

CURING CHARACTERISTICS OF UNSATURATED POLYESTER/ARAMID REINFORCED COMPOSITE: MICROWAVE VS. THERMAL ENERGY

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Abstract. Conventional curing processes for producing thermoset composites use a thermal approach, which suffers from numerous disadvantages, including a long curing cycle time. This paper reports on an alternative curing process of an unsaturated polyester/aramid composite using microwave energy. The differences in curing characteristic of the composites fabricated between microwave and conventional ovens method were compared. Differential Scanning Calorimeter (DSC) analysis showed that microwave curing of composite was much faster than thermal curing while Fourier Transform Infrared Spectroscopy (FTIR) analysis was found to be very much significant in comparing the conversion of polyester C=C and styrene C=C undergoing microwave and thermal curing.

Keywords: Microwave curing, unsaturated polyester/aramid composite, Resin Transfer Moulding (RTM), Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR)

Abstrak. Proses pematangan yang biasa digunakan untuk menghasilkan komposit termoset ialah dengan kaedah terma. Terdapat banyak kelemahan untuk kaedah ini, termasuklah kitaran masa pematangan yang panjang. Kertaskerja ini melaporkan alternatif lain bagi proses pematangan komposit poliester tak tepu/aramid iaitu dengan menggunakan tenaga gelombang mikro. Perbezaan ciri pematangan bagi komposit yang dihasilkan melalui kaedah oven gelombang mikro dan oven lazim telah dibandingkan. Analisis kalorimetri pengimbas pembezaan (DSC) menunjukkan bahawa pematangan komposit dengan kaedah gelombang mikro adalah lebih cepat berbanding dengan kaedah terma. Analisis Spektroskopi inframerah transformasi Fourier (FTIR) pula menunjukkan keberkesanan alat ini membandingkan pertukaran poliester C=C dan stirena C=C yang menjalani pematangan gelombang mikro dan terma.

Kata kunci: Pematangan gelombang mikro, komposit poliester tak tepu/aramid, Resin pengacuan pindah (RTM), Kalorimetri pengimbas pembezaan (DSC), Spektroskopi inframerah transformasi Fourier (FTIR)

1.0 INTRODUCTION

One of the main disadvantages in the use of thermoset matrices for reinforced composite structures and components is the time lengthy required for a thermal curing process to be fully achieved. This is because during curing, heat is transferred to the material through conduction from the surfaces of the material. The thermal conductivity of

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polymeric materials is extremely poor, typically 0.3 W/m.K [1]. Microwave energy has been identified as a potential method to accelerate curing reaction [2]. Unlike conventional heating, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. There is thus potential savings to be made in commercial manufacture through shorter cure cycles and greater efficiency.

The objective of this work was to investigate the incorporation of microwave technology in processing of unsaturated polyester/aramid composite using Resin Transfer Moulding. The approach was to make the mould microwave transparent. However, if microwave heating is to be used for the manufacture of composites with thermosetting matrices, it is important to study the characteristics of the composites fabricated between microwave and conventional ovens method. It is possible that the use of microwave heating will result in a different chemical reaction path. The present paper reports on the differences in curing characteristics of the composites cured by both microwave and conventional ovens methods. Differential Scanning Calorimeter (DSC) was used to determine the degree of cure while Fourier Transform Infrared Spectroscopy (FTIR) was used to investigate in detail the copolymerisation reaction of styrene-unsaturated polyester in the composites.

2.0 EXPERIMENTAL PROCEDURE

2.1 Resin Transfer Moulding

Resin Transfer Moulding involves impregnation of the reinforced material, in a mould cavity, with a resin which is then cured. Moulding was carried out using a Hypaject 3/6 MK II machine manufactured by Plastech T.T. A simple mould with cavity dimensions of 150 × 50 × 2 mm was fabricated from 10 mm thick poly(tetrafluoroethylene) (PTFE) sheet. Composites were moulded using Beetle R 8952 unsaturated polyester resin, with 1% benzoyl peroxides as initiator and a unidirectional high modulus aramid fibre as reinforcement. Once the resin had been injected, the mould was either placed in conventional or microwave ovens.

