

Fracture Toughness of Phenol Formaldehyde Composites Reinforced with E-spheres

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Abstract: A commercial phenol formaldehyde based resole thermosetting resin supplied by Borden Chemical Australia Pty. was reinforced with ceramic-based fillers (SLG) to increase its fracture toughness. This is the second study of the same series. By testing fracture toughness and viscosity at a range of filler addition levels, the optimal addition of SLG was determined in terms of workability, cost and performance. The composites obtained were post-cured in conventional oven as in the previous study. The original contributions of this paper include lowering the cost of the composite (35% w/t of SLG) by 50 % but at the same time its the fracture toughness was reduced only by 20 % (compared to the neat resin), and increasing the fire resistance of the resins tremendously. It was also found that the values of fracture toughness of the samples in this study were higher than those obtained in the previous study when the percentage by weight of SLG varies from 0 to 35%. The shapes of the plots of fracture toughness against percentage by weight of SLG were also different. The possible reasons for the differences were explained.

Keywords: Phenol formaldehyde, phenolic resin, microwaves, envirospheres, SLG, short bar test and viscosity.

1. Introduction

Phenolic thermosetting materials were amongst the first major polymeric material used by industry. They are still among the most widely used thermosetting resins due to their excellent high temperature and fire performance. Phenolics are formed from the condensation of polymerization reaction between phenol and formaldehyde. The condensation reaction for phenolics can be carried out under two different conditions, resulting in two different intermediate materials. One of the intermediates is called resoles

and the other novolacs [1, 2]. The single-stage resole resins do not liberate ammonia during or after moulding, and are preferred for applications in which metal corrosion or odour may be a concern. In addition, they show good resistance to stress cracking in parts that are wet on one side and dry on the other. Two-stage novolac resins are the most widely used and offer wider moulding latitude, better dimensional stability, and longer shelf life than resole materials. In this study, resole resin was used.

The various fillers used can vary from 50 to 80 % by weight. The fillers reduce shrinkage during molding, lower cost and improve strength. They are also used to improve electrical and thermal insulating properties and chemical resistance [1-4]. The high cross-linking of the aromatic structure (Figure 1) produced high hardness, rigidity and strength combined with good heat and electrical insulating properties. Because of high impact strength required in the applications of this composite, it was decided to use SLG to fill the phenolic resin. Some of the various types of phenolic moulding compounds are [3]:

- ❖ General purpose compounds. These materials are usually wood flour-filled to increase impact strength.
- ❖ High-impact strength compounds. They are usually filled with cellulose (cotton, flock and chopped fabric), mineral and glass fibres to provide impact strength of up to 961 J/m.
- ❖ High electrical insulating compounds. These materials are mineral- (e.g., mica) filled to increase electrical resistance.
- ❖ Heat-resistant compounds. They are mineral- (e.g., asbestos) filled and are able to withstand long-term exposure to temperatures of 150 to 180^oC.

This research project is aimed at investigating the fracture toughness of a commercial resole phenol formaldehyde resin reinforced with ceramic microsphere (SLG) filler. The filler

percentage by weight is varied from 0 to 35%. Short bar testing has been used to determine the fracture toughness of the specimens in this work [5-7]. The advantages and methods of using short bar tests were provided by the literature. On account of its simplicity and advantages, they were used in this project.

2. Materials

The commercial resole resin used in this study was J2027 and manufactured by Borden Chemical Pty. Its official name is now Hexion Cellobond J2027L because the company had been taken by Hexion [8]. The acid catalyst used to crosslink the resin was Hexion Phencat 15 [9]. The molecular weight of the commercial resin used is approximately 600 and its functionality 2, one on each end of the molecule. The ratio by weight of the resin to hardener for all samples in this work was chosen to be 50: 1. In the previous study the ratio was 20:1 as the resin used in the previous study was much more viscous.

The polymer based on phenolic resin is Phenol-formaldehyde (PF). The PF resins are formed by the reaction of phenol with formaldehyde. By varying the reaction time, reaction temperature, catalyst type, and the ratio of formaldehyde to phenol, a number of adhesive systems with different characteristics can be produced.

