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Fracture Toughness of Phenol Formaldehyde Composites: Pilot Study

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A commercial phenol formaldehyde based resole thermosetting resin (Hexion "J2027L") was filled with ceramic-based fillers (Envirospheres "slg") to increase its strength and fracture toughness. By testing viscosity, strength, and fracture toughness at a range of filler addition levels, the optimal addition level of SLG was able to be determined in terms of workability, cost, and performance. It was found that the fracture toughness of this resin could be significantly increased through the addition of the slg filler. The results show that composite with 20% by weight of the slg produces the best balance between ease of casting and impact performance.

Keywords Envirospheres, phenol formaldehyde, phenolic resin, SLG, short bar test, viscosity

1. Introduction

Phenolic thermosetting materials were amongst the first major plastic 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 is novolacs (Ref 1, 2).

In the resole process, the condensation polymerization is performed in an alkali solution with excess formaldehyde and is carefully controlled so that a linear, noncross-linked polymer liquid, resole, is produced. The resole can then be molded. When molding, the cross-linking is achieved by heating the viscous liquid. Since a cross-linked part can be obtained by simply heating the resoles, which are called one-stage resins. Alternatively, resole phenolic resins are cured at room temperature via the addition of acid catalysts, typically sulphonic acids (Ref 2).

Novolac phenolic resins are formed by reacting phenol and formaldehyde in an acid solution, but with insufficient formaldehyde to complete the reaction at 100 °C (the opposite of forming resoles). About one mole of phenol is reacted with 0.70-0.85 mole of formaldehyde. This is the first stage of the reaction and a brittle thermoplastic resin is produced which can be melted but cannot cross-link to form a solid network.

The polymerization reaction is shown in Fig. 1. The addition of hexamethylenetetramine (hexa), a basic catalyst, to the first stage phenolic resin makes it possible to create methylene crosses linkages to form a thermosetting-material. When heat and pressure are applied to the hexa-containing novolac resin, the hexa decomposes, producing ammonia which provides methylene cross-linkages to form a network structure. On account that hexa, a second material, must be added to novolacs, they are called two-stage resins. The temperature required for the cross-linking of the novolac resin ranges from 120 to 177 °C.

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 (Ref 1-4). This research project is aimed at investigating the fracture toughness of a commercial resole phenol formaldehyde resin reinforced with ceramic microsphere ("Envirospheres slg") filler. Short bar testing has been used to determine the fracture toughness of the specimens in this work (Ref 5-7).

2. Materials

The commercial resole resin used in this study was J-2027L produced by Hexion Speciality Chemicals Pty Ltd. Its official name is Hexion Cellobond J2027L (Ref 8). The acid catalyst used to cross-link the resin was Hexion Phencat 15 (Ref 9). The ratio by weight of the resin to hardener for all samples in this work was chosen to be 20:1. With reference to phenolic molecule of Fig. 1, 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 Fig. 2 (Ref 3, 10). As the functionality of the phenolic molecules is greater than two, the molecules can react with formaldehyde molecules to form 3D network polymer (Ref 1).

Envirospheres slg (E-spheres) is a commercial ceramic microsphere product obtained as a fly ash by-product. The particle size of this general purpose E-spheres ranges from 20

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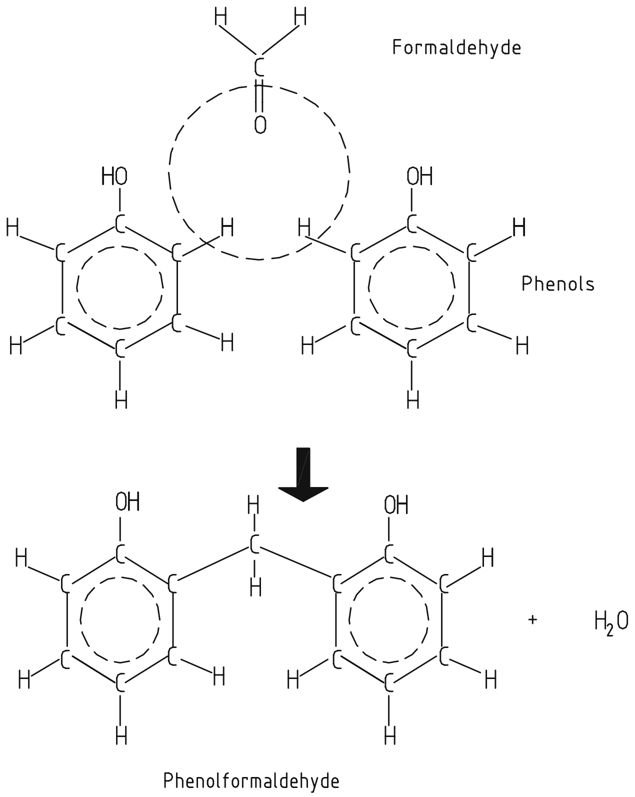


