

# MICROWAVE ASSISTED RESIN TRANSFER MOULDING OF POLYESTER/ARAMID COMPOSITES

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**SUMMARY:** The application of microwave energy in the processing of polymers and composites offers significant advantages over conventional processing technologies in reduced process time and cost. Resin transfer moulding (RTM) is one of the composite fabrication processes that can suffer because of the slow curing time of many thermosetting polymers. This paper reports an investigation in which microwave technology was incorporated into the process. One simple approach to enable microwave heating of a resin transfer moulding is to make the mould microwave transparent. Using Fourier Transform Infrared Spectroscopy (FTIR) it was found that an unsaturated polyester resin cured much faster in the microwave than in the oven. Identically shaped plots of styrene vinyl conversion versus polyester vinyl conversion for both microwave and oven curing suggest that the reaction mechanisms for materials prepared by the two routes are similar. Flexural modulus and strength of the composite samples obtained using microwave heating were higher than those of thermally cured composites.

**KEYWORDS:** Resin transfer moulding, microwave heating, aramid fibre, polyester resin

## INTRODUCTION

A disadvantage of using thermosetting matrices for reinforced composites is the long times which can be required to obtain full cure. This is because during processing heat is supplied to the sample by conduction and/or convection from a thermal energy source and polymers tend to possess poor thermal conductivities. In the search for an alternative energy source for composite cure, there has been considerable interest in the application of electromagnetic waves in the microwave frequency range. There are a number of reports in the literature of composites being prepared by use of microwave heating [1–9]. In contrast to thermal heating which involves heat conduction, microwave energy can directly penetrate the sample and then generate heat internally. This process is sometimes referred to as volumetric heating. Potential advantages offered by microwave heating are higher efficiency, faster production rate, lower cost of components, less energy used, more uniform cure and less equipment required for the same output.

There are two main issues which need to be addressed if microwave heating is to be used for the manufacture of composites with thermosetting matrices. The first of these is the effect of the type of heating used upon the chemical and physical properties of the resulting composites. It is possible that the use of microwave heating will result in a different chemical

reaction path. The second issue is how microwave heating can be incorporated into existing or new composite moulding technology.

Resin transfer moulding (RTM) is a process in which a pre-form of fibres is placed in a closed mould and a thermosetting resin is subsequently injected and cured to form a composite. This process has two slow steps. The first is the placement of fibres in the mould and the second is the curing of the resin. Curing can require times of minutes to hours depending upon the type of resin and its formulation. Microwave heating has the potential to reduce the cycle time of this process. Johnson *et. al* [10] have examined the use of an in-line microwave system to ramp the resin temperature during injection and thus reduce the time required to warm the resin in the mould. This decreased the cycle time by about 36% over that required for the same moulding produced by the conventional RTM process. The use of microwave heating in the mould could yield greater benefits. There are considerable technical difficulties which need to be solved before this could be achieved in a system with commercial potential. One simple approach to enable microwave heating of a resin transfer moulding is to make the mould microwave transparent. This has been used in the work presented here and shown to be a viable method for making microwave cured composites on a laboratory scale.

