Flexural Tests of Phenol Formaldehyde and Slg Composites: Preliminary Results

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Abstract: Phenol formaldehyde was filled with Envirospheres slg to increase the strength of the composite for structural applications by a research Centre on composites, University of Southern Queensland (USQ). In order to reduce costs, the Centre wishes to fill as much slg as possible subject to maintaining sufficient strength of the composites in structural applications. This project varies the percentage by weight of the slg in the composites which are then subjected to flexural tests. The results show that composite with 25 % by weight of the slg produces the highest flexural strength and Young's modulus combined with a reasonable fluidity for casting; the highest flexural strain was achieved when the percentage by weight of slg is 10 %.

Keywords: Flexural strength, flexural strain, Young's modulus, phenol formaldehyde, phenolic resin, envirospheres and slg.

1. Introduction

Phenolic thermosetting materials were the first major plastic material used by industry. They are still among the most widely used thermosets because they are some of the lowest-cost engineering material on a cost-per-volume basis. 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 (Shackelford, 1992; Smith and Hashemir, 2006).

In the resole process, the condensation polymerization is performed in an alkali solution with excess formaldehyde and is carefully controlled so that a linear, non-crosslinked polymer liquid, resole, is produced. The resole can then be molded. When molding, the crosslinking is achieved by heating the viscous liquid. Since a crosslinked part can be obtained by simply heating the resoles, which are called one-stage resins (Smith and Hashemir, 2006).

The novolacs are formed by reacting phenol and formaldehyde in an acid solution but with insufficient formaldehyde to complete the reaction at 100 ^{o}C (the opposite of forming resoles). About one mole of phenol is reacted with 0.7 to 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 crosslink to form a solid network. 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 ^{o}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 (Shackelford, 1992; Smith and Hashemir, 2006; Strong, 2006; Clarke, 1996).

This research project is to investigate the flexural strength, flexural strain and Young's modulus of phenol formaldehyde composites reinforced with varying percentage by weights of Enviro spheres, the filler, with a view to finding out the optimum percentage by weight of the Enviro spheres used in the composites.

2. Phenol formaldehyde

In this research, the resin used is phenol formaldehyde resin solution J-2027L produced by Hexion Speciality Chemicals Pty Ltd. Its official name is Hexion Cellobond J2027L (Chemwatch, 2005a). The catalyst used to crosslink the resin is phenolic resin hardener catalyst produced by the same company. The official name of the catalyst is Hexion Phencat 15 (Chemwatch, 2005b). The ratio by weight of the resin to hardener is 20: 1.

Most molded phenolic parts are made from novolacs. Without filers or reinforcements, the parts are brittle and have high shrinkage in the mold because of the crosslinked nature of the cured resin. The most common filler is wood flour. Other common fillers and reinforcements are cotton fibres, fiberglass, chopped thermoplastic fibres, e.g. nylon.

The high number of OH groups in the resin gives it excellent adhesive qualities. However, this adhesive nature of phenolics causes molding problems. They tend to stick to the molds. Release agents have to be sprayed into the mold surface to solve this problem. The nonflammability of the resin leads to its wide applications. When phenol formaldehyde resin is subjected to a flame, they char rather than melt or burn. They are therefore widely applied in situations where avoiding flammability and smoke is vital. Furthermore, the char has a very low thermal conductivity so that surrounding materials are protected by the decomposed phenolic. Low thermal conductivity of the resin promote its used as bases for toasters and knobs for appliances. Most phenol formaldehyde parts are dark because the dark color is inherent to it and this also limits its use in some applications. A dark pigment is usually added to the resin to standardize the color and to decrease its sensitivity to UV light. Its high electrical resistance wins its applications in electrical switches and circuit breakers. The abrasive nature of the phenolic formaldehyde makes its machining difficult; they are therefore molded to near net shape. The resin is cured by condensation polymerization which results in the evolution of water as a by-product of the curing process and extensive microvoiding within the matrix. The microvoids have little effect on the composite properties except that significantly higher water absorption is observed. High water content can cause structures to delaminate when exposed to heat (Strong, 2006; Clarke, 1996).

3. The Envirospheres

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. 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. Its cost is also low.

4. Three Point Bending Test

The three point bending flexural test provides values for the modulus of elasticity in bending E_B, flexural stress σ_f, flexural strain ε_f and the flexural stress-strain response of the material. The main advantage of a three point flexural test is the ease of the specimen preparation and testing. However, this method has also some disadvantages: the results of the testing method are sensitive to specimen and loading geometry and strain rate (Shackelford, 1992; Wikipedia, 2006).

