of the temperature probe. The thermometer was connected to a PID temperature controller manufactured by CAL Control Ltd., with a model number CAL 9500. This temperature controller was designed to give it the desired heating rate.

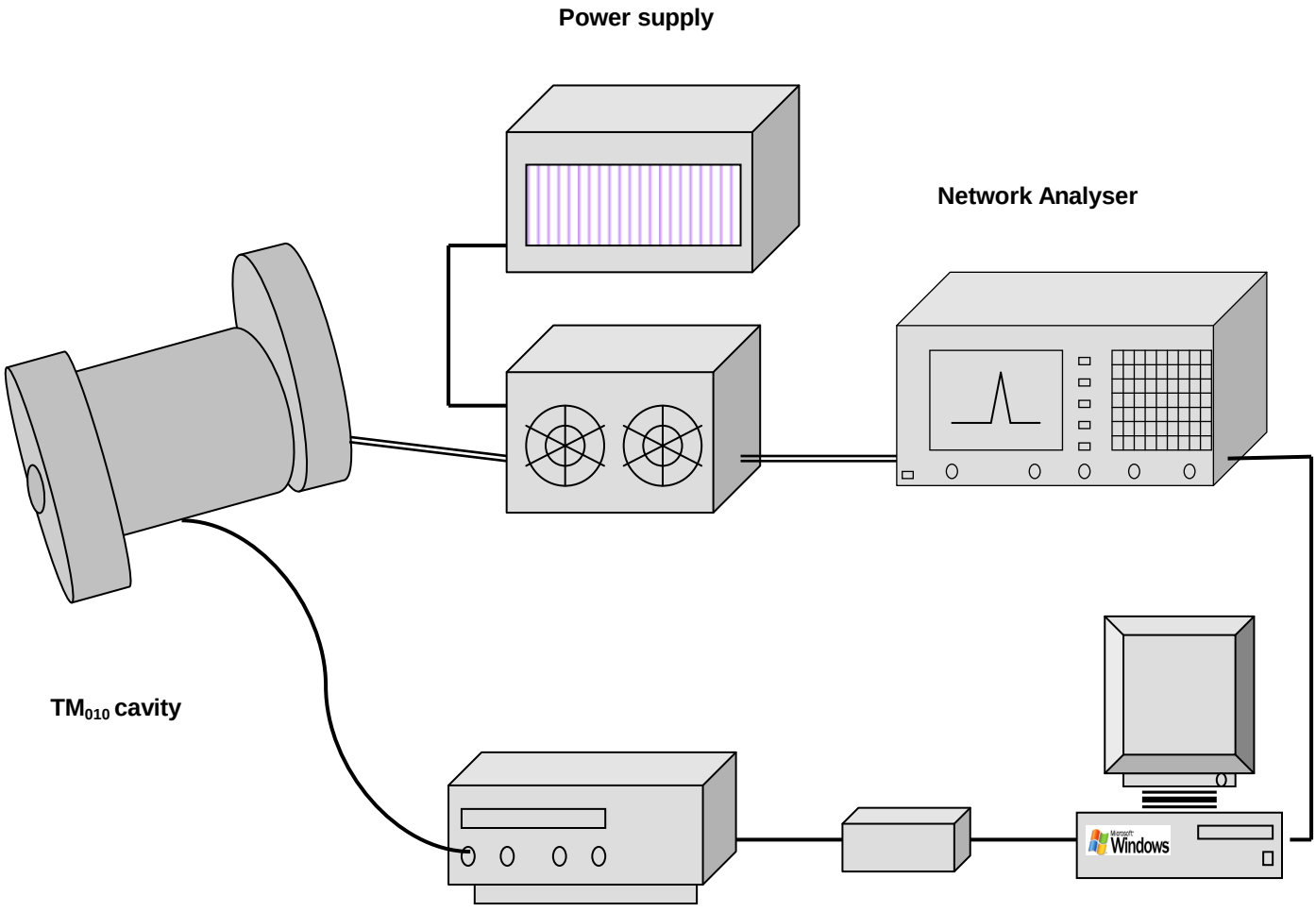


Fig. 2 A schematic diagram of a microwave heating system using a single mode cavity operated in TM_{010} mode [5]

A PTFE mould with dimensions 120mm length x 30mm breath x 5mm height was designed to fit into the cylindrical cavity. Samples were prepared and poured into the mould. The PTFE mould was then placed in the centre of the cavity. The samples were programmed to heat from room temperature to 180^{o}C at 2K min $^{-1}$.