## EXPERIMENTAL

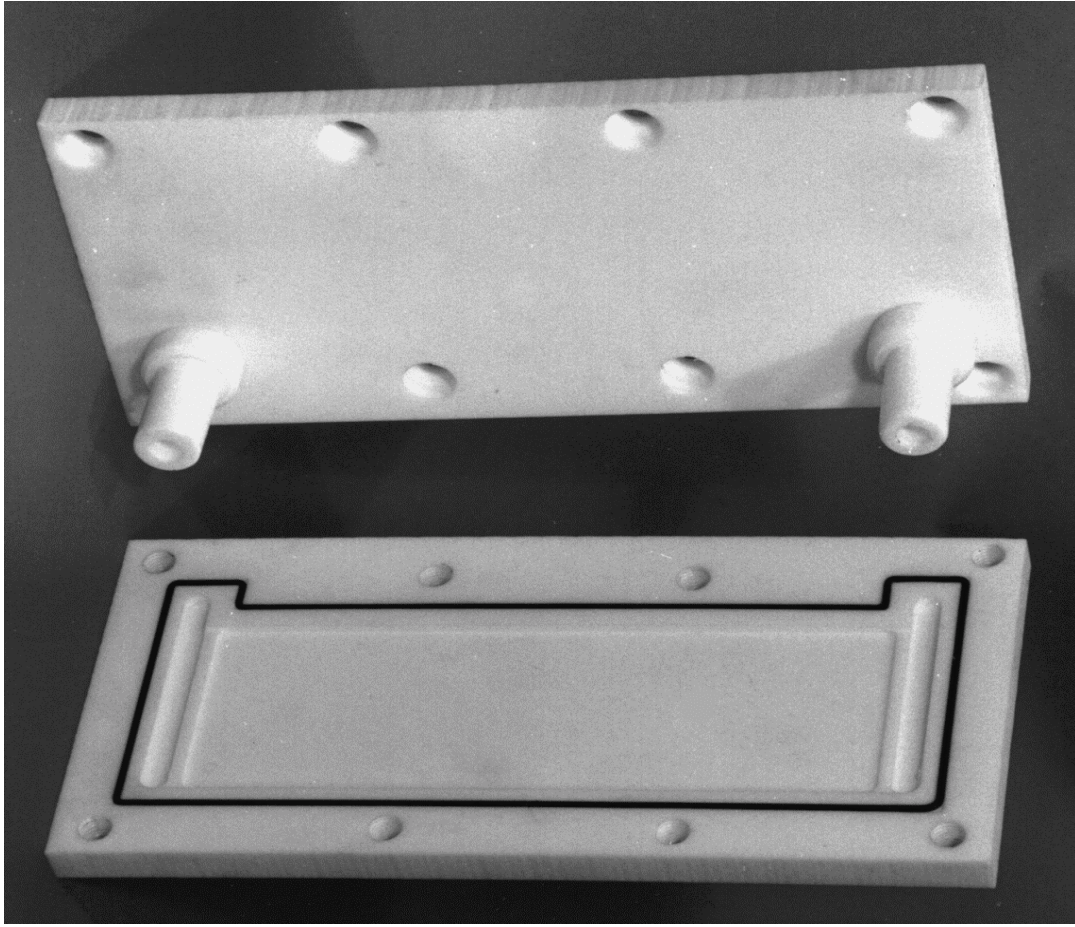
### Resin Transfer Moulding

In this work a simple resin transfer mould with cavity dimensions of 150 x 50 x 2 mm was fabricated from 10 mm thick poly(tetrafluoroethylene) (PTFE) sheet as shown in Fig.1. Composites were moulded using Beetle R 8952 polyester resin, (BIP Chemicals Limited) with 1% benzoyl peroxide as initiator and a unidirectional high modulus aramid fabric (Heinsco) as reinforcement. The mould was placed so that the plane of the cavity was vertical. The resin was injected at the bottom of the cavity and a vent was positioned at the top to prevent air from being entrained. An injection pressure of 0.25 Bar was used. Once the resin had been injected the mould was either placed in a conventional oven at 110°C or in a microwave oven. The power supply of the latter was modified in order to control the accelerating voltage supplied to the magnetron and thus the microwave power.

### Fourier Transform Infrared Spectroscopy (FTIR)

In order to study the cure behaviour of composites in a conventional oven and a microwave, samples were cured for different times. As a comparison, the cure behaviour of the unreinforced resin was also determined. Detailed reaction mechanism analysis of the partially cured samples was done using Fourier Transform Infrared Spectroscopy. There was no problem identified while curing small amount of neat resin (~ 4 grams) at high power (400W), however for the composite samples, some sparking was observed. Thus, the curing of composite samples was carried out at reduced power (120W).