2.2 Microwave Oven

The microwave heating was carried out using a commercial multimode oven (Philips M790), operating at 2.45 GHz. However, in this microwave the power supply was modified in order to control the accelerating voltage supplied to the magnetron and thus the microwave power. With this approach the microwave output could be controlled. The curing of composite samples was carried out at a low power, which was 120 W, since at high power some sparks were observed in the mould. In order to study the curing behaviour, composite samples were cured at different times and then the degree of cure was determined by DSC. Detailed analysis of the reaction mechanism in the partially cured samples was undertaken using FTIR.

2.3 Conventional Oven

A Towson & Mercer model 9-300 conventional oven was used for thermal curing. The oven temperatures were set at 110, 130 and 150°C. These temperatures were selected after studying a DSC dynamic scan for the uncured sample which showed that curing took place at temperature above 90°C. Curing of composite sample was done for different times and the partially cured sample subsequently analysed by DSC and FTIR.

2.4 Differential Scanning Calorimetry (DSC)

A Du Pont 2000 Thermal Analyst DSC was used to investigate the curing behaviour of composites cured in microwave and conventional ovens. Samples with weights between 10 and 30 mg were placed in an open aluminium pan. All samples were cured in a nitrogen atmosphere. Initially a dynamic scan was performed at a heating rate of 20°C/min from 0 to 200°C for the uncured unsaturated polyester resin to determine the curing temperature and also the total heat of reaction (ΔH_R). This scan showed that curing would only take place at temperatures above 90°C. For this reasons the curing temperatures in a conventional oven of 110, 130 and 150°C were selected. The heat of reaction (ΔH_{res}) for the partially cured composites, which have been cured in the conventional oven at different times were analysed using dynamic scans at the same heating rate and temperature range. Samples which had been heated in the microwave oven for different times were also analysed using the same technique. The degree of cure was calculated from the ΔH_{res} of the partially cured samples and from ΔH_R associated with the complete conversion of all reactive groups, as:

$$\text{Degree of cure } (\alpha) = \frac{\Delta H_R - \Delta H_{res}}{\Delta H_R} \quad (1)$$

The overall reaction rate was calculated from the rate of heat released measured as

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_R} \frac{d\Delta H_t}{dt} \quad (2)$$

where $d\alpha/dt$ is the overall reaction rate, ΔH_t is the heat released before time t (i.e., $\Delta H_t = \Delta H_R - \Delta H_{res}$). ΔH_R is known and $d\Delta H_t/dt$ can be solved using the *equal area differentiation technique* [3].

2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra for conversion measurements of styrene and polyester C=C bonds following reaction in either microwave or conventional were obtained using a *Perkin Elmer 2000 FTIR spectrometer*. There are two types of partially cured samples

depending upon the extent of cure, one was in liquid form and the other was in solid form. For 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. 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 scans from 450 to 4500 cm^{-1} were taken for each sample and their average was stored.

In this study, the absorbance at 1730 cm^{-1} (stretching mode of the carbonyl groups) was chosen as an internal standard. The consumption of polyester C=C bonds, α_E was determined from the peak at 982 cm^{-1} , while that of C=C bonds of styrene α_{ST} was determined from the peak at 912 cm^{-1} . These peaks, *i.e.*, 982 cm^{-1} for polyester C=C bonds and 912 cm^{-1} for C=C bonds of styrene were also assigned by other researchers [4-7].

$$\alpha_E = 1 - \left(\frac{\tilde{A}_{982}^t}{\tilde{A}_{982}^o} \right) \quad (3a)$$

$$\alpha_{ST} = 1 - \left(\frac{\tilde{A}_{912}^t}{\tilde{A}_{912}^o} \right) \quad (3b)$$

where \tilde{A}^o and \tilde{A}^t are normalised absorbance of the functional group before reaction and after reaction time t ; $\left(\tilde{A}_{982}^o = \frac{A_{982}^o}{A_{1730}^o}; \tilde{A}_{912}^o = \frac{A_{912}^o}{A_{1730}^o}; \tilde{A}_{982}^t = \frac{A_{982}^t}{A_{1730}^t}; \text{ and } \tilde{A}_{912}^t = \frac{A_{912}^t}{A_{1730}^t} \right)$.

3.0 RESULTS

3.1 Differential Scanning Calorimetry (DSC)

The degree of cure for the partially cured unsaturated polyester/aramid composites undergoing microwave and thermal heating was calculated using Equation 1. Figure 1 compares the degree of cure obtained at different times for the composite samples cured by both methods.