3. RESULTS AND DISCUSSION

3.1 EFFECT OF CURING ON POLYMER DENSITY

Fig. 3Fully cured sample of Araldite LY 5052 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8 with microwave heating at 180^{0}C for 240 minutes.

The density gives us an indication of how tightly or loosely packed the molecules are in the network structure. The difference in the network packing between the samples cured using conventional and microwave heating can be investigated through this method. A pycnometer was used to measure the density of the fully cured samples. A plot of average density for the fully cured samples prepared using conventional and microwave curing for Araldite DLS 772 / 4 4 DDS epoxy system is shown in fig. 4.

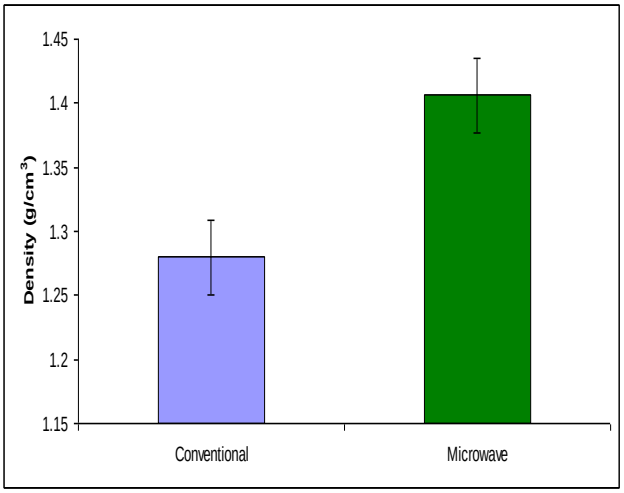
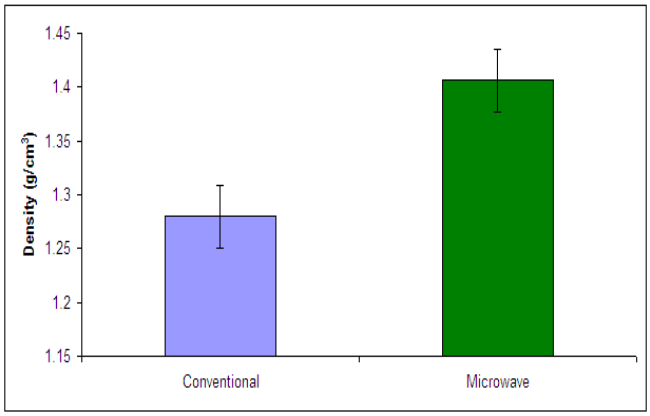


Fig. 4 Plot of Average Density for conventionally and microwave cured samples of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8

From fig. 4, the density of the microwave cured samples for the epoxy system Araldite DLS 772 / 4 4' DDS were slightly higher than the densities of the conventionally cured samples, meaning that the molecules are more tightly packed.



This reveals that the network structure in the microwave-cured samples were more compact than the conventionally cured samples. This suggests a different morphology in microwave compared to conventionally prepared samples, indicating a more compact network structure for the microwave cured samples.

3.2. EFFECT OF CURING ON DYNAMIC MECHANICAL PROPERTIES.

Dynamic Mechanical Thermal Analysis was used to study the morphology of the network structure of the polymer materials. The effect of curing method on the glass transition temperature of the microwave and conventionally cured samples was determined and compared.

Figs.5 and 6 show the typical DMA results for conventionally and microwave-cured samples of Araldite DLS 772 / 4 4' DDS epoxy system.

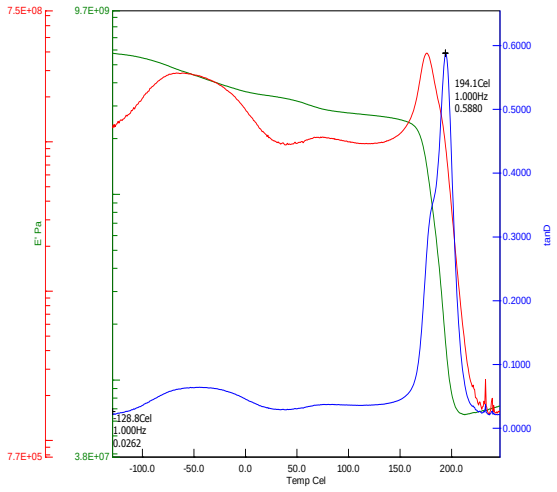


Fig. 5 Dependence of storage modulus (G'), Loss modulus (G") and tan δ with temperature for a fully cured sample of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8 prepared using conventional heating at 180^{0}C for 240 mins.