A disadvantage of phenolic resins is that they are characterized by a complex process of polymerization (cure) with generation of water and formaldehyde, with consequent formation of voids. Therefore, the processing of phenolic materials requires careful temperature control and gradual heating to allow continuous elimination of volatiles and to reduce the number of

defects in final components. Normally the time required for these operations is incompatible with common industrial process schedules.

Initially formaldehyde reacts with phenol to form hydroxymethyl derivatives preferentially at the aromatic ring carbon para to the phenolic hydroxyl as depicted in Figure 1. As the reaction proceeds, substitutions also take place between the hydroxymethyl groups and the aromatic ring carbons of phenol or another hydroxymethyl group to form methylene linkages. In this manner, the polymeric structure of the resin shown in Figure 2 is produced.

With reference to phenolic molecule of Figure 3, there are five 5 hydrogen atoms in the benzene ring but because of limited space, there are only three possible sites for reaction and the phenolic molecule is said to have a functionality of three and this is shown in Figure 4 [3, 10]. As the functionality of the phenolic molecules is greater than two, the molecules can react with formaldehyde molecules to form 3-D network polymer [1].

The Enviroshperes (E-spheres) SLG is a mineral additive that can improve product by reducing product's weight, improving its performance and lowering its cost. E-spheres are white microscopic hollow ceramic spheres that are ideal for a wide range of uses. The particle size of this general purpose E-spheres ranges from 20 – 300 μm with approximate mean of 130 μm . The relative density of E-spheres is 0.7. E-spheres are a combination of Silica, SiO_2 (55-60%), Alumina, Al_2O_3 (36-44%), Iron Oxide, Fe_2O_3 (0.4-0.5%) and Titanium Dioxide, TiO_2 (1.4-1.6%). E-sphere is an inert material similar to talc, etc (E-spheres, undated). The material may be prone to dusting in use. Grinding, milling or otherwise generating dust may create a respiratory hazard. In high dust areas the use of

goggles and a National Institute of Occupational Health and Safety (NIOSH) approved dust respirator is recommended.

They are used in a variety of manufacturing applications because of their unique properties and they are (E-spheres, undated):

- extreme heat resistance;
- high compressive strength;
- pure, clean and white.

In addition to these unique features, E-spheres provide all the benefits you would expect from a microsphere. The typical applications in composites include casting, spray-up, hand lay-up, cold/hot press molding, resin transfer molding and syntactic foam.

3. Fracture toughness

Unlike the result of an impact test, it is a property that can be quantitatively measured. A typical fracture toughness test may be performed by applying a tensile stress to a specimen prepared with a flaw of known geometry and size and is shown in Figure 5. The stress applied to the material is intensified at the flaw [10]. For a simple test the stress intensity factor,

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

where f is a geometry factor for the specimen and flaw.

σ is the applied stress; a is the flaw size. If the specimen is assumed to have 'infinite' width then $f \cong 1.0$; for 'semi-infinite' width, $f \cong 1.1$ [11, 12].

The critical stress intensity factor is defined as fracture toughness, K_c is the K required for a crack to propagate and

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

K_c is a property that measures a material's resistance to brittle fracture when a crack is present and its unit is $\text{MPa}\sqrt{m}$. The value K_c for this thick-specimen situation is known as the plane strain fracture toughness K_{Ic} ; furthermore, it is also defines by [13]:

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

4. Short Bar Test and the Composite Samples

Baker described the background, selection criteria and specimen geometry options for short rod and short bar methods [5]. The background, selection criteria and specimen geometry options for the samples were clearly explained, which made the manufacture of the samples easier. Figure 6 shows the short rod and short bar specimens with straight chevron slots. 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 diameter (for short rod) or breath (for short bar). The other parameter, W, is the length of the specimen. The relationship between the peak load (to fracture the sample), the breath and the length of the specimen was given in equation (4). 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 requirements for LEFM were explained clearly, which were used in this study. The equation for the material plane strain critical stress intensity factor, K_{ICSB} [13]:

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

where F_{\max} = Peak load;

B is the breath of the sample;

W is the length of the sample;

Y_m^* is the compliance calibration according to ASMT E-399-78 and

$$Y_m = 17.1645$$

$$\omega = \frac{W}{H} = 1.96$$

$$\alpha_0 = \frac{a_0}{W} = 0.342$$

$$\alpha_1 = \frac{a_1}{W} = 0.969$$

All parameters like a_0 , a_1 , W and H are shown in Figures 6 and 7. Also, $B = 50$ (by design), and $F_{\max} = 222$ N (average peak load of six samples, 222 N was used in the calculation of K_{ICSB}).