The standard used is ISO 14125:1998(E) because the results can then be compared with the work of others. (ISO 14125, 1998). The centre uses a universal machine MTS Alliance RT/10 at 10kN couple with the software TESTWORK 4.   The dimensions of the specimens of resins were 250mm x 10mm x 4mm and tested at a crosshead speed of 4 mm/min.

The equation used for calculating the flexural stress,

$$\sigma_f = \frac{3PL}{2bh^2} \qquad (1)$$

The equation used for calculating the flexural strain,

$$\varepsilon_f = \frac{6Dh}{L^2} \qquad (2)$$

The equation used for calculating the Young's modulus,

$$E_B = \frac{L^3 m}{4bh^3} = \frac{Flexural \quad strength}{Flexural \quad strain} \qquad (3)$$

where: σ_f : stress in outer fibre at midpoint, MPa;

ε_f : strain in the outer surface, %;

E_B: modulus of elasticity in bending, MPa;

P: load at a given point on the load deflection curve, N;

L: support span, mm;

b: width of test beam, mm;

h: depth of test beam, mm;

D:maximum delection of the centre of the beam, mm;

m: slope of the tangent to the initail straight line portion of the load deflection curve, N/mm.

5. The Composite Samples

The reinforcer was E-sphere slg (ceramic hollow sphere) particulates and they were made 10 % to 30% by weight in the cured phenol formaldehyde composite PF/E-SPHERES (X %), where x is the percentage by weight of the filler. As the raw materials of the composites are liquid and ceramic hollow spheres, the flexural test specimens were cast to shape. The resin is a dark brownish liquid and is first mixed with the dark brownish catalyst. After that 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 1000 grams of uncured composite of 30 % by weight of slg. The uncured composite was then cast into the moulds curing in ambient conditions. In this project, the x % by weight of PF/E-SPHERES (X %) was varied from 10 to 30% in step of 5 % by weight. The number of samples used for each percentage by weight of E-spheres will be six.

After initial 24-hour curing when the test pieces were removed from the mould, they were post-cured. This was achieved by baking the pieces in an oven. Oven temperatures and times were:

- 4 hours at 50°C

- 4 hours at 80°C
- 2 hours at 100°C

During the initial baking process of 4 hours at 50°C, it was observed that a number of test pieces were developing a bow in middle. This bowing was between 1mm and 4mm in the middle of the piece and seemed to be exacerbated by the higher temperature baking processes. To counteract this, after they were removed from each baking session, all test pieces were subject to an approximate 2kg load while between two pieces of toughened glass. The time for this weighting was approximately 16 hours as they cured overnight. The test pieces were then tested.

6. Results and Discussion

Figure 1 illustrates the flexural strength of varying by weight of E-sphere (slg) reinforced phenol formaldehyde matrix composite. At 5 percent by weight of the slg, the flexural strength is highest at 42.39 MPa; at 10 – 20 percent by weight of slg reinforcement, the values of flexural strength drop and vary from 17.22 to 17.18 MPa, they are very stable. At 25 % by weight of slg the flexural strength increased again to 26.48 MPa; it dropped back to 22.07 MPa at a weight reinforcement of 30 percent.

The flexural strength is highest at 5 percent by weight of slg reinforcement because at this low percentage of reinforcement, the slg has less impact on the flexural strength of the composite; the fact that the unfilled phenolic formaldehyde has a higher flexural strength than its filled counterpart had been evaluated by Wang et al. (1997). If the left hand side of the graph in Figure 1 is extrapolated so that it intersects with the y-axis, the flexural strength of unfilled phenolic resin was 73.18 MPa; Wang et al. (1997) found that the flexural strength of unfilled phenolic resin was 71.3 MPa, and that of 20 percent by weight ceramic powder reinforced phenolic formaldehyde matrix composite was 10.5 MPa. In this research the corresponding by weight slg reinforced phenolic formaldehyde matrix composite was 17.18 MPa. The difference in flexural strength of the unfilled resin for both studies is only 2.6%; the difference in values obtained because the phenolic resin used in the two cases are not identical but