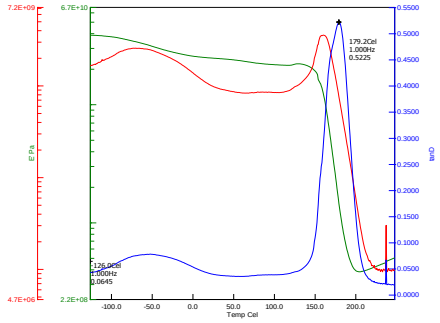


Fig. 6 Dependence of storage modulus (G'), Loss modulus (G") and tan δ with temperature for a fully cured sample of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8 prepared using microwave heating at 180 ^{o}C for 240 mins.

We notice from figs. 5 and 6 that the temperature dependence of the dynamic mechanic thermal analysis properties for the conventional and microwave cured Araldite DLS 772 / 4 4' DDS epoxy system follow the same course. The shear modulus (G') decreased as the temperature increased At the point where the storage modulus decreased sharply, the damping curve (tan δ) went through a maximum. The loss modulus also went through a maximum, but its peak was not as striking as the damping curve peak. The peak in the loss modulus curve occurred at a temperature slightly lower than the peak in the tan δ curve. Usually, the tan δ is the most sensitive indicator of the molecular motions which are occurring in the material. The tan δ peak is associated with the main glass-to-rubber transition. The temperature at the maximum of this tan δ peak is known as the glass transition temperature, T_g of the material. Two peaks were observed in the tan δ curve in both conventional and microwave-cured epoxy systems as shown in figures 5 and 6. A smaller peak was observed below 0oC in all the plots. The presence of two peaks means that a secondary transition occurred in the samples during the thermal analysis. The secondary transition is attributed to the crankshaft motion of the hydroxyl-ether group [6]. The crankshaft motion is usually found in amine cross linked systems [6]. The width of the tan δ peaks for all the figures appeared to be similar. However, the tan δ peak temperature was found to be higher in the microwave cured samples. The difference in the T_g values was attributed by Wei *et al*[7] to the existence of different network structures and cross-links within the conventional and microwave cured samples. The higher T_g in the microwave cured samples also suggested that the cross-link density was probably higher in the microwave cured samples than conventionally cured samples.

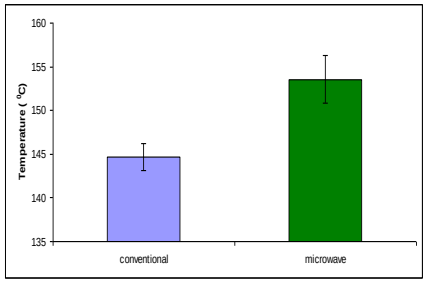


Fig 7 Bar chart of Average Tg values of conventional and microwave cured samples of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8.

TABLE I
GLASS TRANSITION VALUES FOR FULLY CURED SAMPLES OF ARALDITE DLS 772 / 4 4' DDS EPOXY SYSTEM WITH AN AMINE / EPOXY RATION OF 0.8.

Epoxy System	Tg1 (^{o}C)	Tg2 (^{o}C)	Tg3 (^{o}C)	Tg4 (^{o}C)	Tg5 (^{o}C)	Average Tg (^{o}C)	Standard Deviation
Conventional	178.6	179.2	177.5	175.6	172.8	177.7	1.57
Microwave	197.3	194.1	192.3	195.7	197.6	195.4	2.30

3.3 CROSS- LINK DENSITY

It is necessary to determine the cross-link density of the fully cured samples. This will enable us to investigate the variations in the structure of the materials produced by microwave and conventional heating. The Cross-link density (v) is defined as the number of moles of cross-linked chains per cubic centimeter of polymer [109]. The cross-link density can be determined by modulus measurements in the rubbery plateau. The relationship between rubbery plateau modulus and the cross-link density is given by

$$v = \frac{G'}{RT} \quad (1)$$

G' is the shear storage modulus which is obtained in the rubbery plateau. R is the gas constant, while T is the temperature in Kelvin which corresponds to the storage modulus value. The shear storage modulus is defined in the rubbery region at the temperature of Tg + 50.[8]. Bar chart plots of the cross-link density for both conventionally and microwave cured samples for both epoxy systems are shown in the figures below. The overall results reveal that microwave cured samples have a higher cross-link density than conventionally cured samples. This is an indication of a more compact network structure within the microwave cured samples.