Fracture toughness for 20% by weight of SLG is calculated as:

$$K_{\text{ICSB}} = \frac{(F_{\max} Y_m^*)}{B\sqrt{W}} = 8.800 \text{ MPa}\sqrt{m}$$

They also show two slot bottom geometries which result from two useful methods of machining the chevron slots.

The reinforcer was SLG (ceramic hollow sphere) particulates and they were made 0 % to 35 % by weight in step of 5 % in the cured phenol formaldehyde composite PF/E-SPHERES (X %), where X is the percentage by weight of the filler; the 40% by weight was tried but it was found to be too viscous for mixing. As the raw materials of the composites are liquid and ceramic hollow spheres, the short bar specimens were cast to shape. The resin is mixed with the catalyst, after which the SLG is added to the mixture and they are then mixed to give the uncured composite. Table 1 shows the mass in grams of resin, catalyst and slg required respectively to make 1000 grams of uncured composite of 25 % by weight of SLG. The mould was made from PVC (poly vinyl chloride) sheets with six pieces of short bar specimen each. This is depicted in Figure 8. The slots were made by inserting plastic sheets of suitable

thickness. Figure 9 shows some of the PF/E-SPHERES (X %) short bar specimens ready for the tests. After preliminary curing, the samples were taken out of the mould and post-cured in an oven at 50 °C for 4 hours followed by 80 °C for 4 hours and finally by 100 °C for 2 hours. The degree of curing of the samples was 85% to 90 % as measured by differential scanning calorimeter (DSC). These specimens were then subjected to short bar test.

5. Sample Size

The number of samples for each percentage by weight of E-spheres is six. An MTS 810 Material Testing Systems was used for the test. The rate of extension was 1 mm per minute. The short bar tests involve an opening load being applied near the mouth of the specimen, causing a crack to initiate at the point of the chevron slot. Ideally, the opening load should be less than the load that will be required to further advance the crack. A continually increasing load must be supplied until the crack length reaches the critical crack length, a_c . Beyond a_c , the load should decrease, as shown in Figure 10.

6. Results and Discussion

Figure 11 shows the of fracture toughness J2027 (Brendon Chemical) specimens filled with varying weight percentages of E-spheres SLG. Table 2 depicts the fracture toughness of PF/E-SPHERES with varying percentage by weight of SLG with the standard deviation given in bracket. It was found that the fracture toughness is highest with the neat resin (0 % by weight of SLG); its value was $14.74 \text{ MPa}\sqrt{m}$. The value dropped to a low of $7.37 \text{ MPa}\sqrt{m}$ when the SLG by weight is 10%; after this the values varied from 8.08 to $8.81 \text{ MPa}\sqrt{m}$ as the percentage by weight of SLG increases from 15 to 25%. All the values were within the

two percent markers of $7.37 \text{ MPa}\sqrt{m}$ (10% SLG). The fracture toughness increases back to $11.88 \text{ MPa}\sqrt{m}$ when the percentage by weight of SLG is 35%. It appears that when the percentage by weight of SLG was be further increased, the values of the fracture toughness would also increase but the fact was that composites with SLG higher than 35 % by weight would be too viscous; they cannot be mixed properly and be poured into the moulds. As the standard deviation is small (Table 2), it can be argued that the values of fracture toughness obtained are reliable.