It shows that the composite curing in the microwave oven was faster than that of the conventional oven. The curing time required in the microwave oven was 25 minutes and for the conventional oven at 150°C was 30 minutes. There is not much difference in time. This is because the experiments in the microwave oven were conducted at lower power to avoid the arcing problems.

As expected the overall reaction rate for the composite sample cured in microwave oven was also much faster as shown in Figure 2. The overall reaction rate was calculated according to Equation 2.

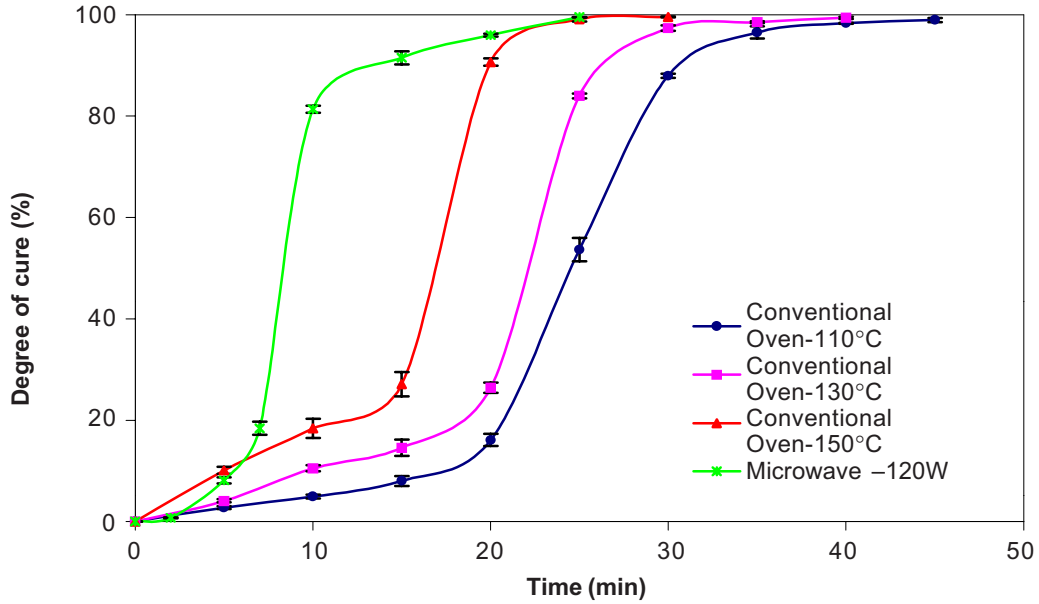


Figure 1 Comparison between degree of cure vs. time for the unsaturated polyester/aramid composites cured in conventional and microwave ovens using DSC.

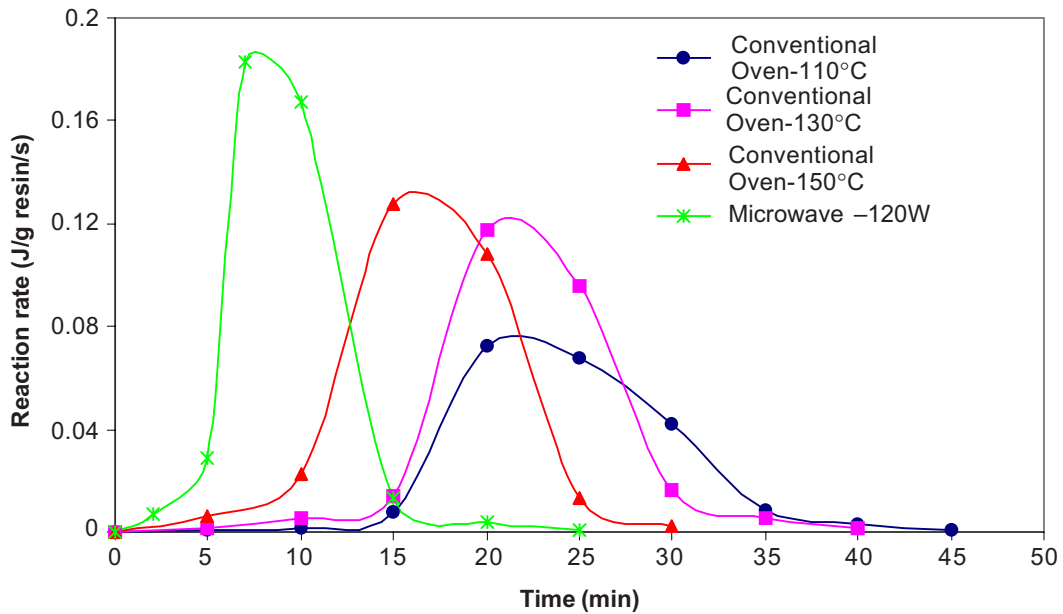


Figure 2 Reaction rate vs. time for the unsaturated polyester/aramid composites cured in conventional and microwave ovens.

