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An Evaluation of Fracture Toughness of Vinyl Ester Composites Cured under Microwave Conditions

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The shrinkage of vinyl ester particulate composites has been reduced by curing the resins under microwave conditions. The reduction in the shrinkage of the resins by microwaves will enable the manufacture of large vinyl ester composite items possible (H.S. Ku, G. Van Erp, J.A.R. Ball, and S. Ayers, Shrinkage Reduction of Thermoset Fibre Composites during Hardening using Microwaves Irradiation for Curing, Proceedings, Second World Engineering Congress, Kuching, Malaysia, 2002a, 22-25 July, p 177-182; H.S. Ku, Risks Involved in Curing Vinyl Ester Resins Using Microwaves Irradiation. *J. Mater. Synth. Proces*. 2002b, 10(2), p 97-106; S.H. Ku, Curing Vinyl Ester Particle Reinforced Composites Using Microwaves. *J. Comp. Mater*., (2003a), 37(22), p 2027-2042; S.H. Ku and E. Siores, Shrinkage Reduction of Thermoset Matrix Particle Reinforced Composites During Hardening Using Microwaves Irradiation, *Trans. Hong Kong Inst. Eng*., 2004, 11(3), p 29-34). In tensile tests, the yield strengths of samples cured under microwave conditions obtained are within 5% of those obtained by ambient curing; it is also found that with 180 W microwave power, the tensile strengths obtained for all duration of exposure to microwaves are also within the 5% of those obtained by ambient curing. While, with 360 W microwave power, the tensile strengths obtained for all duration of exposure to microwaves are 5% higher than those obtained by ambient curing. Whereas, with 540 W microwave power, the tensile strengths obtained for most samples are 5% below those obtained by ambient curing (H. Ku, V.C. Puttgunta, and M. Trada, Young's Modulus of Vinyl Ester Composites Cured by Microwave Irradiation: Preliminary Results, *J. Electromagnet. Waves Appl*., 2007, 20(14), p. 1911-1924). This project, using 33% by weight fly ash reinforced vinyl ester composite [VE/FLYSH (33%)], is to further investigate the difference in fracture toughness between microwave cured vinyl ester particulate composites and those cured under ambient conditions. Higher power microwaves, 540 and 720 W with shorter duration of exposure are used to cure the composites. Short-bar method of fracture toughness measurement was used to perform the tests. Plastic (PVC) re-usable molds were designed and manufactured for producing the test samples. The results show that the fracture toughness of specimens cured by microwave conditions are generally higher than those cured under ambient conditions, provided the power level and duration of microwave irradiation are properly and optimally selected.

Keywords composites, fly ash, fracture toughness, and vinyl ester resin, microwaves, short-bar test, shrinkage

1. Introduction

Vinyl ester resins have strong and growing applications in corrosion environments in the USA. Other significant markets for vinyl esters include pultruded construction and electrical components, automotive structural applications, polymer concrete vessels for mining and chemical operations and sporting goods because they exhibit excellent chemical resistance, low-maintenance requirements, design flexibility, and ease of installation (Ref 1, 2). The Centre of Excellence for Engineered Fibre Composites, University of Southern Queensland (USQ) also designs and manufactures a significant amount of equipment and structures for local governments and industries using vinyl ester resins, which suffer considerable shrinkage during hardening.

Fracture toughness measures the ability of a material containing a flaw to withstand an applied load. Unlike the results of an impact test, fracture toughness is a quantitative property of the material (Ref 3). Fracture toughness can be used to calculate the load which a structure can withstand without experiencing catastrophic failure due to fracture; hence it is an important material property in many engineering designs. As in the previous study, the short-bar method will be used (Ref 3-8).