Fig. 1 Formation of phenol formaldehyde

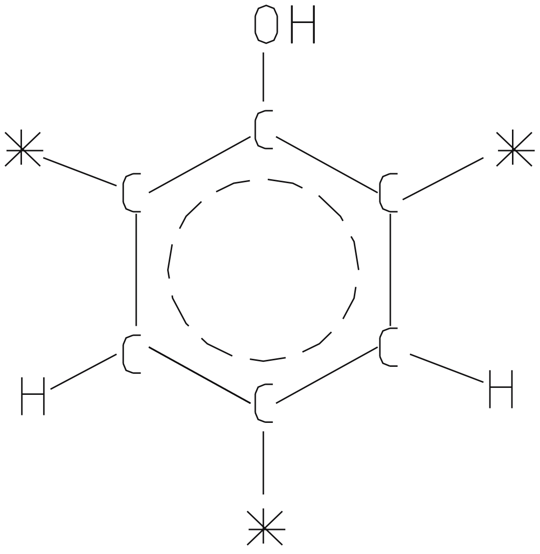


Fig. 2 Phenol with active sites marked *

to 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%).

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 Fig. 3. The stress applied to the material is intensified at the flaw (Ref 11). For a simple test, the stress intensity factor,

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

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 11, 12). σ is the applied stress and a is the flaw size.

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

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

where 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 defined by (Ref 12):

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

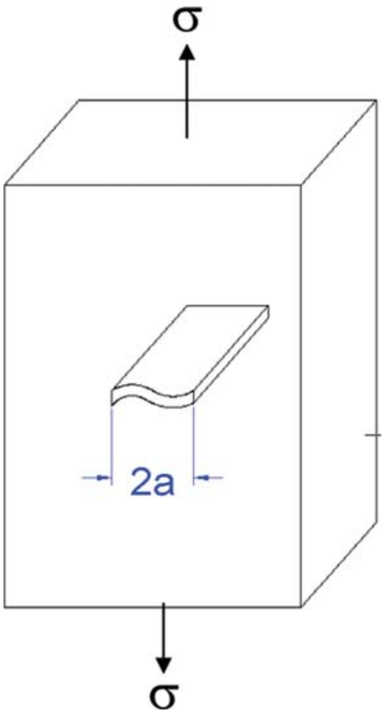
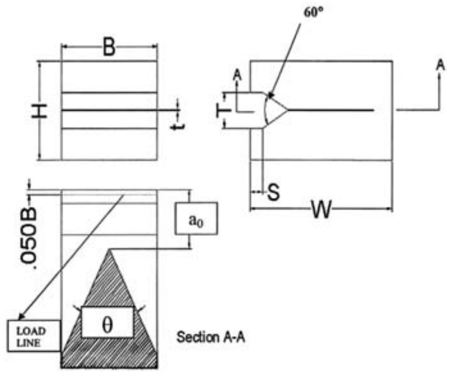


Fig. 3 Schematic drawing of fracture toughness specimens with edge and internal flaws

4. Short Bar Test and the Composite Samples

Baker (Ref 7) described the background, selection criteria, and specimen geometry options for short rod and short bar methods. Figures 4 and 5 show 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). They also show two slot



SYMBOL	DEFINITION	VALUE	TOLERANCE
B	BREADTH	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. 4 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