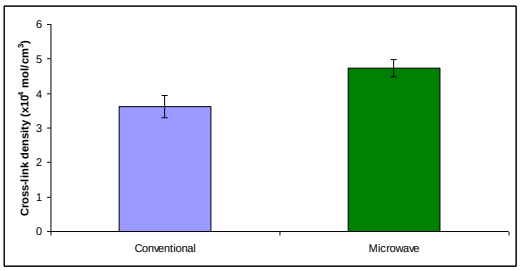


Fig 8 Plot of Bar chart of cross-link density values of conventional and microwave cured samples of Araldite DLS772 / 4 4' DDS epoxy system with an amine / epoxy system of 0.8

TABLE II
CROSS-LINK DENSITY VALUES FOR FULLY CURED MICROWAVE AND CONVENTIONALLY CURED SAMPLES OF ARALDITE DLS 772 / 4 4' DDS EPOXY SYSTEMS.

Epoxy System	Value 1	Value 2	Value 3	Value 4	Value 5	Average	Standard Deviation
Conventional	3.82	3.76	3.56	3.87	3.09	3.62	0.32
Microwave	4.75	4.56	4.44	5.08	4.86	4.74	0.25

3.4 AVERAGE MOLECULAR WEIGHT BETWEEN CROSS-LINKS

The difference in the network structure formed by conventional and microwave heating can be investigated from the average molecular weight between cross-links (M_c) of each sample. As the cross-link density represents the 'tightness' of the network links characterize the 'looseness' of the network. The average molecular weight between cross-links(M_c) is defined as the total sample weight that contains one mole of effective network chains. The determination of M_c is based on the simple rubber elasticity theory and can be calculated from [9, 10];

$$\mathrm{M_c} = \frac{\rho RT}{G'} \quad (2)$$

Where ρ is the density, R is the gas constant, T is the temperature in Kelvin and G' is the shear storage modulus in the rubbery region. The unit of M_c is the same as for molecular weight, g/mol. Comparison of Equations 1 and 2 shows that M_c is the proportional to cross-link density and can be expressed as follows;

$$M_c = \frac{\rho}{\nu} \quad (3)$$

Nielsen, however, claimed the equations of the kinetic theory of rubber predict moduli far too small for extremely highly cross - linked materials [9]. He has proposed an empirical equation that agrees much better than equation 3 with the experimental results at very high degrees of cross-linking.

$$\log G' = 7.0 + \frac{293\rho}{M_c} \quad (4)$$

The average molecular weight between cross-links for conventionally and microwave-cured samples were calculated using equations 3 and 4. The results both suggest that the M_c value of conventionally cured samples was generally higher than of microwave-cured samples. Bar chart plots of the average molecular weight between cross-links of microwave and conventionally cured samples of both epoxy systems is shown in figure 9. These results suggest that conventionally cured samples had larger 'free volume' between polymer chains. This result is consistent with the lower density observed in the conventionally cured samples.

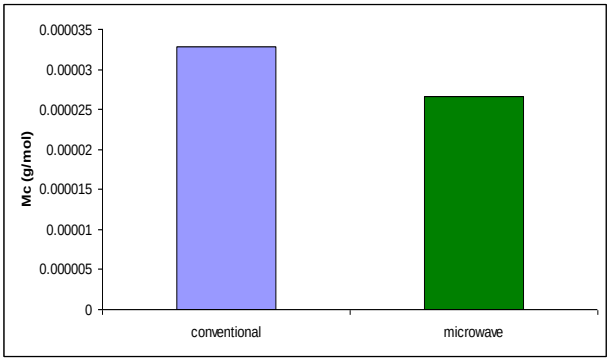


Fig. 9 Plot of average molecular weight between cross-links (M_c)of conventional and microwave cured samples of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8 using Nielsen's equation.