this is not critical. Wang et al. (1997) used ICI Fiberite resol-type CMXR-6055 phenolic formaldehyde resin; this research used Chemwatch Hexion Cellobond J2027L phenolic formaldehyde resin. On top of it, Wang el al. (1997) did not mention they way they cured the resin and its filler. The difference in flexural strength of the reinforced phenolic formaldehyde composites for both studies is 64%, which is a significant difference. Wang et al. (1997) used ceramic particles of diameters between 300 – 600 μm with a specific gravity of 1.05 g/cm^3; no other details of the filler were mentioned. In this study, the diameters of the ceramic particles were between 20 -300 μm; it can be argued that the smaller diameters of the ceramic particles (slg) can be wetted by and mixed with the resin and this results in higher flexural strength. The resin used in this study is newer than in its counterpart and may wet and mix with the ceramic particles better. Moreover, the post-curing process of this study may also contribute significantly to the higher flexural strength.

Table 2 shows the values of flexural strength mentioned above with their standard deviation. It can be found that the maximum flexural strength, 26.48 MPa, is obtained when the percentage by weight of slg is 25 % (36.6 % by volume). It appears that if the right hand side of the graph in Figure 1 is extrapolated, the flexural strength will approach zero when the percentage by weight of the reinforcer is 43%. Hence, the maximum slg by weight that can be added to the phenol formaldehyde resin is 25 percent; at this point, maximum flexural strength can be achieved together with significant reduction in material cost. At 25 percent by weight of slg, the viscosity of the slurry mixture was 5,565 cP which is very fluid and can be cast into moulds and then manipulated with ease (Ku et al., 2006).

Figure 2 shows the flexural strain of varying by weight of E-sphere (slg) reinforced phenol formaldehyde matrix composite. The value (0.019 mm/mm) peaked at a percentage by weight of filler of 10 percent. At other percentages by weight of slg, the flexural strains vary from 0.013 to 0.014; the change is not much. From Figure 4, it can be found that the strain varies from one percentage to the next, though it can be observed that there is a general downward trend from the lower values of filler (left hand side) to the higher values of filler (right hand side). The values found seem to be reasonable when they are compared with those of aluminum oxide (0.007 mm/mm) and glass (0.009) (Callister, 2005).

Redjel (1995) found the flexural strain of pure phenolic resin to be 0.0143 mm/mm. The material used for his work was a pure phenolic resin 84055 manufactured by CDF-Chimie (France) and catalyzed by 3 % of C1650 and cured at 80 $^{\circ}$C for 8 days. In this study, it was found that the flexural strain of 5 percent by weight reinforced phenolic resin was 0.014 which is very near to that found by Redjel (1995) for pure phenolic resin (0.0143); even at 10 percent by weight of slg, the flexural strain was only 0.019 which is only 1.3 times higher than that obtained by Redjel (2006). This is because the reinforcement did not have any impact to the flexural strain of the composite.

Table 3 illustrates the values of flexural strain mentioned above with their standard deviation. It can be found that the maximum flexural strain, 0.019, is obtained when the percentage by weight of slg is 10 %. It appears that except for the peak value, the flexural strain from 5 – 30 percent is around 0.014. Hence, the flexural strain, at the maximum flexural strength of 26.48 MPa, i.e. 25 percent by weight of slg, will not be compromised.

Figure 3 shows the Young's modulus of varying by weight of E-sphere (slg) reinforced phenol formaldehyde matrix composite. At 5 percent be weight of the slg, the Young's modulus is highest at 3,005 MPa; at 10 – 20 percent by weight of slg reinforcement, the values of flexural strength drop and vary from 979 to 1,114 MPa, they are very stable. At 25 % by weight of slg the Young's modulus increased again to 1,995 MPa; it dropped back to 1,707 MPa at a weight reinforcement of 30 percent. The values found seem to be reasonable when they are compared with those of phenolic (2,760 – 4,830 MPa) (Callister, 2005). Moreover, the extrapolated value of Young's modulus of pure phenolic resin in this study is 5,730 MPa, which is quite close to that found by Redjel (1995) for pure phenolic resin (4,401 MPa).

Table 4 illustrates the values of Young's modulus mentioned above with their standard deviation. It can be found that the maximum Young's modulus, 1,995MPa, is obtained when the percentage by weight of slg is 25 % (36.6 % by volume). It appears that if the right hand side of the graph in Figure 7 is extrapolated, the modulus of elasticity will approach zero when the percentage by weight of the reinforcer is

40%, which is not far from the percentage (43%) at which the flexural strength approaches zero. Hence, the maximum slg by weight that can be added to the phenol formaldehyde resin is 25 percent; at this point, maximum modulus of elasticity and flexural strength can be achieved together with significant reduction in material cost. Moreover, the flexural strain, at the maximum flexural strength of 26.48 MPa, and Young's modulus of 1,995 MPa i.e. 25 percent by weight of slg, will not be compromised.