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis is based on the changes of peaks associated with some of the functional groups. Thus, there are several peaks that may change when the reaction takes place. The consumption of styrene monomer was followed by the change in peak area at 912 cm^{-1} , while the consumption of C=C bond in unsaturated polyesters was followed by the change in the peak area at 982 cm^{-1} . As shown in Figure 3, the styrene and polyester C=C bonds can be easily determined from the peak changes at 912 cm^{-1} and 982 cm^{-1} respectively. When the curing proceeds these peaks will decrease.

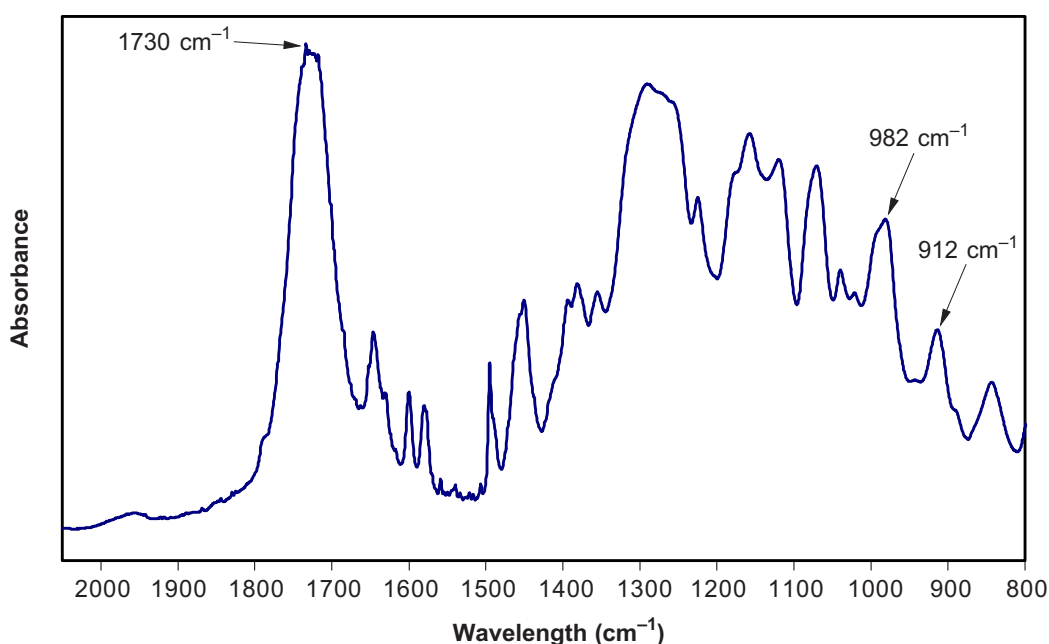


Figure 3 IR spectra obtained for the uncured unsaturated polyester resin

The consumption of C=C bond in unsaturated polyesters and C=C bond in styrene monomer was calculated using Equations 3a and 3b, respectively. The relative consumption of C=C bond in styrene to C=C bond in unsaturated polyesters can then be used to calculate the average crosslink length of styrene n , as follows;

$$n = \text{relative consumption of styrene to polyesters C=C multiplied by initial molar ratio (MR) of styrene to polyester C=C (initial MR is 1.48)}$$

where n is the average crosslink length of styrene through which the vinylene groups either in two adjacent polyester molecules (*i.e.*, intermolecular crosslinking) or in the same polyester molecule (*i.e.*, intramolecular crosslinking) are connected [8].

Table 1 shows the results obtained from FTIR for unsaturated polyester/aramid composites cured in a conventional oven at 110°C and Figure 4 shows the conversion of polyester C=C bonds and styrene C=C bonds vs. time profiles. For comparison, the bell-shaped DSC rate profile was also plotted.