2. Fracture Toughness and Short-Bar Geometry

A typical fracture toughness test is performed by applying a tensile stress to a specimen prepared with a flaw of known geometry and size as shown in Fig. 1. The stress applied to the material is intensified at the flaw (Ref 2). For a simple test the stress intensity factor,

$$K = f\sigma\sqrt{\pi a} \quad \text{(Eq 1)}$$

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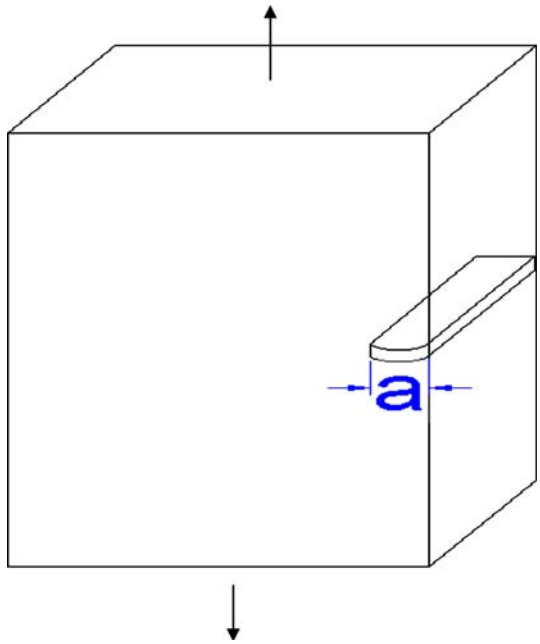


Fig. 1 Schematic drawing of fracture toughness specimens with edge and internal flaws

where f is a geometry factor for the specimen and flaw. If the specimen is assumed to have 'infinite' width then $f \cong 1.0$; for 'semi-infinite' width, $f \cong 1.1$ (Ref 3, 9), where σ is the applied stress in N/mm^2; a is the flaw size in mm.

By performing a test on a specimen with a known flaw size, the value of K that causes the flaw to grow and cause failure can be determined. Fracture toughness, K_c, is defined as the critical stress intensity required for a crack to propagate and

$$K_c = f\sigma_c\sqrt{\pi a} \quad \text{(Eq 2)}$$

K_c is a property that measures a material's resistance to brittle fracture when a crack is present and its unit is MPa $\sqrt{m}$.

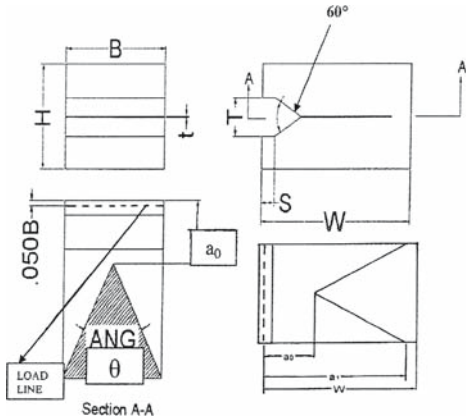
For relatively thin specimens, the value of K_c will depend on specimen thickness but when the specimen thickness is much larger than the crack, it becomes independent of thickness. Under these conditions, a condition of plane-strain exists. Plain strain means that when a load operates on a crack in a manner represented in Fig.1, there is no strain component perpendicular to the front and back faces. The value K_c for this thick-specimen situation is known as the plane strain fracture toughness K_{Ic}; furthermore, it is defined by (Ref 9).

$$K_{Ic} = f\sigma\sqrt{\pi a} \quad \text{(Eq 3)}$$

Figure 2 shows the short-bar specimen with straight chevron slots (Ref 4-6). The load line is the line along which the opening load is applied in the mouth of the specimen. The specimen parameter, B, is the specimen breadth.

3. The Composite Samples

In current study, Hetron 922 PAW (recommended vinyl ester resin used in winter) was used. The vinyl ester is dissolved in 50% by weight of styrene. It is formed from the reaction between methacrylic acid and the diglycidylether of bishphenol



SYMBOL	DEFINITION	VALUE	TOLERANCE
B	BREADT	B	
W	LENGTH	1.5B	± .010B
H	HEIGHT	.870B	± .005B
a_0	INITIAL CRACK LENGTH	.513B	± .005B
θ	SLOT ANGLE	55.2	± 1/2
t	SLOT THICKNESS	SEE TABLE III (of Barker, 1981)	
S	GRIP GROOVE DEPTH	.130B	± .010B
T	GRIP GROOVE WIDTH	.313B	± .005B
R	RADIUS OF SLOT CUT	SEE FIG 4 (of Barker, 1981)	2.5B

Fig. 2 Short-bar specimen with straight chevron slots

A. The resin hardener (MEKP) used in the experiment was 2% by volume (Ref 10). The reinforcer was fly ash (ceramic hollow spheres) particulate which constituted 33% by weight of the cured vinyl ester composite [VE/FLYASH (33%)]. This is the same composition as used in the previous study (Ref 7).