A Perkin Elmer 2000 FTIR spectrometer, with a resolution of 4 cm<sup>-1</sup> in the transmission mode was used for measurements of the conversion of the styrene and polyester C=C bonds following reaction in the microwave and conventional ovens. The partially cured samples were either in liquid form or in solid form depending upon the extent of cure. For the liquid samples, one drop was cast as a thin film on a sodium chloride (NaCl) plate. It was then transferred to a liquid sampling cell holder located in the FTIR. On the other hand, solid samples were filed to form a finely powdered material before being pressed together with dried potassium bromide (KBr) to produce a disc. Sixteen consecutive spectra from 450 to 4500 cm<sup>-1</sup> were taken of each sample and their average was stored.



*Fig. 1: Poly(tetrafluoroethylene) (PTFE) Mould*

The conversion of styrene and polyester C=C bonds were measured by following the changes in the area of their characteristic peaks. In this study, the absorbance at  $1730\text{ cm}^{-1}$  (stretching modes of carbonyl groups) was chosen as an internal reference. The consumption of polyester C=C bonds,  $\alpha_E$ , was determined from the peak at  $982\text{ cm}^{-1}$ , while that of C=C bonds of styrene,  $\alpha_{ST}$ , was determined from the peak at  $912\text{ cm}^{-1}$ .

$$\alpha_E = 1 - \frac{\bar{A}^t_{(982)}}{\bar{A}^o_{(982)}} \quad (1)$$

$$\alpha_{ST} = 1 - \frac{\bar{A}^t_{(912)}}{\bar{A}^o_{(912)}} \quad (2)$$

where  $\bar{A}_t$  and  $\bar{A}^0$  are the normalised absorbance of the functional group before reaction and after reaction time  $t$ ; ( $\bar{A}_{982}^0 = A_{982}^0 / A_{1730}^0$ ;  $\bar{A}_{912}^0 = A_{912}^0 / A_{1730}^0$ ;  $\bar{A}_{982}^t = A_{982}^t / A_{1730}^t$ ; and  $\bar{A}_{912}^t = A_{912}^t / A_{1730}^t$ ).

### **Mechanical properties**

A three point bending test, according to BS 2782, was used to determine the flexural properties of samples using an Instron mechanical testing machine. Six rectangular samples were prepared for each set. There were four sets of samples as follows:

- i. Unsaturated polyester resin cured in oven at 110°C for 45 minutes
- ii. Unsaturated polyester resin cured in microwave at 120W for 25 minutes.
- iii. Aramid/polyester composite cured in oven at 110°C for 45 minutes.
- iv. Aramid/polyester composite cured in microwave at 120W for 25 minutes.

Rectangular samples with dimensions of approximately 70 mm (length) x 10 mm (width) x 2 mm (thickness) were cut using different techniques for neat resin and composite. For the resin, samples were cut using band saw, while the composites were cut using a diamond slitting wheel. All samples were polished before being placed in the testing machine. The machine crosshead speed was 5 mm/min and the span (L) was 40 mm.

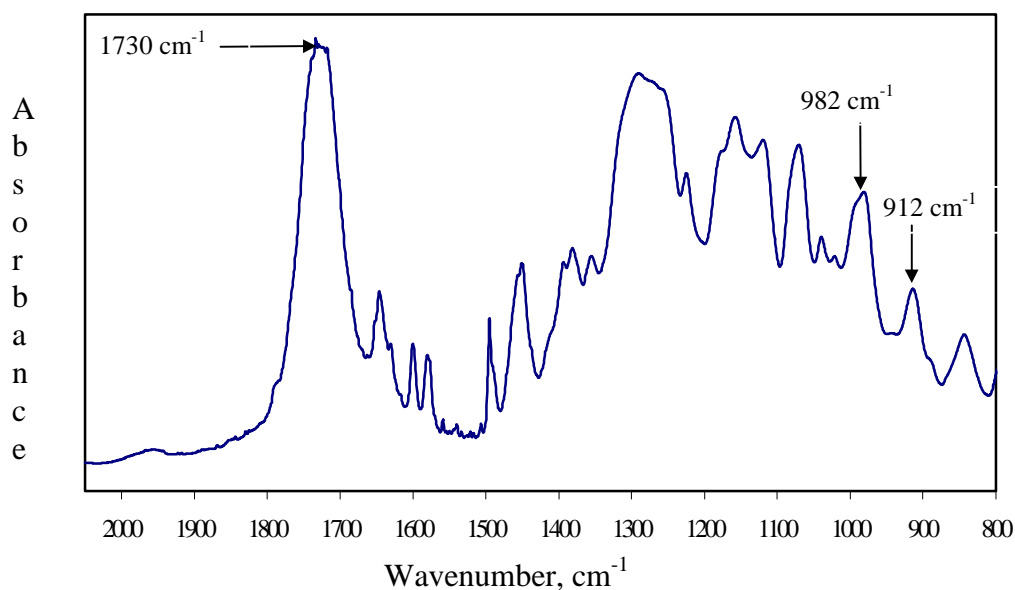
### **Fibre volume fraction determination**