Table 1 Percentage of polyester and styrene C=C bonds conversion for the unsaturated polyester/aramid composites cured in a conventional oven at 110°C

Time (min)	% cure based on polyester C=C	% cure based on styrene C=C	Relative consumption of styrene/polyester
5	2.4 ± 0.2	1.5 ± 0.1	0.63 ± 0.05
10	3.4 ± 0.4	2.4 ± 0.2	0.71 ± 0.03
15	7.8 ± 0.6	5.7 ± 0.5	0.73 ± 0.06
20	12.5 ± 1.3	9.4 ± 0.7	0.75 ± 0.04
25	44.3 ± 3.4	29.3 ± 2.0	0.66 ± 0.03
30	75.6 ± 4.8	52.4 ± 3.1	0.69 ± 0.03
35	89.2 ± 1.6	67.1 ± 0.9	0.75 ± 0.01
40	91.7 ± 2.3	77.0 ± 1.4	0.84 ± 0.03
45	92.3 ± 1.8	80.8 ± 1.7	0.88 ± 0.02

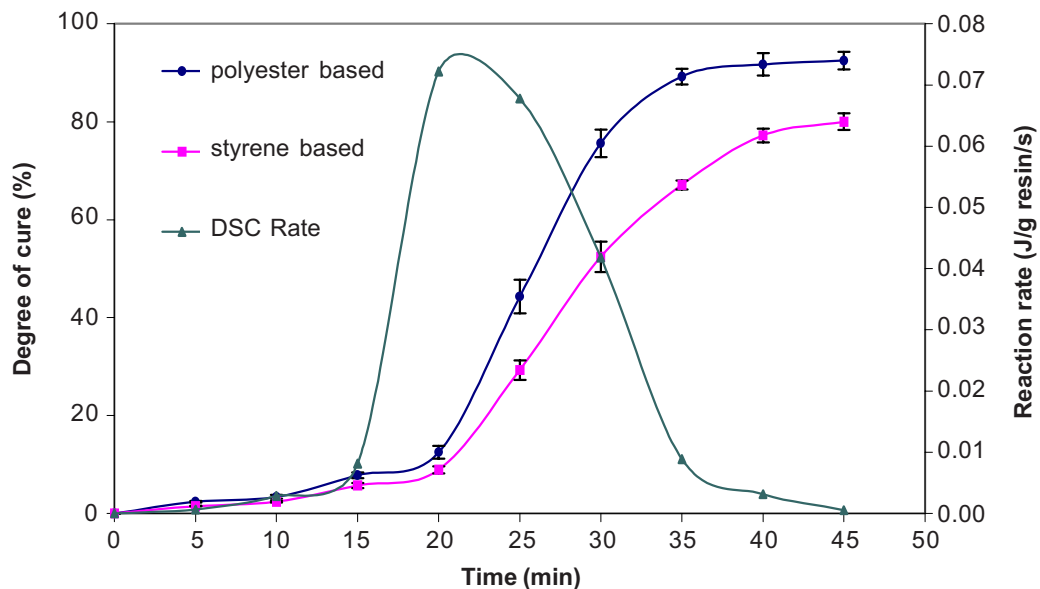


Figure 4 Conversion and DSC rate vs. time profiles for the unsaturated polyester/aramid composites cured in a conventional oven at 110°C

It can be seen that before the peak of DSC rate profile, the difference in conversion of polyester C=C bonds and styrene C=C was small. However, after the peak of DSC rate profile, the difference in conversion was slightly higher. The final conversions of polyester C=C and styrene C=C were 92.3 ± 1.8 and $80.8 \pm 1.7\%$, respectively. The calculated average crosslink length of styrene for the final composite formed was 1.30 ± 0.02 .

Figures 5, 6 and 7 show the conversion against time profile for the unsaturated polyester/aramid composites cured in the conventional oven at 130 and 150°C and