The short-bar specimens were cast to shape. The resin is a colorless liquid and is first mixed with the red accelerator. The fly ash is then added to the mixture which is then mixed to give the uncured composite. Table 1 shows the mass in grams of resin, accelerator, and fly ash required respectively used to make 1000 g of uncured composite.

The uncured composite was then poured into the molds for curing at ambient or microwaved conditions (Ref 11). The mold was made from 6-mm PVC sheets with six pieces of short-bar specimen each (Fig. 3). The slots were made by inserting plastic sheets of suitable thickness into the castings.

4. Short-Bar Method Test and Microwaves

Vinyl ester resins have been proved to absorb microwaves readily. The risks associated with microwave processing have also been discussed in previous studies (Ref. 7). In this study, the selection of exposure times and power levels was based on the combination of power level and exposure time which resulted in minimum shrinkage of vinyl ester composites. These results were experimentally determined. The degree of curing after each treatment has not been determined. However, after leaving the treated samples in ambient conditions for 24 h, the resin would be fully cured (Ref 7, 8, 11-14). The microwave facility used in this project is a modified microwave oven with a maximum power of 1800 W; the power levels can be increased in steps of 180 W.

Table 1 Weight of materials required to make 000 g of VE/FLYASH (33%)

Parameters	Materials	Resin	MEKP	Fly ash	Composite
Relative density		1.05	1.18	0.7	...
Percentage by volume		56.5	1	42.6	100
Percentage by weight		67	...	33	100
Weight for 600 g of composite		657 (g)	13 (g) or 11 (mL)	330 (g)	...

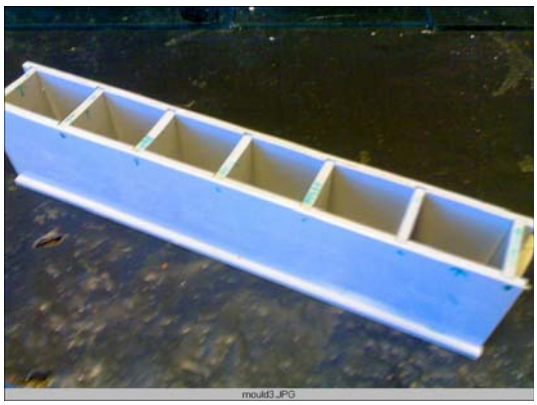


Fig. 3 The external view of short-bar specimen mold

An MTS 810 Material Testing Systems was used for the test. The rate of extension was set at 1 mm per minute. In current study, VE/FLYASH (33%) was exposed to microwave irradiation of 180 and 360 W, respectively, with exposure times for both power levels at 60, 70, and 80 s, respectively; VE/FLYASH (33%) was also exposed to microwave irradiation of 540 and 720 W, respectively with exposure times for both power levels at 15, 20, and 25 s, respectively.

One mold or six uncured short-bar specimens were exposed to microwaves at a time. At the same time, one mold of composite was cured under ambient conditions and their fracture toughness values used as a benchmark for comparison.

The equation for fracture toughness in a short-bar test can be derived from basic fracture mechanics using the assumptions of linear elastic fracture mechanics (LEFM). The equation for the material plane-strain critical stress intensity factor, K_{ICSR} is as follows (Ref 15):

$$K_{ICSB} = \frac{(F_{max} Y_m^*)}{B\sqrt{W}} \quad \text{(Eq 4)}$$

where F_{max} = Peak load

$Y_m^* = 16.5013$

$Y_m{}^*$ is the compliance calibration according to ASTM E-399-78 and

$$Y_m^* = \{-0.36 + 5.48\omega + 0.08\omega^2 + (30.65 - 27.49\omega + 7.46\omega)\alpha_0 + (65.90 + 18.44\omega - 9.76\omega)\alpha_0^2\}\left\{\frac{\alpha_1 - \alpha_0}{1 - \alpha_0}\right\}^{\frac{1}{2}} = 16.5013$$