Figure 12 shows the of fracture toughness of Borden J2027 specimens filled with varying weight percentages of E-spheres SLG in the previous study. It was found that the values of fracture toughness in this study were generally higher than those of previous study. The shape of the curves is also different. These are due to the fact that the two batches of phenolic resins were different [14]. The ratio of resin to catalyst in the previous study was 20 :1 while that of this study was 50:1 which was a 'must' in this study because any ratio of less than 50 would result in very vigorous reaction and the specimens cast would have a lot of blow holes. After casting, the samples were allowed to harden in room temperature for 72 hours not the 24 hours in the previous study before they were taken out for post-curing in an oven [14]. This is due to the fact that the ratio of resin to catalyst used in this study was 50:1 and the hardening of the samples became much slower. The relative density of resin used in this study is 1.23 while that in the previous study was 1.225. The relative density of the post-cured composites manufactured for this study ranges from 1.185 (5% of SLG) to 0.972 (35% of SLG); the density decreases with increasing percentage by weight of SLG because the relative density of SLG is only 0.7. At the same time, their corresponding tensile strengths range from 16.1 MPa (5% of SLG) to 7.9 MPa (35% of SLG); the light SLG reduces the tensile strength of the composites [15]. By comparing these data with those of

materials in other study, it can be found that the composites made in this study have lower densities and therefore lower tensile strengths [2]. It can be argued that other properties of composites made in this study will be inferior to those of materials listed in Table 3 [15]. However, the cost of materials in this study will be cheaper because SLG is the unwanted by product of fly ash. Provided, the application requirements of the materials are not too stringent, these composites can be cheaper alternatives. The viscosity of the neat resin used in this study was 700 cP while that of the previous study was 3240 cP. These differences lead to the different in values of fracture toughness of the composites manufactured. Aierbe et al. also found that phenolic resins supplied by different manufacturers were different [16]. They would have different viscosity and density; this indicates that the degree of water content is different; one company can produce phenolic resins with 8 % water content and the other will sale one with 12~15 % water content. Also the composition of the 'phenolic prepolymers' is different when the resin have been prepared with different experimental conditions like synthesis temperature, time, and different C:P and F:P ratios; all these differences give rise to different mechanical and thermal properties [17]. The values of fracture toughness of the composites done in the other study were mentioned, which were used for comparison [14]. A concurrent study about post-curing the samples in microwaves shows that the shape of the curve in this study is the same as that in microwave study and has the same trend. It can be argued that the shape of this study is more reliable than that in the previous study [18].

7. Conclusion

This study confirms that by adding SLG to phenolic resin by up to 35% by weight, the fracture toughness of composites obtained would be 20% weaker than that of the neat resin

but the cost reduced could be more than 50%. Redjel found that the fracture toughness of pure phenolic resin was $1.51 \text{ MPa}\sqrt{m}$ [19]; the fracture toughness of neat resin used in this study was $14.75 \text{ MPa}\sqrt{m}$, which is 8.77 times the fracture toughness of pure phenolic resin, an increase of 877%. Hence, the fracture toughness of resulting composites obtained from current resin could be used in many applications. The trend of the fracture toughness of phenolic resin reinforced with varying SLG by weight was also conformed by this study.

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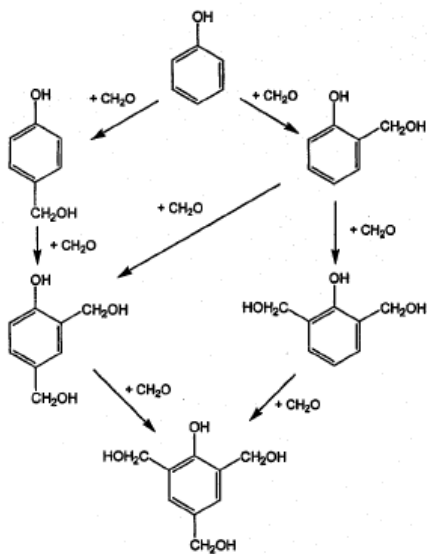