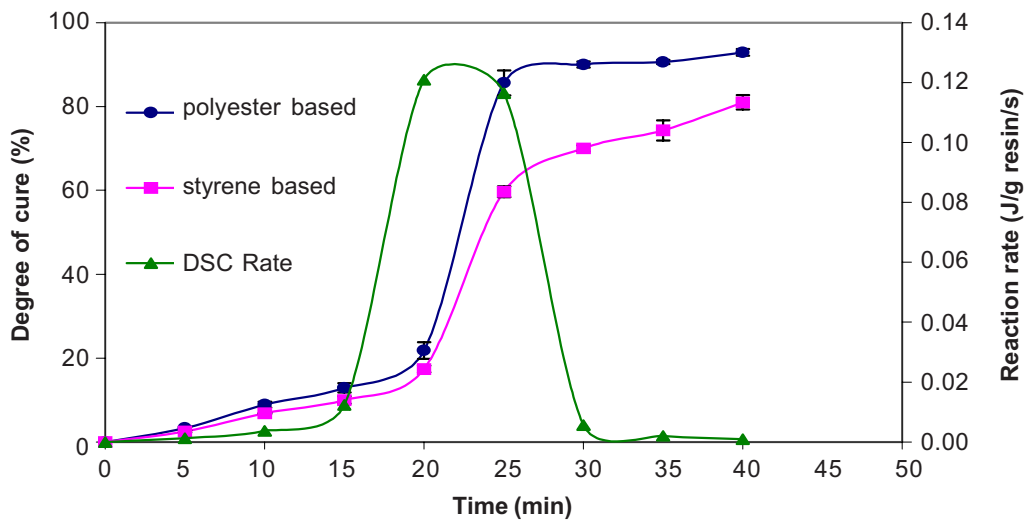


Figure 5 Conversion and DSC rate *vs.* time profiles for unsaturated polyester/aramid composites cured in a conventional oven at 130°C

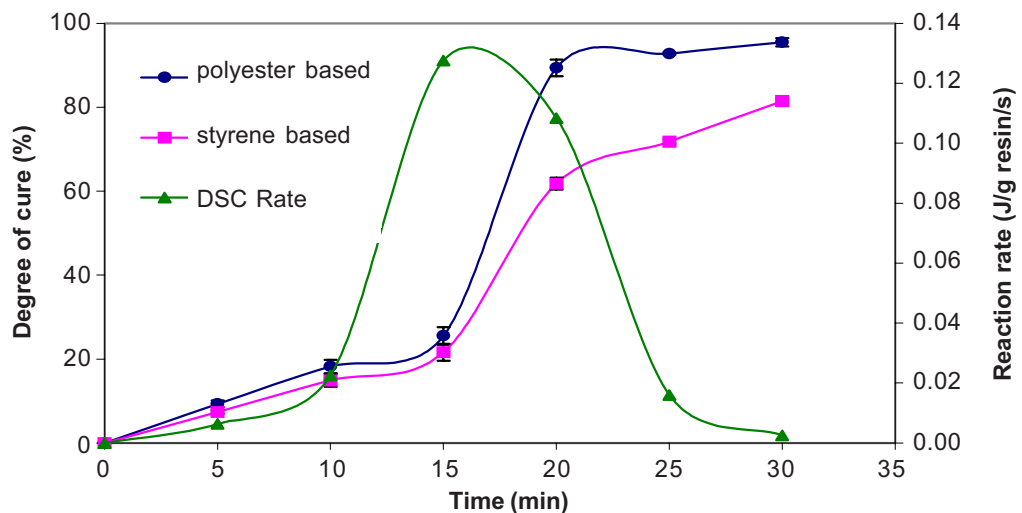


Figure 6 Conversion and DSC rate *vs.* time profiles for unsaturated polyester/aramid composites cured in a conventional oven at 150°C