$$\text{and } \omega = \frac{W}{H} = \frac{73.7}{44.2} = 1.667$$

$$\alpha_0 = \frac{a_0}{W} = \frac{24.4}{73.7} = 0.331$$

$$\alpha_1 = \frac{a_1}{W} = \frac{63.8}{73.7} = 0.866$$

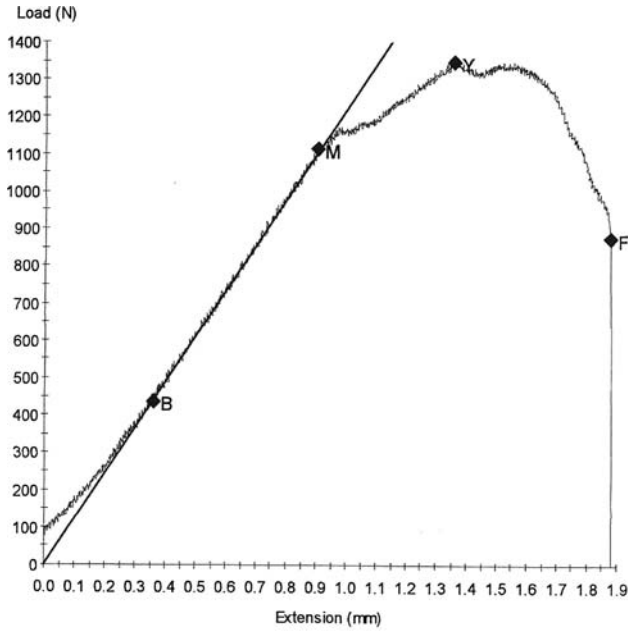


Fig. 4 The change of load versus crack length of a sample cured under ambient condition

An example of how K_{ICSB} is determined is demonstrated here using the data collected from ambient cured samples.

Using Eqn. (4) $K_{ICSB} = \frac{(F_{max} Y_m^*)}{B\sqrt{W}}$;

B = 50.8 (mm), by design and W = 73.7 (mm) (not 1.5B as in Fig. 2).

The mean of peak load = F_{max} = 1347 N and this is obtained from Fig. 4 which illustrates the change of load versus crack length of a sample cured under ambient conditions from previous study and Y_m = 16.5013.

$$\text{Fracture toughness, } K_{ICSB} = \frac{(1347 \times 16.5013)}{50.8\sqrt{73.7}} = 50.97\,\text{MPa}\sqrt{m}$$

5. Results and Discussion

Table 2 depicts the fracture toughness of VE/FLYASH (33%) cured under different microwave conditions in previous study (Ref 7). Each fracture toughness value is the average value of six samples. The values of fracture toughness of samples cured under ambient conditions, 50.97 MPa $\sqrt{m}$ were converted to 100% for ease of comparison; other values were also similarly converted to percentage using 50.97 as base.

From Table 3 (current study), it can be found that the fracture toughness of the sample treated with 180 W and exposures time of 60, 70, and 80 s is higher than that of the ambient cured samples from 1% to 8%; while that of 360 W and 60-80s microwaved cured ones are higher than the ambient cured one from 1% to 11%. Each fracture toughness value is the average value of six samples. The standard deviation has been calculated from the values of the six samples. With microwave parameters of 540 W and shorter duration of exposures of 15, 20, and 25 s, the fracture toughness is higher than those cured under ambient conditions from 2% to 8%. With microwave parameters of 720 W and shorter duration of exposures of 15, 20, and 25 s, the fracture toughness is higher than those cured under ambient conditions from 5% to 7%.

Referring to Table 2, it can be found that nearly all the values of fracture toughness of VE/FLYASH (33%) cured under microwave conditions are within 5% of those cured under ambient conditions; only those cured by 540 W for 25 s and 720 W for 15 and 25 s are not within 5% of the values of those cured under ambient conditions.