Figure 1: Formation of the hydroxymethyl derivatives phenol

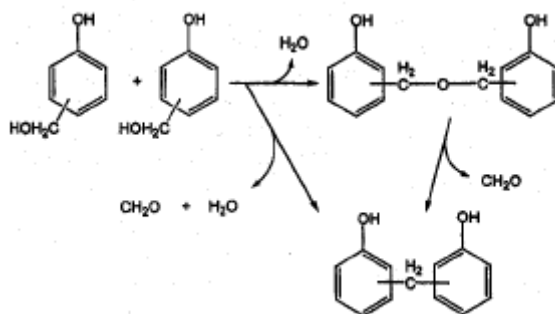


Figure 2: Condensation of the hydroxymethyl derivatives of phenol

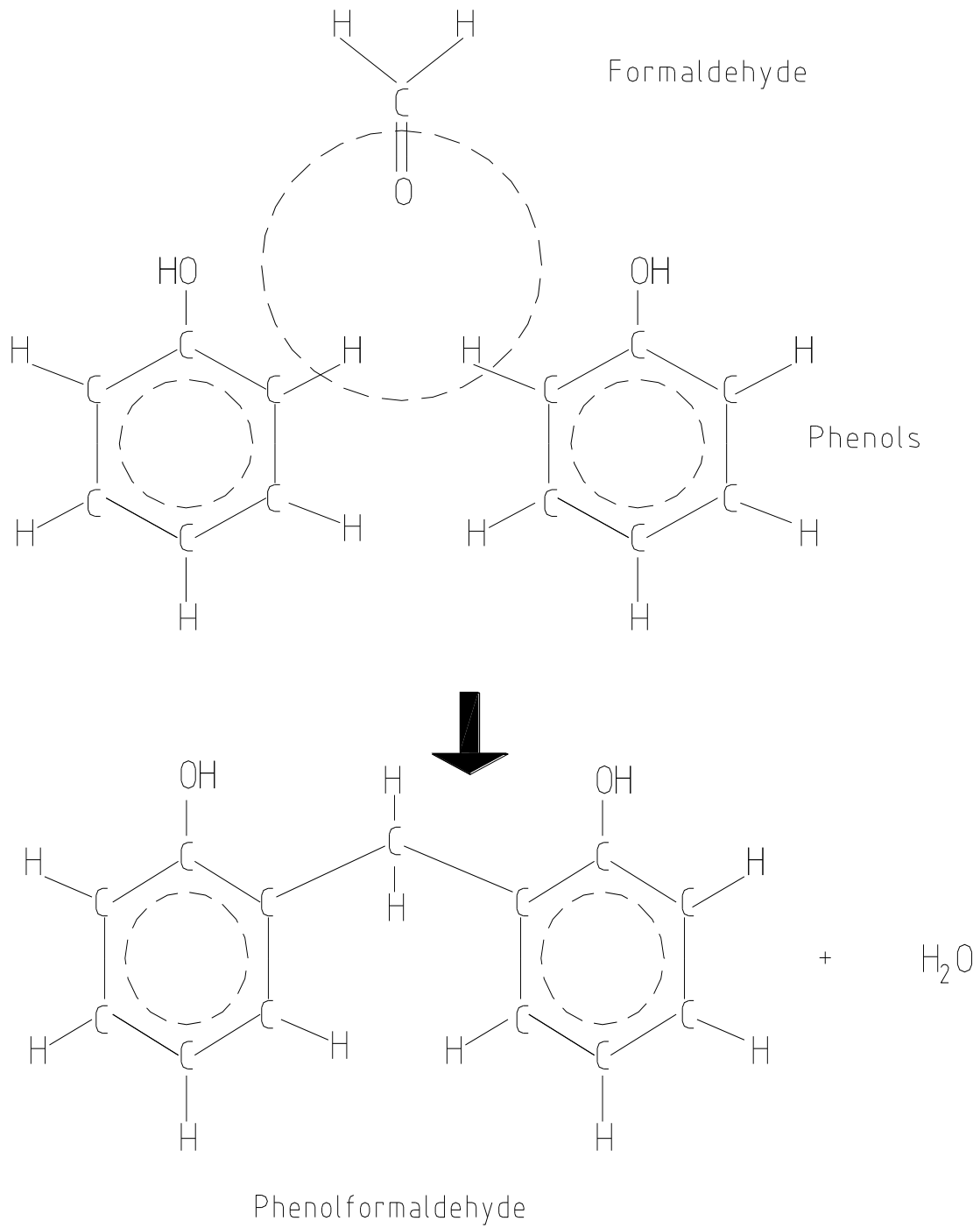


Figure 3: Formation of Phenol formaldehyde

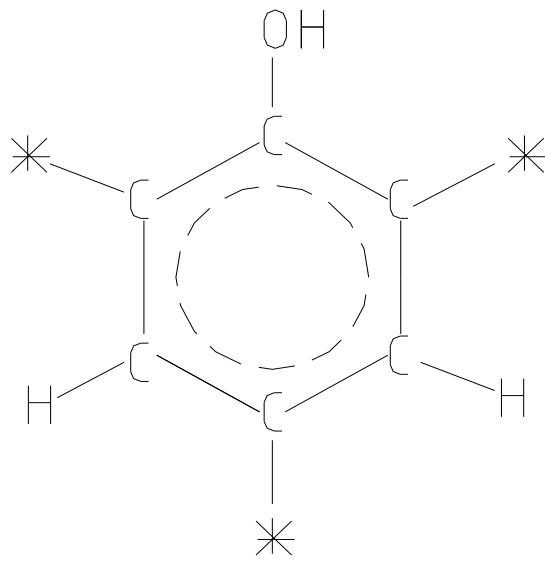


Figure 4: Phenol with active sites marked *