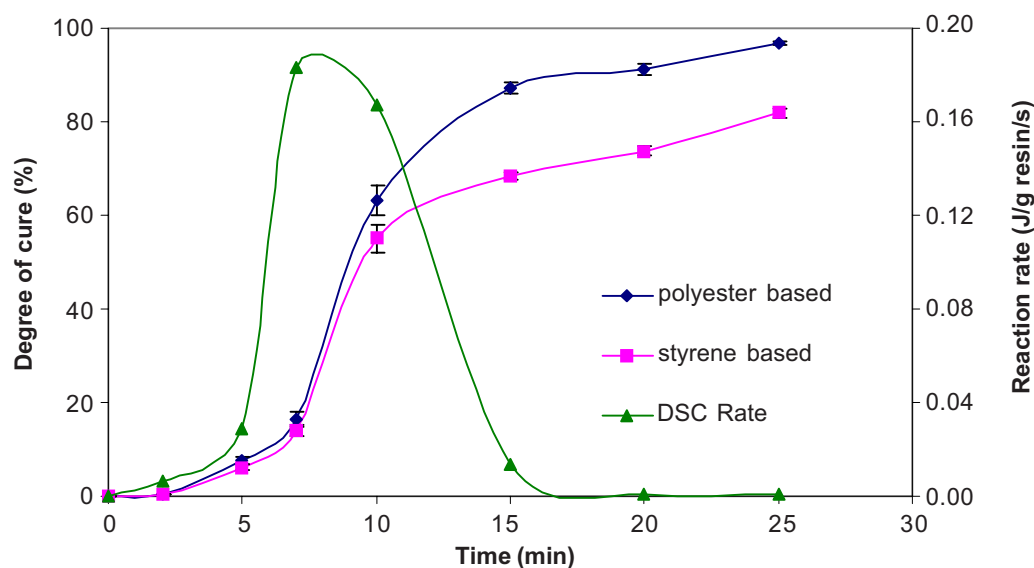


Figure 7 Conversion and DSC rate *vs.* time profiles for unsaturated polyester/aramid composites cured in a microwave oven at 120 W

microwave oven at 120 W respectively. It can be seen that the trends of conversion variations for styrene and polyester C=C bonds were similar to that of composite cured in a conventional oven at 110°C as shown in Figure 4.

Table 2 summarises the final conversion measured by IR and the final average crosslink length of styrene for the composite cured at various temperatures in the conventional oven and in the microwave. It can be seen that the average crosslink length of styrene decreased slightly with increasing temperature, while the average crosslink length of styrene for the microwave cured samples was lower than that of the oven cured materials.

Table 2 Summary of kinetic information obtained using IR for unsaturated polyester/aramid composites cured in conventional and microwave ovens at maximum cure.

Curing conditions	% Cure based on Styrene C=C	% Cure based on Polyester C=C	Average length of styrene, <i>n</i>
Conventional Oven at 110°C	80.8 ± 1.7	92.3 ± 1.8	1.30 ± 0.02
Oven at 130°C	81.2 ± 1.7	92.9 ± 0.8	1.29 ± 0.02
Oven at 150°C	81.5 ± 0.4	95.5 ± 1.0	1.26 ± 0.01
Microwave at 120 W	81.9 ± 1.0	96.8 ± 0.5	1.24 ± 0.01

4.0 DISCUSSION

For the highly crosslinking reaction system of styrene/unsaturated polyester, the initial reaction mechanism was proposed by Yang and Lee [9] as shown in Figure 8. After the reaction starts, the initiator decomposes to generate free radicals, which link the C=C bonds of the system through either inter or intra-molecular crosslinking reaction to form long chain polyester molecules (see Figure 8a). These long chain polyester molecules tend to form spherical type of structure due to the intra-molecular crosslinking of pendant C=C bonds and the microgel particles are thus formed (see Figure 8b).

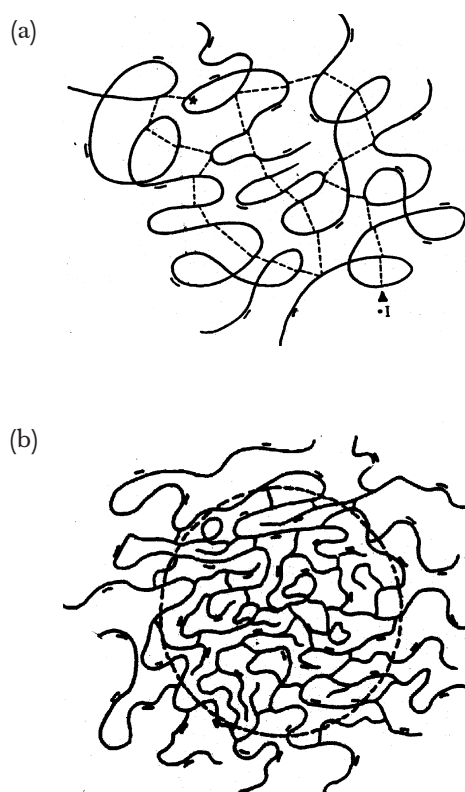


Figure 8 Schematic diagram showing microgel formation through the growth of free radicals (a) growth of free radicals; (b) formation of microgel particles [9]

Based on the DSC rate profiles and conversion profiles obtained by IR for both samples cured in conventional and microwave ovens, the microgel based reaction mechanism can be stated as follows.