Fibre volume fraction for the composites undergoing flexural testing was measured using a Magiscan Image Analyzer attached to an optical microscope. Each specimen undergoing flexural testing was sectioned about 5 mm from the end. Then, it was polished thoroughly until the cross section of the fibres was clearly visible. The volume fraction was measured from the ratio of the area occupied by the fibre to overall area. Three areas were examined for each sample and the average value was recorded.

## **RESULTS AND DISCUSSION**

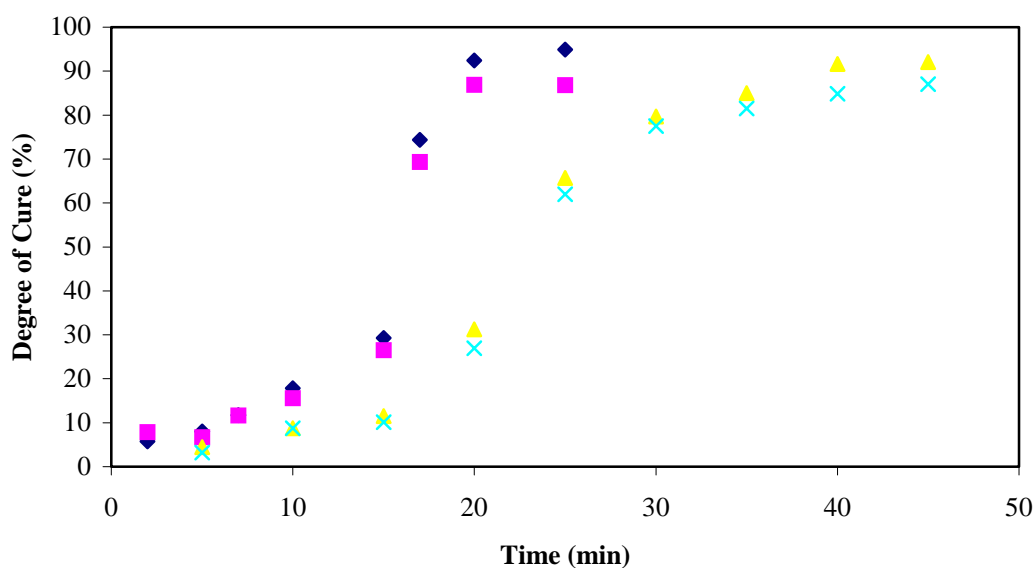
### **Infra red spectroscopy of the partially cured composites**

The FTIR analysis is based on the peak changes of functional groups. There are several peaks that may change when the reaction takes place. A typical IR spectrum for the uncured resin is shown in Fig. 2. The proportion of styrene and polyester C=C can be easily determined from the change in the height of the peaks at 912 cm<sup>-1</sup> and 985 cm<sup>-1</sup>, respectively. When the curing proceeds these peaks will decrease.



*Fig.2 : IR obtained for the uncured unsaturated polyester resin*

Fig. 3 shows the plot of degree of cure as measured by disappearance of the styrene and polyester chain double bonds during microwave and oven heating. It can be seen that for almost the entire reaction course in microwave and oven, the conversion of polyester is higher than that of styrene. According to Yang and Lee [11] who studied three different polyester resins with different amounts of unsaturation, the difference between them is due to the higher degree of unsaturation of C=C in polyester molecules. Polymer molecules tend to form ‘microgel’ structure, which is caused by an intramolecular cyclization reaction.



