

Tensile Tests of Phenol Formaldehyde SLG Reinforced Composites: Pilot Study

H Ku^{*+}, W Jacobson^{*}, M Trada^{*} and F Cardona⁺, D Rogers[#]

^{*}Faculty of Engineering and Surveying,

⁺Centre of Excellence in Engineered Fibre Composites

University of Southern Queensland, Australia.

[#]Loklite Pty Ltd, PO Box 178, Darling Heights, Queensland, 4350, Australia.

H Ku, W Jacobson , M Trada, F Cardona and D Rogers, Tensile Tests of Phenol Formaldehyde SLG Reinforced Composites Pilot Study, Journal of Composite Materials, 2008 (accepted for publication).

Corresponding Author:

Title : Dr.
Name : Harry Siu-lung Ku
Affiliation : Faculty of Engineering and Surveying,
University of Southern Queensland.
Tel. No. : (07) 46 31-2919
Fax. No. : (07) 4631-2526
E-mail : ku@usq.edu.au
Address : Faculty of Engineering and Surveying,
University of Southern Queensland,
West Street, Toowoomba, 4350,
Australia.

Abstract: Phenol formaldehyde was filled with Envirospheres SLG to increase the strength and impact toughness of the composite for structural applications by the Centre of Excellence in Engineered Fiber Composites (CEEFC), 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 and impact toughness of the composites in structural applications. This project varies the percentages by weight of the SLG in the composites which are then subjected to tensile tests. The results show that composite with 10 % by weight of the SLG produces the highest yield, tensile strengths and Young's modulus combined with a reasonable fluidity for casting.

Keywords: Yield strength, tensile strength, 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 [1, 2].

The novolacs 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 0.7 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 °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 [1-4].

This research project is to investigate the yield strength, tensile strength and Young's modulus of phenol formaldehyde composites reinforced with varying percentages by weight 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

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 [5]. 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 [6]. The ratio by weight of the resin to hardener is 50: 1, which may be changed when the resin is supplied by other manufacturer.

Most molded phenolic parts are made from novolacs. Without fillers 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 [3-4].

3. The Envirospheres

The Envirospheres (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 [7]:

- 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.

4. Stress and strain curve

In the tensile test, the force and extension of the test pieces were recorded. Figure 1 shows a typical curve for the specimen undergoing the test. This graph gives the information of tensile force versus tensile elongation.

4.1 Yield Strength

It is the strength at which a definite amount of plastic strain has occurred. Figure 1 shows that 0.2 % proof load could not be determined because line passing the 0.2 % elongation and parallel to the most approximated linear portion of the curve will never cut the curve. The gauge length used should be the separation of the grips and 105 mm because the elongation of non-ductile material, e.g. this phenolic composite, when subjected to tensile force will spread along the sample evenly and not restricted to the conventional gauge length of 50 mm [9, 10]. Figure 1 also illustrates how the 0.1 % proof load was determined.

When the intersection was projected to the y-axis, the load found was 355 N which is the 0.1 % offset yield load. Yield strength is calculated using the relationship below [8]:

$$\text{Yield strength} = \frac{\text{Yield load}}{\text{Original cross-sectional area}} \quad (1)$$

For example, the yield strength of the sample illustrated in Figure 1

$$= \frac{0.1\% \text{ offset load}}{\text{Original cross-sectional area}} = \frac{355}{14.8 \times 3.8} = 6.31 \text{ (MPa)}$$

4.2 Tensile strength

This tensile strength can be calculated by dividing the maximum load with the original cross sectional area of the specimen as follows [8]:

$$\text{Tensile strength} = \frac{\text{Maximum load}}{\text{Original cross-sectional area}} \quad (2)$$

or

$$\sigma = \frac{P_{\max}}{A_o} \quad (3)$$

where P_{\max} is the maximum load in Newton and A_o is the original cross-sectional area in mm^2 .

For example, the tensile strength of sample illustrated in Figure 1

$$= \frac{370}{14.8 \times 3.80} = 6.58 \text{ (MPa)}.$$

The tensile strength is most sought after result of a tensile test. It is easy to determine and has become a familiar property and is useful for the purposes of specifications and quality control of a product.