Figure 4 shows the scanning electron microscopy image of phenolic resin post-cured for 4 hours at 80 ^{o}C at a magnification of 3,500 times. Voids are found left by the evaporation of water formed during condensation polymerization of phenol formaldehyde. Its flexural strength was 73.18 MPa and this is high compared with those of varying percentage by weight of slg reinforced phenolic resin (Figure 3). Despite the voids, its flexural strength was high because the structure is better than that shown in Figure 5, which illustrates the scanning electron microscopy image of phenolic resin reinforced by 20% by weight of slg and post-cured for 4 hours at 80 ^{o}C at a magnification of 25,000 times. It can be found that the voids were partially filled by the slg but the reinforcer did not fuse with the matrix and a gap was found between them. The lack of fusion brought about failure of the composite by cutting through the weak slg when bending load was applied. On the other hand, the presence of these slg particles made the flexural strain of the composite higher as depicted in Figure 2. The relationship between the micro structure of the composite and its Young's modulus is quite similar to that of its flexural strength. To improve the fusion between the reinfoircer and the matrix, other fillers or resin will have to be added and this will also be research focus of the Centre of Excellence for Engineered Fibre Composites in the near future.

7. Conclusions

This study has evaluated the flexural strength, flexural strain and Young's modulus of varying percentage by weight of slg reinforced phenolic resin; in all cases, the fluidity

of the slurry composite was high and could be cast easily into moulds. The values with no filler (extrapolated) had also been compared with those found by other studies and they agreed with each other very well. . It can be argued that when the fusion between phenolic resin (matrix) and slg (reinforcer) is improved by adding some other fillers and resins to the composite, its flexural strength will be improved.

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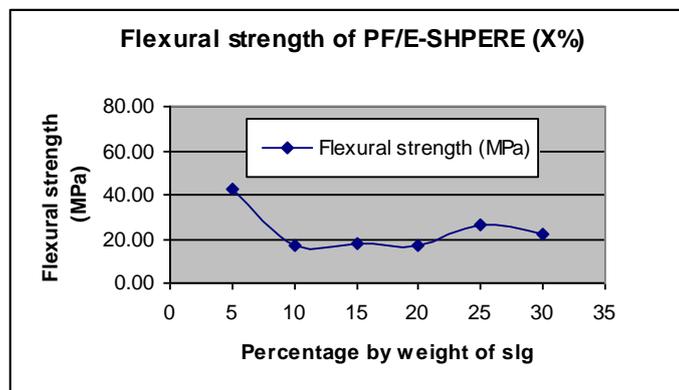
Figure 1: Flexural strength of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite
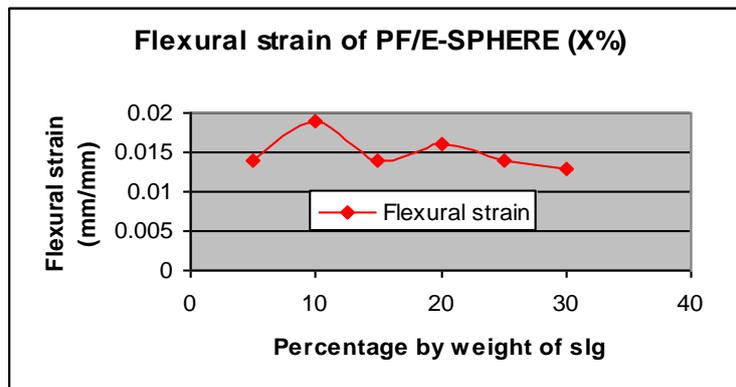