*Fig. 3 : Degree of cure vs. time for composite samples cured in microwave and oven using FTIR: Microwave; polyester C=C (◆), styrene C=C (■), Oven; polyester C=C (▲), styrene C=C (×)*

Inside the microgel, there can be a substantial amount of homopolymerization of the polyester vinyl groups. This is because the local polyester vinyl concentration is extremely high. Thus, at the same curing time, more double bonds in the polyester have been reacted than in the styrene.

As can be seen from Fig. 3, the curing of composites is much faster in the microwave than in the oven under the conditions used in this study. In the microwave oven, polymer molecules are heated directly due to the relaxation of the polarisation of the dipoles along the electric field. Legros *et. Al* [12] concluded from their dielectric properties study of an unsaturated polyester resin that C=O segments of fumaric residues are the most dielectrically active polar groups. Therefore, inside the network structure, the induced polyester polarisation will increase the molecular mobility. This results in acceleration of the curing reaction.

Since the reaction between styrene and unsaturated polyester is a copolymerization, the copolymer structure depends strongly on the relative reaction rates of the polyester vinyl groups and the styrene compared to homopolymerization of the styrene. Fig. 4 shows a plot of styrene conversion versus polyester vinyl group conversion for both microwave curing and oven. The trend emerging from this plot reveals that the cure kinetics of the unsaturated polyester are identical in the microwave and in the oven. In other words, the techniques have the same copolymerization route.

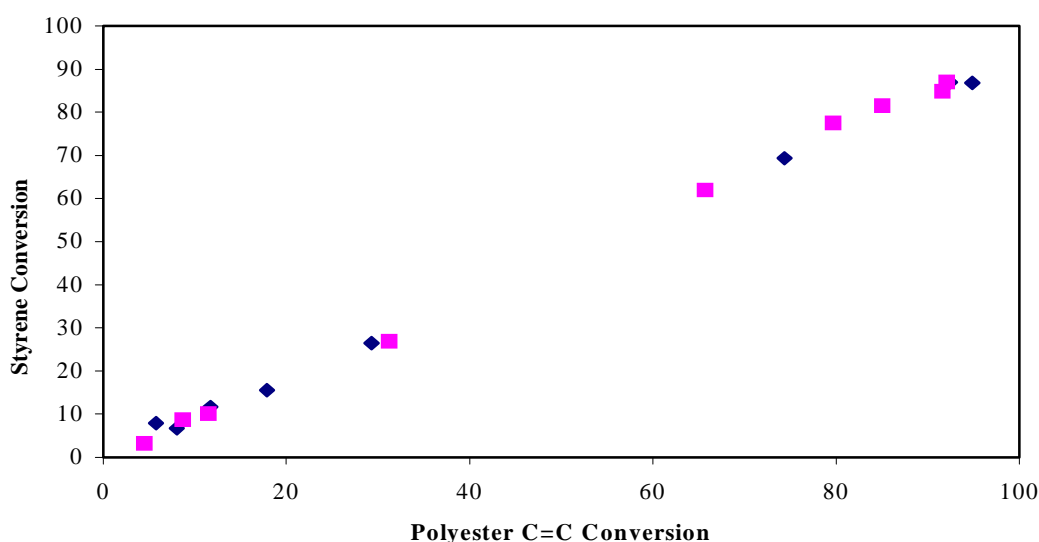
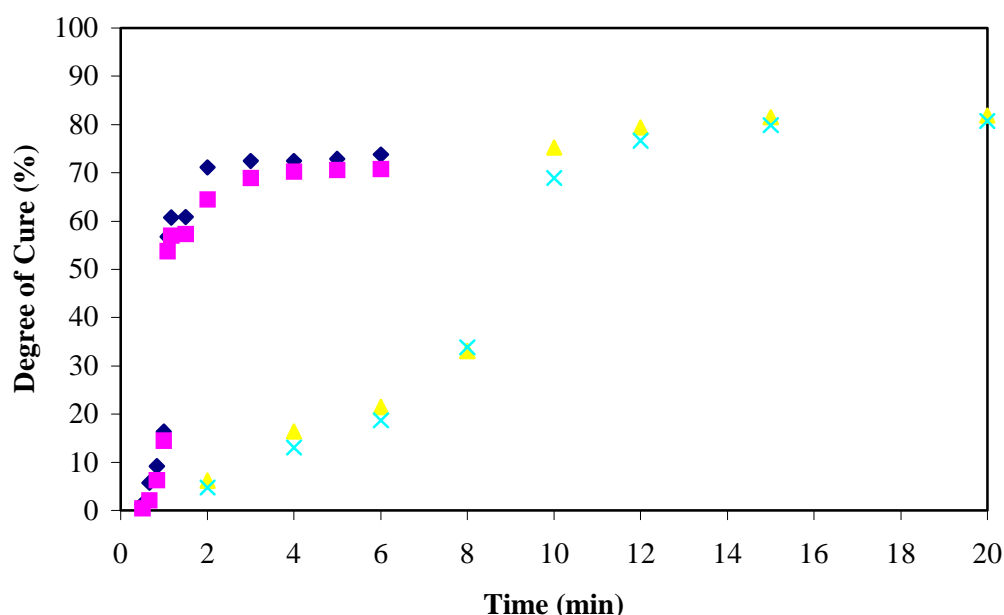