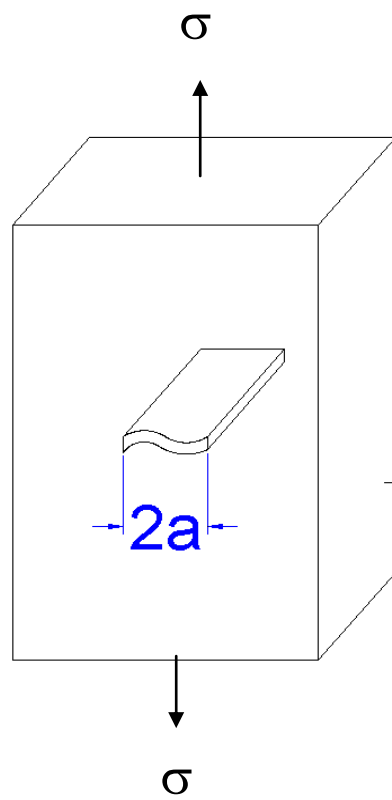
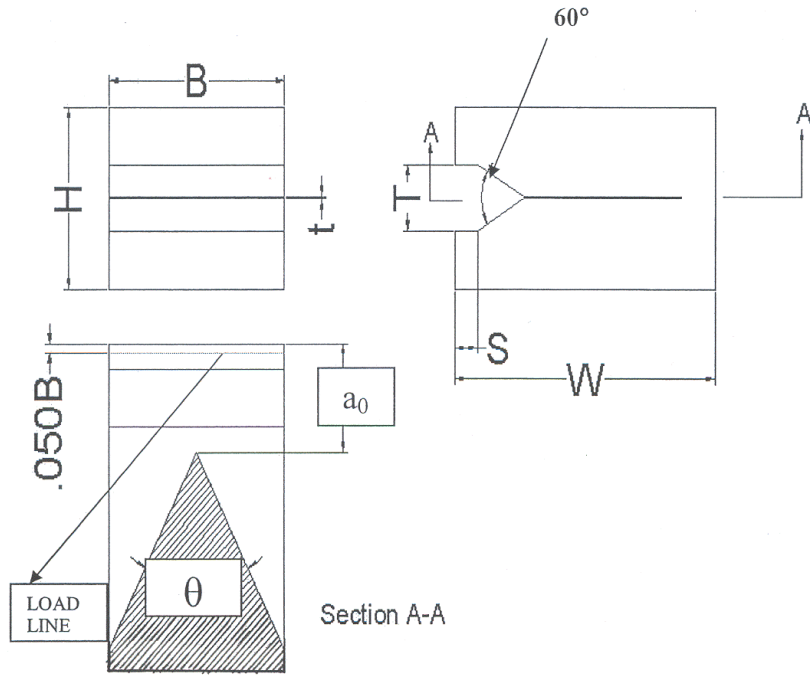


Figure 5: Schematic Drawing of Fracture Toughness Specimens with Edge and Internal Flaws



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

Figure 6: Short Bar Specimen with Straight Chevron Slots. The LOAD LINE is the line along which the opening load is applied in the mouth of the specimen.