4.3 Young's modulus

The Young's modulus (E) or modulus of elasticity is to measure the stiffness of the material. The Young's modulus can be calculated by calculating the slope of the initial linear portion of the stress-strain curve. As the force-extension curve of the material does not possess a perfectly linear portion (Figure 1), the Young's modulus quoted is the secant modulus at a strain of 0.1 percent [11, 12]. The Young's modulus [8]:

$$E = \frac{\text{stress}}{\text{strain}} = \frac{\sigma}{\varepsilon} \quad (4)$$

From (1) and (2), (6) becomes

$$E = \frac{\frac{F}{A_o}}{\frac{\Delta L}{L_o}} \quad (5)$$

For example, the Young's modulus of sample illustrated in Figure 1 was calculated using the data provided from Figure 2, in which a portion of the most linear part of the curve was selected; after projecting the top point of the selected linear portion into the x- and y- axis respectively, the force (= 250 N) and the extension (= 0.186 mm) were obtained and used in the calculation.

$$E = \frac{\frac{250 - 0}{14.8 \times 3.8}}{\frac{0.186 - 0}{105}} = 2509.40 \text{ (MPa)} = 2.509 \text{ (GPa)}.$$

5. The Composite Samples

The reinforcer was E-sphere slg (ceramic hollow sphere) particulates and they were made 0 % to 35% 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 tensile 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 mixture of SLG, resin and accelerator was blended with mechanical blender to ensure a more homogenous mixture. The upper and lower plates and the mould were illustrated in Figure 3. They were clamped by nine screws and springy plastic clamps as illustrated in Figure 4. This proved to be effective and no seeping of the slurry took place when the samples were cured under ambient conditions. The screwed and tightened mould combination was slightly vibrated to facilitate the escape of the gases and this will certainly reduce the porosity of the specimens. Finally, before pouring the uncured composite into the mould, the upper surface of the lower plate, the cavities of the mould, the two faces of the mould and the lower surface of the upper plate were sprayed with more releasing agent (canola oil) to enable easy release of the samples after curing. The uncured composite was then cast into the moulds (Figure 3) curing in ambient conditions.

An MTS 810 Material Testing Systems was used for the tests. The rate of extension was made at 1 mm per minute.

After initial 72-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 5 illustrates the yield strengths of varying percentage by weight of E-sphere (SLG) reinforced phenol formaldehyde matrix composite. The yield strength of the neat resin was 13.00 MPa. At 10 percent by weight of SLG, the yield strength was highest at 15.80 MPa; after this SLG reinforcement lowered the values of yield strength; it dropped dramatically from 9.05 to 4.00 MPa when the percentage by weight of SLG were 15 % to 20 % respectively. From 20% to 35 % by weight of SLG, the yield strength values did not vary much but were relatively low and the

composite will not be suitable for most applications. Table 2 shows the values of yield strength mentioned above with their standard deviation in brackets.

Figure 6 shows the tensile strengths of phenolic composite with varying SLG by weight. The tensile strength of the neat resin was 15.00 MPa. At 5 percent by weight of SLG, the tensile strength was highest at 13.4 MPa and at 10 percent by weight of SLG, the tensile strength was still at 13.3 MPa; after this SLG reinforcement dragged the values of tensile strength down; it dropped dramatically from 13.30 to 3.00 MPa when the percentage by weight of SLG were 10 % to 15 % respectively. The variation of tensile strength with respect to percentage by weight of SLG is the same as that of yield strength. Table 2 shows the values of tensile strength mentioned above with their standard deviation in brackets.