Basically the formation of microgel particles would continue from the beginning of the reaction until the microgels meet and closely overlap with one another throughout the system. After the peak of the DSC rate profile, the rate of microgel formation

would then slow down considerably due to the diffusion controlled propagation reactions for polyester C=C bonds. Sometime later, when the existing microgels were highly overlapped via crosslinking and a compact network structure was formed, no new microgel particles would be generated.

Because of the presence of fibre in an unsaturated polyester/aramid composite, the surface area of the resin would be further increased. This is due to the combination of macro-flow and micro-flow in RTM as illustrated in Figure 9 [10]. Mould filling to distribute resin throughout the fibre-loaded cavity can be considered as macro-flow. Fibre wetting to penetrate fibre bundles can be considered as micro-flow.

The increase in a surface area of the resin will create a looser microgel structure during curing and a greater amount of monomer could participate in the self-bonding in the crosslinking reactions inside the microgels.

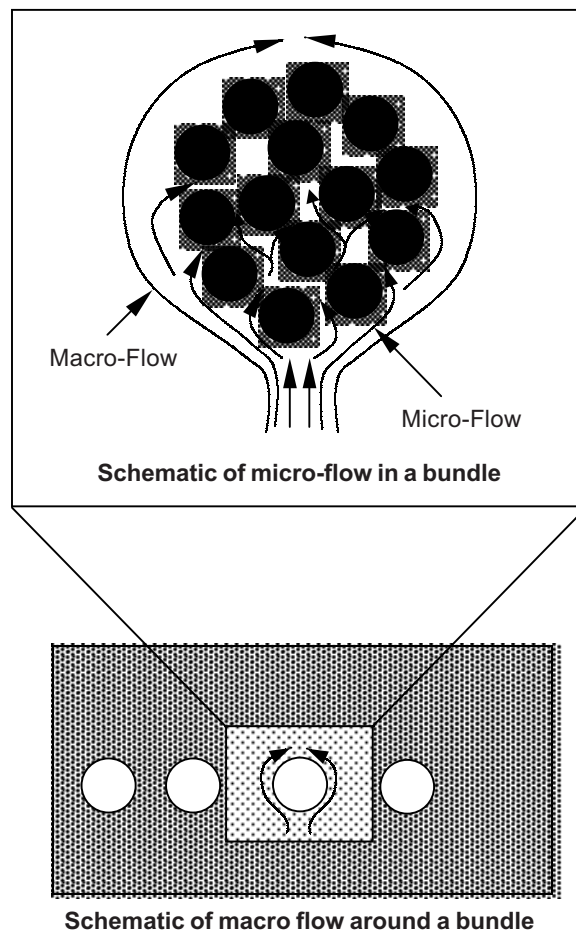


Figure 9 Schematic displaying micro-flow in a fibre bundle and macro-flow around a fibre bundle [10]

The formation of microgel particles would continue until the microgels meet and closely overlap with one another. After the peak in the DSC rate profile, the microgel structure would be so compact that it would be difficult for styrene monomers to diffuse into the microgel to crosslink with the pendant C=C bonds of polyester molecules inside. Most of the styrene would be consumed in the intermicrogel crosslinking reaction with polyester C=C. Hence, this leads to a lower conversion of styrene in a later reaction processes.

A similar explanation of the formation of microgels mechanism can be applied to microwave cured sample. However, in microwave cure, microwave radiation heats up polymer molecules directly inside the network structure, the induced polymer and monomer molecule polarization along the applied electromagnetic field may greatly increase the molecular mobility. Hence, this would reduce the rigidity of the formed network structure so that more polyester and styrene C=C could be consumed as shown in Table 2. This would lead to an increase in crosslinking inside the microgels (lower average crosslink length of styrene), leading to higher overall crosslink density. Higher overall crosslink density would be expected to increase the mechanical properties of the microwave cured composite sample.

5.0 CONCLUSIONS

Microwave curing of unsaturated polyester/aramid composites was found to be faster than that of 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 the greatest possible reduction in cycle time.

Fourier transform infrared spectroscopy (FTIR) showed that the consumption of styrene monomer can be determined by measuring the change in the peak area at 912 cm^{-1} , while the consumption of C=C bond in an unsaturated polyesters resin could be observed by the change in the peak area at 982 cm^{-1} . When the curing proceeded these peaks decreased.

FTIR analysis revealed that the microwave cured composite produced lower average crosslink length of styrene for the final conversion. This would lead to an increase in overall crosslink density and would be expected to enhance the mechanical properties of the microwave cured composite sample.

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