3.5 EFFECT OF CURING ON FLEXURAL PROPERTIES

A 3-point bending test was used to determine the flexural mechanical properties of the fully cured samples. The 3 point bending test is a stress-strain test whereby the specimen is deformed under bending conditions. Fully cured samples of Araldite DLS 772 / 4 4' DDS epoxy systems were subjected to three point bending tests. Fig. 10 shows flexural stress-strain curves obtained from conventional and microwave cured samples. The flexural load-displacement plots for the conventionally and microwave cured samples show similar patterns.

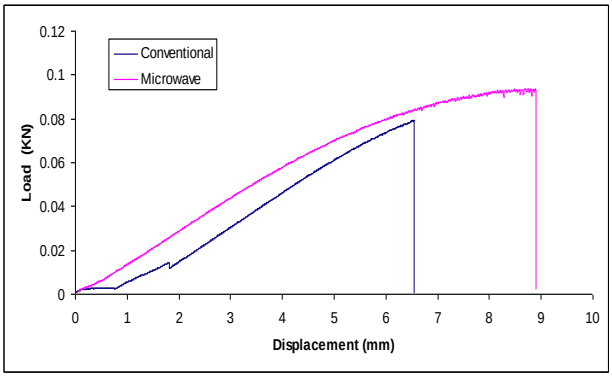


Fig. 10 Load vs Displacement plot for conventional and microwave cured samples of Araldite DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8.

The results showed that the microwave cured samples had higher flexural strengths and modulus than conventionally cured samples. This suggests that microwave cured samples are stronger and stiffer than conventional cured samples, giving more credence to the argument that the molecular network structure are more packed in microwave cured samples.

TABLE III

FLEXURAL STRENGTH VALUES FOR FULLY CURED SAMPLES OF ARALDITE DLS 772 / 4 4' DDS WITH AN AMINE / EPOXY RATIO OF 0.8

Epoxy System	Flexural Strength 1	Flexural Strength 2	Flexural Strength 3	Flexural Strength 4	Flexural Strength 5	Average	Standard Deviation
Conventional	107.3	113.6	117.9	105.3	110.6	110.9	5.01
Microwave	147.6	140.7	139.7	143.8	134.6	144.2	4.85

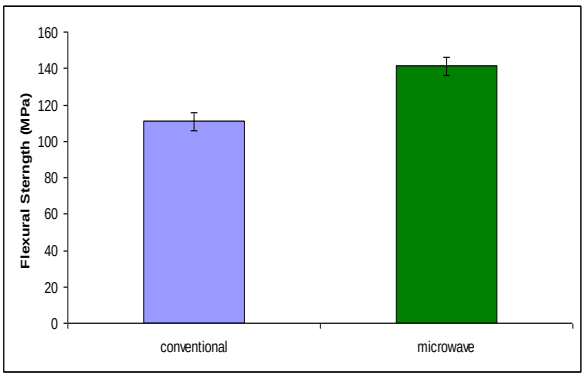


Fig.11 Bar chat of Average flexural strength values of conventional and microwave cured samples of Araldite.

These results are in good agreement with the higher Tg and higher cross-link density. Singer *et al.,*[11] attributed their findings to a better alignment of the molecules exposed to the electric field. This alignment may produce a higher molecular packing with lower free volume and higher density resulting in a higher modulus for microwave-cured samples. Bai *et al.,*[12] suggested that the differences in tensile properties could be attributed to a greater homogeneity of the microwave cured resin. This DLS 772 / 4 4' DDS epoxy system with an amine / epoxy ratio of 0.8.Navabnour *et al*[4, 13] observed a fifteen percent increase in the flexural modulus and the flexural strength of microwave cured samples, suggesting that enhancement was as a result of a reduction in the residual stresses in the microwave cured samples brought upon as a result of a better temperature control associated with microwave heating.

4. CONCLUSIONS

In this research, we observed that for Araldite DLS 772 / 4 4' DDS epoxy systems, the density of the fully cured microwave samples was higher than the density of the conventionally cured samples. Furthermore, the glass transition temperatures for the microwave cured samples were higher than the glass transition temperature of conventionally cured samples. The microwave cured samples had higher cross-link densities and lower average molecular weight between crosslinks than the conventionally cured samples. This indicated that the microwave cured samples were more compact. The microwave cured samples also had a higher flexural strength and modulus than conventionally cured samples.

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