Fig.4 : Total styrene conversion vs. polyester C=C conversion of composites : Microwave (◆); Oven (■).

### Infra red spectroscopy of the partially cured resin

As a comparison with composite, the cure behaviour of the unreinforced resin was also determined. Fig. 5 shows the plot of degree of cure for the unreinforced unsaturated polyester resin cured in an oven and microwave. As has been shown for the composites, during almost the entire reaction course, microwave curing is much faster than the oven.

It should be remembered that the thermal curing has been undertaken at the same temperature as for the composite samples, but that the microwave cure for the unreinforced resin was carried out at higher powers and hence temperatures. It can be seen that the cure behaviour for both curing techniques is similar to composite (Fig.3), except it is much faster. This is because the amount of resin used while curing the unreinforced resin was about 4 grams, which is somewhat less than the composite. However, the final conversions for the unreinforced resin in the microwave and oven are slightly lower than the composite cure. As the amount of resin used is less (~ 4 grams), heat conduction through the surface of the sample will be faster. This may lead to the formation of tightly bonded microgels. It should be noted that the microwave heating of these samples will also be more rapid than the composite because of the higher power used and lower mass of the sample. Many vinyl groups may be buried inside the microgels, which reduce the reactivity of polyester vinyls and further cause lower overall conversion.



*Fig. 5 : Degree of cure vs. time for the unsaturated polyester samples cured in microwave and oven using FTIR: Microwave; polyester C=C (◆), styrene C=C (■); Oven ; polyester C=C (▲), styrene C=C (×) .*

## Mechanical properties of composites

Fig.6 and Fig.7 summarise the flexural modulus and strength results for the composites as a function of fibre volume fraction. Both plots show that flexural modulus and strength increase with the amount of fibre.