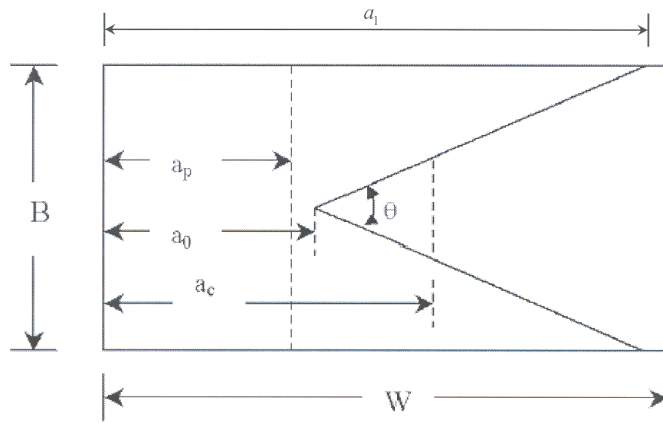


Figure 7: Cross-section dimensions of short bar specimen showing a_1

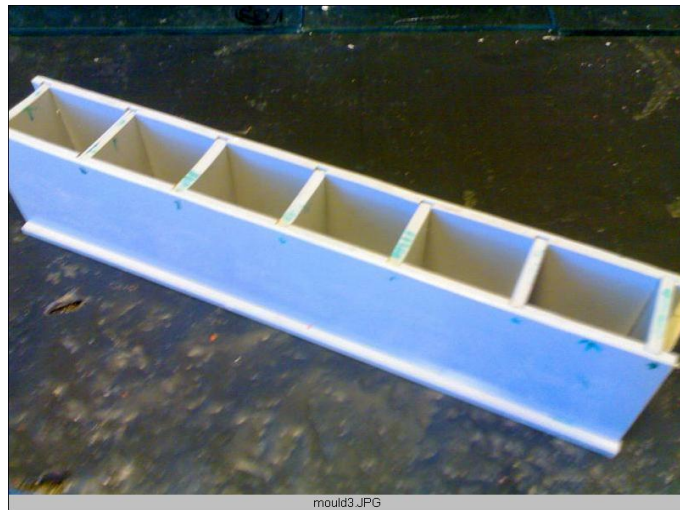


Figure 8: The mould for short bar specimens



Figure 9: The short bar specimens

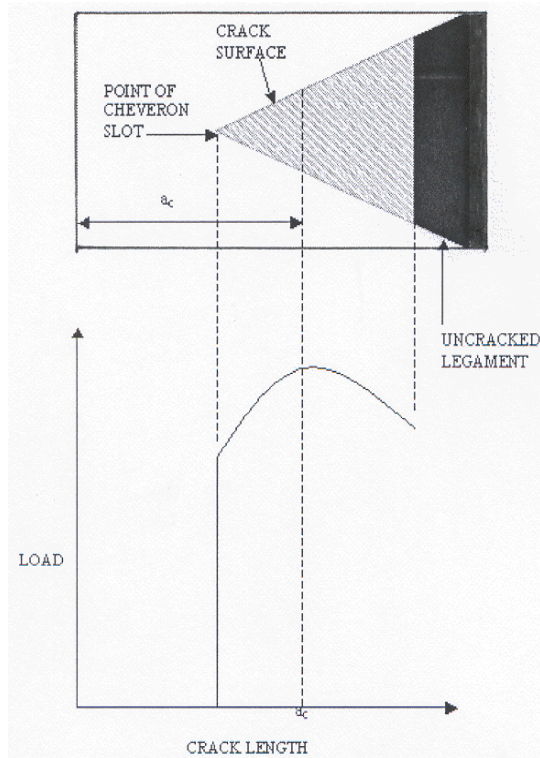


Figure 10: Variation of load versus crack length

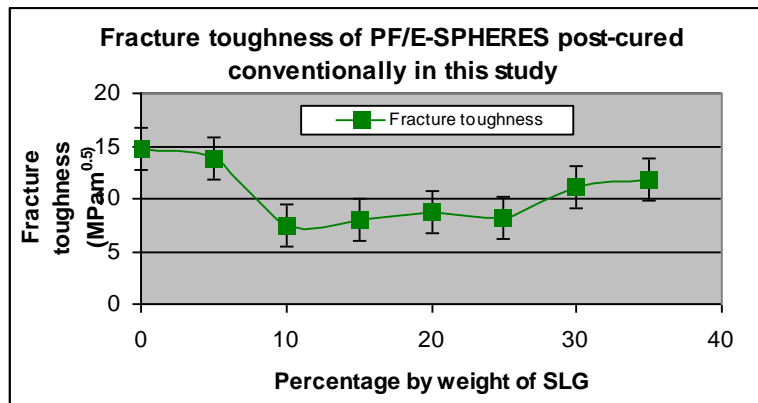


Figure 11: Fracture toughness of PF/E-SPHERES with varying percentage by weight of SLG in this study

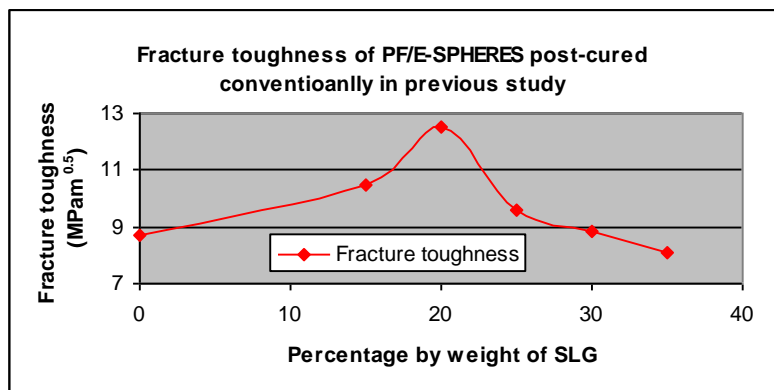


Figure 12: Fracture toughness of PF-E-SPHERES with varying percentage by weight of SLG previous study

Table 1: Weight of materials required to make 1000 g of PF/SLG (25%)

| Parameters | Materials | Resin (R) | Catalyst (C) | R + C | Slg | Composite |
|--|-----------|-----------|--------------|---------|---------|-----------|
| Percentage by weight | | 50 | 1 | --- | --- | --- |
| Percentage by weight | | --- | --- | 3 | 1 | --- |
| Weight of materials in 300 g of PF/SLG (10%) | | 735.3 (g) | 14.7 (g) | 750 (g) | 250 (g) | 1000 (g) |

Table 2: Fracture toughness of different percentage by weight of SLG reinforced phenolic resin