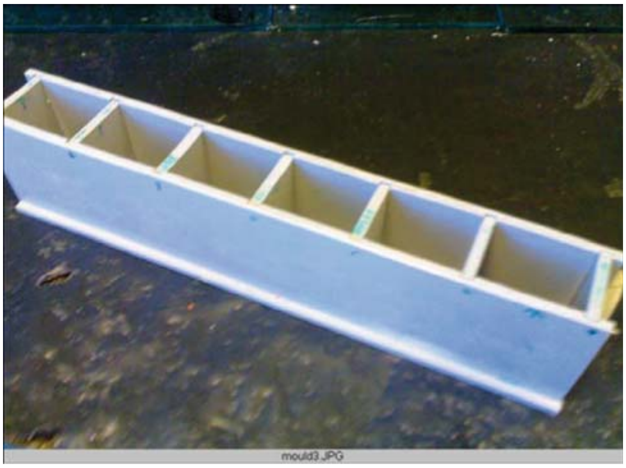


Fig. 5 The mold for short bar specimens

bottom geometries, which result from two useful methods of machining the chevron slots. Figure 4 shows the straight slot geometry, which results from feeding the saw or cutter through the specimen.

The reinforcer was E-sphere slg (ceramic hollow sphere) particulates and they were made 15-35% 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 E-sphere 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 300 g of uncured composite of 20% by weight of slg. The mold was made from PVC (poly vinyl chloride) sheets with six pieces of short bar specimen each. This is depicted in Fig. 5. The slots were made by inserting plastic sheets of suitable thickness. Figure 6 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 mold and post-cured in an oven at 50 °C for 2 h followed by 80 °C for 4 h and finally by 100 °C for 4 h. They 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 made 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 Fig. 7.

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} (Ref 13):

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

where F_{max} = Peak load, Y_m* is the complicance calibration according to ASMT E-399-78 and Y_m = 15.700

$$\omega = \frac{W}{H} = 1.671,$$

$$\alpha_0 = \frac{a_0}{W} = 0.310,$$

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

All parameters like a_0, a_1, W, and H are shown in Fig. 8. Also, B = 50 (by design), and F_{max} = 356N (average peak load of six samples, 356N was used in the calculation of K_{ICSB}).

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

$$K_{ICSB} = \frac{(F_{max} Y_m^*)}{B\sqrt{W}} = 13.070\ \text{MPa}\sqrt{m}.$$

6. Viscosity Measurements

Viscosity was measured using the Brookfield RDVD-II+ viscosity testing machine. Throughout the tests, the viscosity

Table 1 Weight of materials required to make 300 g of PF/SLG (20%)

Parameters	Materials	Resin (R)	Catalyst (C)	R + C	Slg	Composite
Percentage by weight		20	1	...	...	...
Percentage by weight		...	...	8	2	...
Weight of materials in 300 g of PF/SLG (10%)		229 (g)	11 (g)	240 (g)	60 (g)	300 (g)