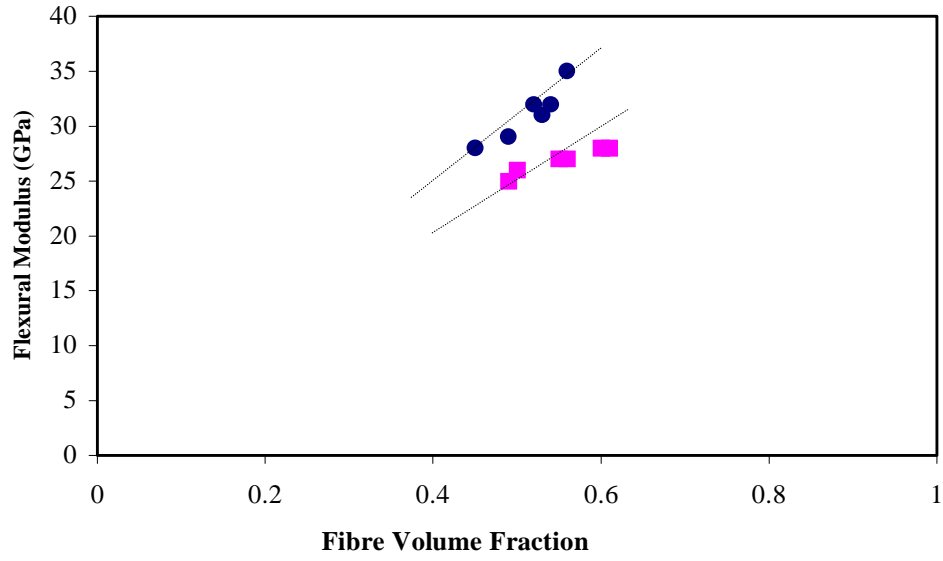


Fig. 6: Flexural modulus vs. fibre volume fraction of composites cured in microwave (●) and oven (■).

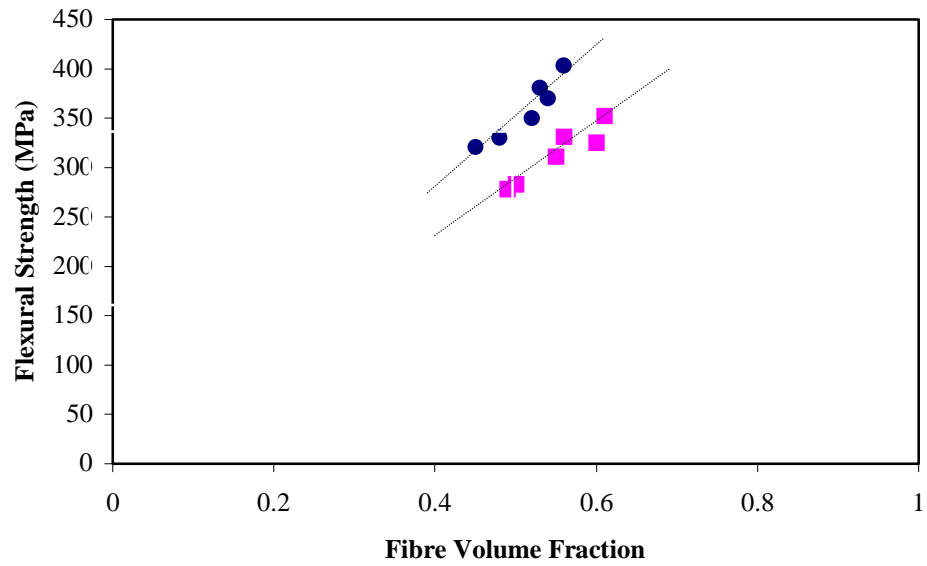


Fig. 7: Flexural strength vs. fibre volume fraction of composites cured in microwave (●) and oven (■)

The average flexural modulus and strength of composites obtained from both techniques are tabulated below:

Table 1: Average flexural modulus and strength of composites (50% fibre volume fraction)

Technique	Flexural modulus (GPa)	Flexural strength (MPa)
Microwave	$31 \pm 3$	$359 \pm 30$
Oven	$27 \pm 1$	$313 \pm 26$



It can be observed that an average flexural modulus and strength for the samples cured in microwave is higher than in the oven. According to Bai *et. al*[3] who studied epoxy resins, the better results obtained from samples prepared using microwave heating is due to better homogeneity of curing.

## CONCLUSIONS

The use of a microwave transparent mould in resin transfer moulding (RTM) has demonstrated the potential for microwave processing of composites. Microwave curing of composites and unreinforced resins were found to be faster than in a conventional oven. However, the time was not optimised since the purpose of the work was to demonstrate the viability of microwave approach rather than to achieve large reduction in cycle time. Identical plots of styrene conversion versus polyester vinyl conversion for both microwave curing and oven suggest that the reaction mechanisms for materials prepared by the two routes is similar. Microwave curing of the composite lead to slightly higher flexural modulus and strength. This improvement may be due to a better homogeneity in the microwave curing route. Further work is now being undertaken to understand and develop this route.

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