Figures 5 and 6 show that all values of fracture toughness of VE/FLYASH (33%) cured under microwave conditions are within or above 5% upper marker of those cured under ambient

Table 2 Results of the fracture toughness and other parameters for VE/FLYASH (33%) cured under different conditions

Conditions	Ambient	180 W		360 W		540 W		720 W	
Time (s)	Nil	60	80	60	80	15	25	15	25
Relative Fracture Toughness (%)	100 (50.97 MPa $\sqrt{m}$)	103	101	97	95	95	92	85	90

Table 3 Fracture toughness of VE/FLYASH (33%) cured under different conditions

Conditions	Ambient	180 W			360 W			540 W			720 W		
Time (s)	Nil	60	70	80	60	70	80	15	20	25	15	20	25
Relative fracture toughness (%)	100	101	108	105	111	103	101	104	108	102	105	107	106
	1.17[a]	2.32	0.68	2.82	3.25	1.65	2.17	3.84	2.98	2.06	3.02	1.23	1.93

[a]standard deviation

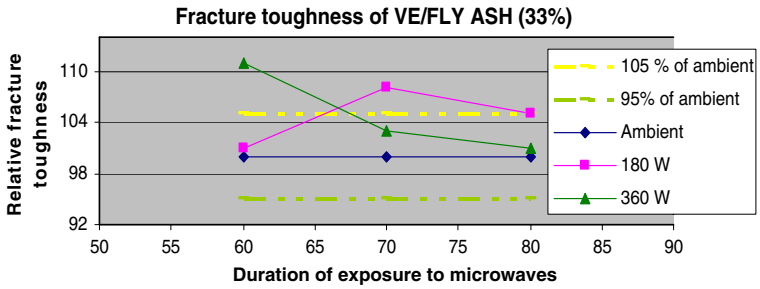


Fig. 5 Fracture toughness of VE/FLYASH (33%) cured under 180 W and 360 W of microwave power

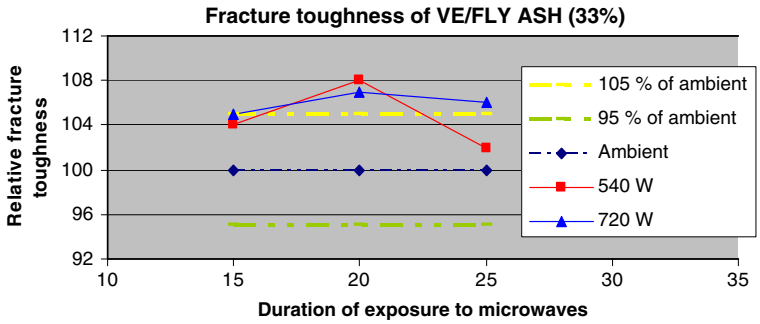


Fig. 6 Fracture toughness of VE/FLYASH (33%) cured under 540 and 720 W of microwave power

conditions. This means microwave irradiation reduces the shrinkage of the composite, but at the same time improves its fracture toughness.

By studying Tables 2 and 3, it can be argued that some discrepancies occur between previous and current study; for power levels of 360 W and higher, the fracture toughness values obtained in current study are higher than those obtained in previous study. In general, the higher fracture toughness values obtained in current study is because of the better material used to make the mold and improvement in design. In previous study, cardboard was used to make the molds and this allows the resin to penetrate into the cardboard and seep through the gaps between the adjoining areas of the cardboard; the resulting composite would then have a higher percentage by weight of fly ash and hence they are less tough. When the samples were cured under microwave conditions, the situation became worse as the initial expansion of the composite due to microwave irradiation forced more resin to penetrate into the cardboard and seep through the adjoining gaps. In current study, this did not happen as the molds were made of plastic, which may deform after several microwave processing and a new mold has to be machined.

6. Conclusion

These studies illustrate that the exposure of the samples by microwave irradiation did reduce the shrinkage of the vinyl ester composite but at the same time the toughness of the material was retained, provided a suitable combination of power level and duration of exposure were selected in the treatment. For lower power levels, e.g., 180 W, a longer exposure time of 30-35 s will do this but for higher power levels, e.g., 540 W, much shorter duration (15-20 s) of exposure is required.

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