Fig. 6 The short bar specimens

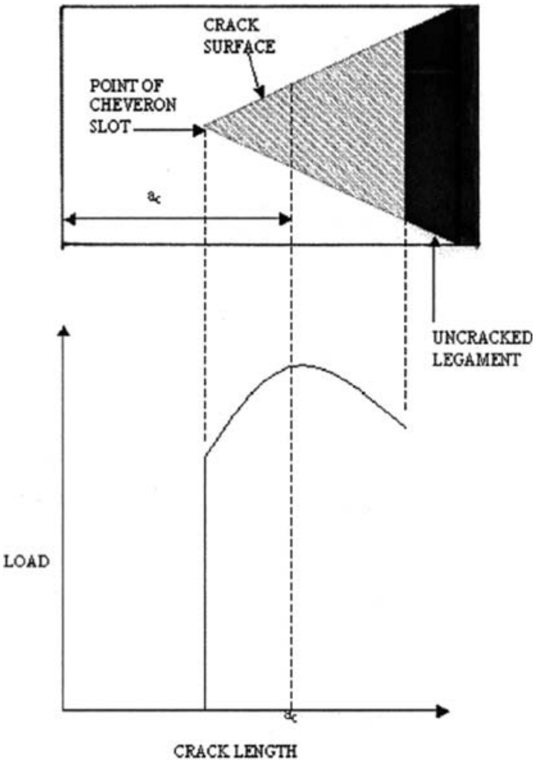


Fig. 7 Variation of load vs. crack length

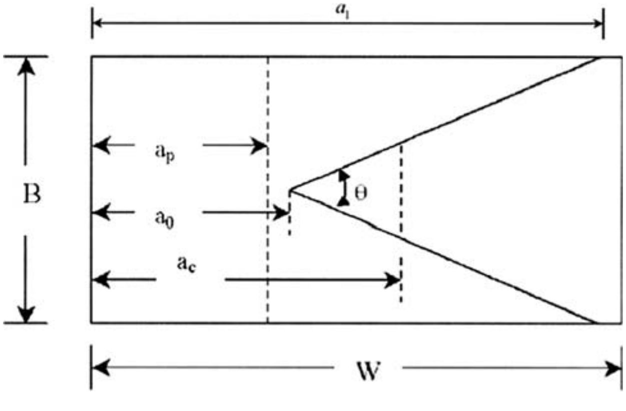


Fig. 8 Cross section dimensions of short bar specimen showing a_1

was recorded at a constant temperature of 26 °C. The temperature of the composite (in liquid form) would rise as time went on due to the curing. Theoretically, one should allow the temperature to rise and viscosity to reduce (Fig. 9) and then pour the liquid form composite into the molds but this may not be achievable because the composite would have cured before one can properly cast the composite into the molds. Viscosity has therefore to be measured as soon as the measuring probe was dipped into the composite.

7. Results and Discussion

Figure 10 shows the of fracture toughness J2027 specimens filled with varying weight percentages of E-spheres slg. Table 2 depicts the of fracture toughness 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 when the percentage by weight of the filler, slg is 20%; its value is 12.47 MPa$\sqrt{m}$. As the standard deviation is small, it can be argued that the values of fracture toughness obtained are reliable. Redjel (Ref 14) found that the fracture toughness of pure phenolic resin was 1.51 MPa$\sqrt{m}$; the fracture toughness of neat resin by weight of slg reinforced phenolic resin, PF/E-SPHERES (0%) in this study was 8.72 MPa$\sqrt{m}$, which is 5.78 times the fracture toughness of pure phenolic resin, an increase of 478%. This may be due to the improved resin used (the work was carried out 11 years later) and better post-curing method of the composite. Figure 11 shows the viscosity of 2027/E-sphere formulations as function of filler weight. This data show that the viscosity increases with increasing percentage by weight of SLG. It has been found by experiment, and been confirmed by other researchers (Ref 15), that there is a viscosity limit of resin/SLG mixtures above which casting is not possible. This is around 38-42% by weight and corresponds to viscosity in the range of 16,000-20,000 cps. This filler content is much higher than that previously determined to be best in terms of fracture toughness, 20% w/w. At 20% w/w, the viscosity of the resin/SLG mixture is around 3140 cps. At this viscosity, workability of the filled resin would be good.

Figure 12 illustrates the scanning electron microscopy image of phenolic resin post-cured for 4 h at 80 °C at a magnification of 3500×. There is evidence of the presence of voids of around 10 μm diameter that have been attributed to the water domains formed during the condensation cure of the