Figure 2: Flexural strain of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite
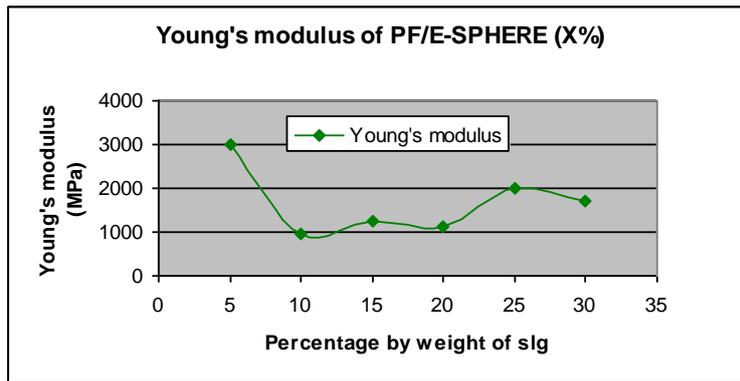
Figure 3: Young's modulus of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite
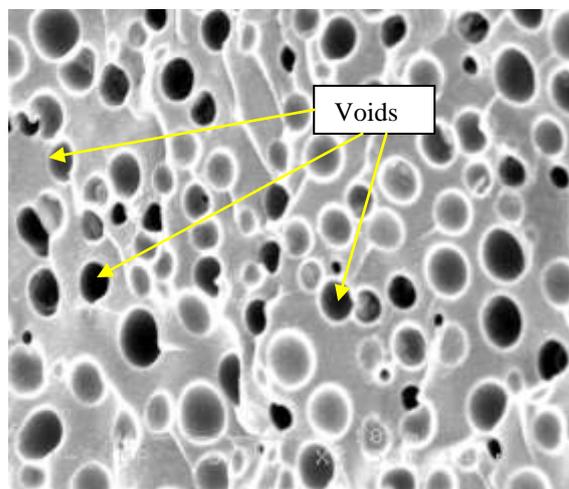

Figure 4: Phenolic resin post-cured for 4 hours at 80 ^{o}C at a magnification of 3,500 times
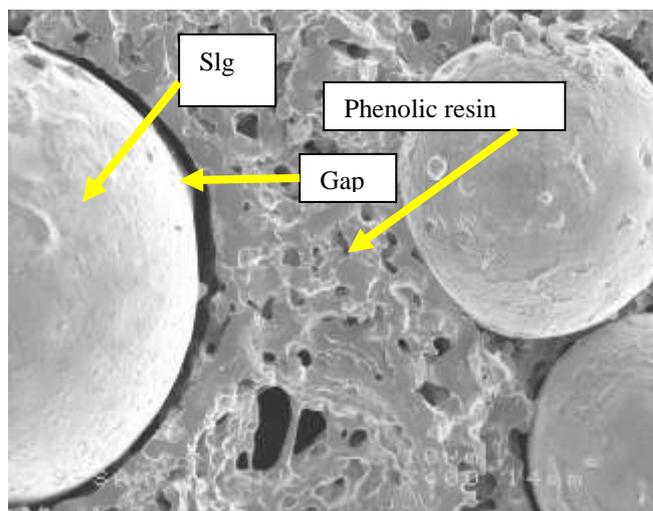

Figure 5: PF/E-SPHERE (20%) post-cured for 4 hours at 80 ^{o}C at a magnification of 25,000 times

Table 1: Weight of materials required to make 1000 g of PF/E-SPHERE (30%)

	Materials	Resin (R)	Catalyst (C)	R + C	Slg	Composite
Parameters						
Percentage by weight		20	1	---	---	---
Percentage by weight		---	---	7	3	---
Weight of materials in 300 g of PF/SLG (10%)		667(g)	33 (g)	700 (g)	300 (g)	1000 (g)

Table 2: Flexural strength and its standard deviation of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite

Percentage by weight of slg	5	10	15	20	25	30
Flexural strength, MPa	42.39 (3.12)[#]	17.22 (2.46)	17.57 (2.54)	17.18 (4.02)	26.48 (1.59)	22.07 (3.09)

[#] standard deviation

Table 3: Flexural strain and its standard deviation of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite

Percentage by weight of slg	5	10	15	20	25	30
Flexural strain, mm/mm	0.014 (0.001)[#]	0.019 (0.004)	0.014 (0.003)	0.016 (0.004)	0.014 (0.002)	0.013 (0.003)

[#] standard deviation

Table 4: Young's modulus and its standard deviation of varying percentage by weight of E-sphere reinforced phenolic formaldehyde matrix composite

Percentage by weight of slg	5	10	15	20	25	30
Flexural strain, mm/mm	3005 (362)[#]	979 (303)	1256 (221)	1114 (263)	1995 (350)	1707 (295)

[#] standard deviation