| Percentage by weight of SLG | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 35 |
|---|------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|------------------|------------------|
| Fracture toughness $\text{MPa}\sqrt{m}$ | 14.75 (0.0603) # | 13.8 (1.007) | 7.37 (0.424) | 8.07 (0.516) | 8.81 (0.333) | 8.21 (0.277) | 11.06 (0.708) | 11.88 (0.524) |

standard deviation

Table 3: Mechanical properties data for some common composites

| Composites | E (MPa) | T.S. (MPa) | K_{IC} ($\text{MPa}\sqrt{m}$) |
|---|-----------------------|---------------|--------------------------------------|
| E-glass (73.3 vol. %) in epoxy (parallel loading of continuous fibres) | 56×10^3 | 1,640 | 42-60 |
| B (70 vol. %) in epoxy (parallel loading of continuous fibres) | $210-280 \times 10^3$ | 1,400 - 2,100 | 46 |
| SiC whiskers in Al_2O_3 | - | - | 8.7 |
| SiC fibres in SiC | - | - | 25 |
| SiC whiskers in reaction-bonded Si_3N_4 | - | - | 20 |
| Douglas fir, kiln-dried at 12% moisture (loaded parallel to grain) | 13.4×10^3 | - | 11 - 13 |
| Douglas fir, kiln-dried at 12% moisture (loaded perpendicular to grain) | - | - | 0.5 - 1 |