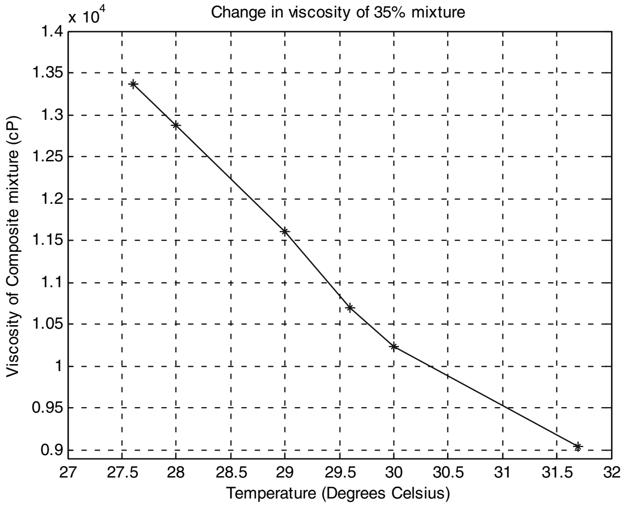


Fig. 9 Viscosity change with temperature of 35% by weight of slg composite

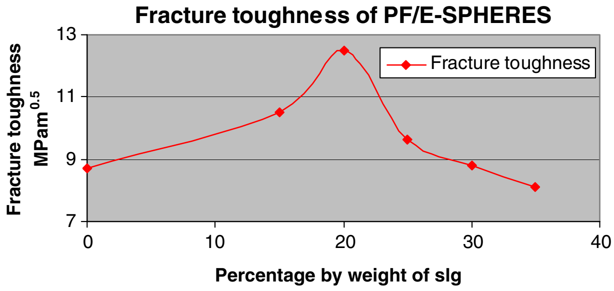


Fig. 10 Fracture toughness of PF-E-SPHERES with varying percentage by weight of slg

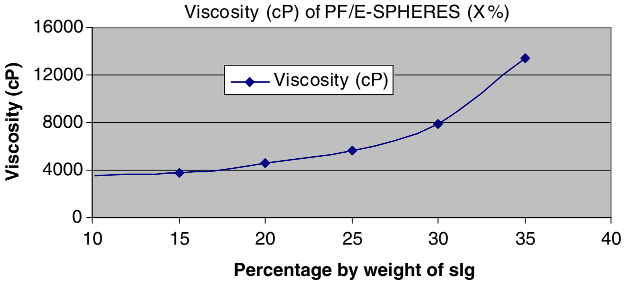


Fig. 11 Viscosity of various composite mixtures at approximately 26 °C

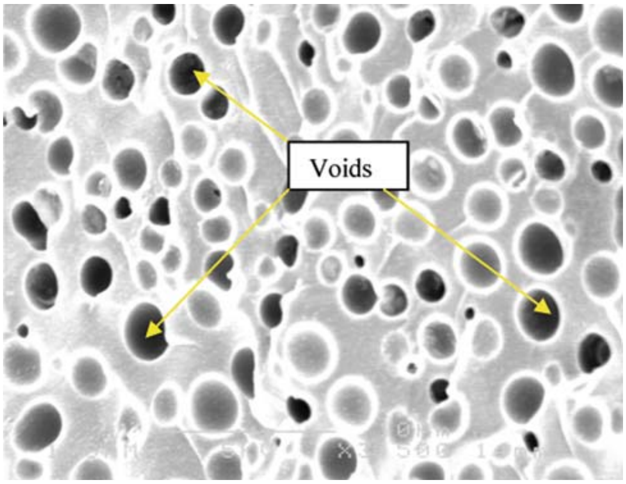


Fig. 12 Phenolic resin post-cured for 4 h at 80 °C at a magnification of 3500 times

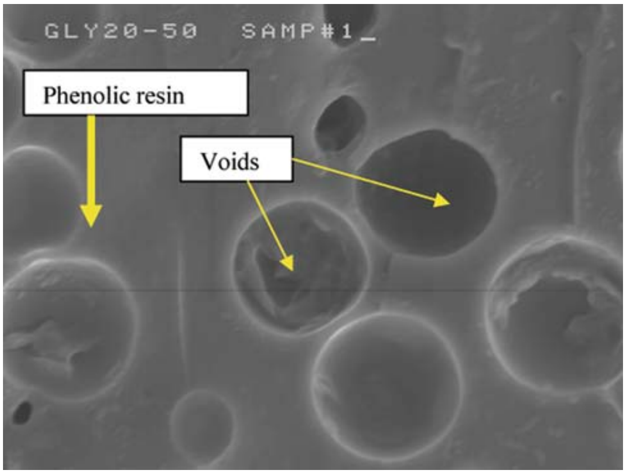


Fig. 13 Phenolic resin post-cured for 4 h at 80 °C at a magnification of 10,000 times

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

Percentage by weight of slg	0	15	20	25	30	35
Fracture toughness MPa$\sqrt{m}$	8.72 (1.94)[a]	10.5 (0.80)	12.5 (0.16)	9.62 (0.24)	8.82 (0.36)	8.12 (0.67)

[a] Standard deviation

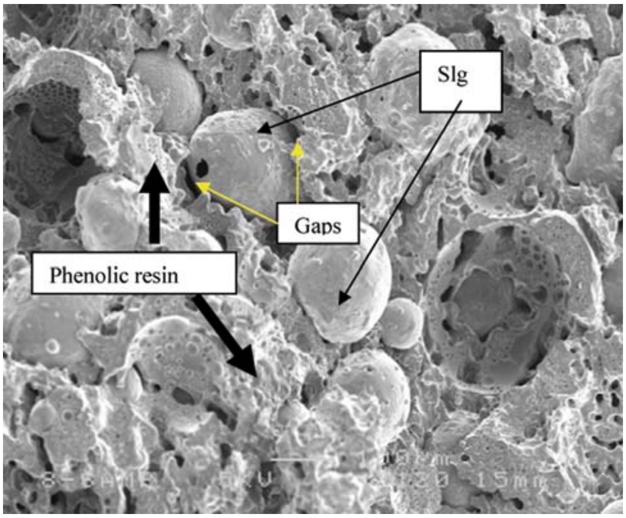


Fig. 14 PF/E-SPHERE (20%) post-cured for 4 h at 80 °C at a magnification of 10,000 times

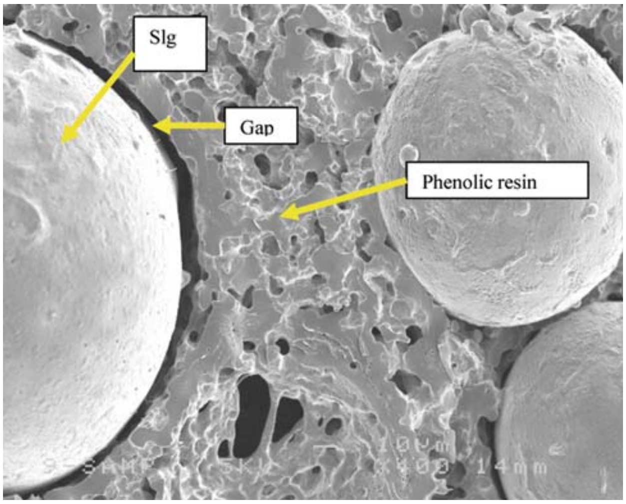


Fig. 15 PF/E-SPHERE (20%) post-cured for 4 h at 80 °C at a magnification of 25,000 times

resole resin. Its fracture toughness is less than those of phenolic resin reinforced with slg of 15-25% by weight. Figure 13 enables one to view the voids of the above composite clearer as the magnification of the image was increased to 10,000×.

Figure 14 illustrates the scanning electron microscopy image of phenolic resin reinforced by 20% by weight of slg and post-cured for 4 h at 80 °C at a magnification of 10,000×. It can be found that the voids were partially filled by the slg but the reinforcer did not fuse with the matrix and gap was found between them. Its facture toughness is 12.50 MPa$\sqrt{m}$ and it can be argued that if the reinforcer and the matrix mix homogenously, the fracture toughness will even be higher. Figure 15 enables one to view the gaps of the above composite clearer as the magnification of the image was increased to 25,000×. With this magnification, it is clear that there is no fusion between the reinforcer and the matrix. To improve the fusion between the reinforcer and the matrix, other fillers or resin will have to be added and this will also be research focus for us in the near future.

8. Conclusions

The project has proved that by adding 20% by weight of slg to phenolic resin, the fracture toughness of the composite is 8.28 times of that of the pure resin. It has also proved that 20% by weight of slg is the most suitable amount of slg added to attain maximum fracture toughness and has no fluidity problem for casting the composite into molds. It can be argued that the fusion between phenolic resin (matrix) and slg (reinforcer) will be improved by adding some other fillers and resins to the composite.

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