Figure 7 shows the Young's moduli of varying by weight of E-sphere reinforced phenol formaldehyde matrix composite. The Young's modulus of the neat resin was 2.51 GPa and it decreased slowly as the percentage by weight of SLG increases (up to 15 %) and dropped significantly to 1.39 when the percentage by weight of SLG was 20 %; after that the values did not change much. The values found seem to be reasonable when they are compared with those of phenolic formaldehyde (2.76 – 4.83 GPa) [13]. However, the Young's modulus of pure phenolic resin in this study is 2.51 GPa, which is 13.5 % lower than that found by a group of researchers for pure phenolic resin (2.9 GPa). The same team used ICI Fiberite resol-type CMXR-6055 phenolic formaldehyde resin; this research used Chemwatch Borden (Hexion) Cellobond J2027L phenolic formaldehyde resin. On top of it, they did not mention the temperatures and duration of soak when they cured the resin and its filler [14].

They 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 [14]. In this study, the diameters of the ceramic particles were between 20 -300 μm . In general, the smaller diameters of the ceramic particles (SLG) can be wetted by and mixed with the resin better and this may result in Young's modulus but this is not the case. More study has to be carried out to remedy this. Table 2 shows the values of Young's modulus mentioned above with their standard deviation in brackets.

Figure 8 shows the scanning electron microscopy image of phenolic resin post-cured for 4 hours at 80°C at a magnification of 3,500 times. Voids are found left by the evaporation of water formed during condensation polymerization of phenol formaldehyde. Despite the voids, its tensile strength was high because the structure is better than that shown in Figure 8, 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°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 tensile load was applied. 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 of the Centre of Excellence for Engineered Fibre Composites in the near future.

7. Conclusions

This study has evaluated the yield strength, tensile strength 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 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. The best percentage of SLG by weight that can be added to the phenolic resin to give maximum yield and tensile strengths is about 10 percent. The Young's modulus is largest with neat resin. Also from table 2, it can be found that the standard deviations of the yield and tensile strengths, and the Young's modulus are small and can be argued that the values of those mechanical properties are reliable.

References

1. Shackelford, J F, Introduction to Materials Science for Engineers, 3rd edition, Macmillan, 1992, pp.435-437, 459.
2. Smith, W F and Hashemir, J, Foundations of Material Science and Engineering, 4th edition, McGraw-Hill, 2006, pp. 523-525.
3. Strong, A B, Plastics: materials and processing, 3rd edition, Pearson/Prentice-Hall, 2006, pp. 182-183, 304-309, 323-333, 620-621.

4. Clarke, J L (Editor), *Structural design of polymer composites*, E & FN Spon, U.K., 1996, pp.59-62, 343-5, 357.

5. Chemwatch, *Material Safety Data Sheet for Hexion Cellobond J2027L*, 2005a, pp. 1-14.

6. Chemwatch, *Material Safety Data Sheet for Hexion Phencat 15*, 2005b, pp. 1-14.

7. E-spheres, www.envirospheres.com.au, Envirospheres Pty Ltd., P O Box 497, NSW 2070, Australia, undated.

8. Wang, H, *Engineering Materials*, USQ Studybook 1, USQ, Toowoomba, Australia, A3-A6, 2.4-2.5, 2008.

9. Ku, H, Trada, M and Puttgunta, V C, *Mechanical Properties of Vinyl Ester Composites Cured by Microwave Irradiation: Pilot Study*, *Key Engineering Materials*, 2006, Vol. 334-335, pp.537-540.

10. Ku, H, Puttgunta, V C and Trada, M, *Young's Modulus of Vinyl Ester Composites Cured by Microwave Irradiation: Preliminary Results*, *Journal of Electromagnetic Waves and Applications*, 2007, Vol. 21. No. 4, pp. 517 - 526.

11. Osswald, T A and Menges, G, *Materials Science of Polymers for Engineers*, Hanser publishers, New York, pp. 103-5, 229- 31, 1995.

12. John, V B, *Engineering Materials*, Macmillan, 1990, p. 209.

13. Callister, W D, *Fundamental of Materials Science and Engineering: An Integrated Approach*, 2nd edition, Wiley International, 2005, pp.184.

14. Wang, S, Adanur, S and Jang B Z, Mechanical and thermo-mechanical failure mechanism analysis of fibre/filler reinforced phenolic matrix composite, *Composites Part B*, 1997, 28B, pp. 215-231.

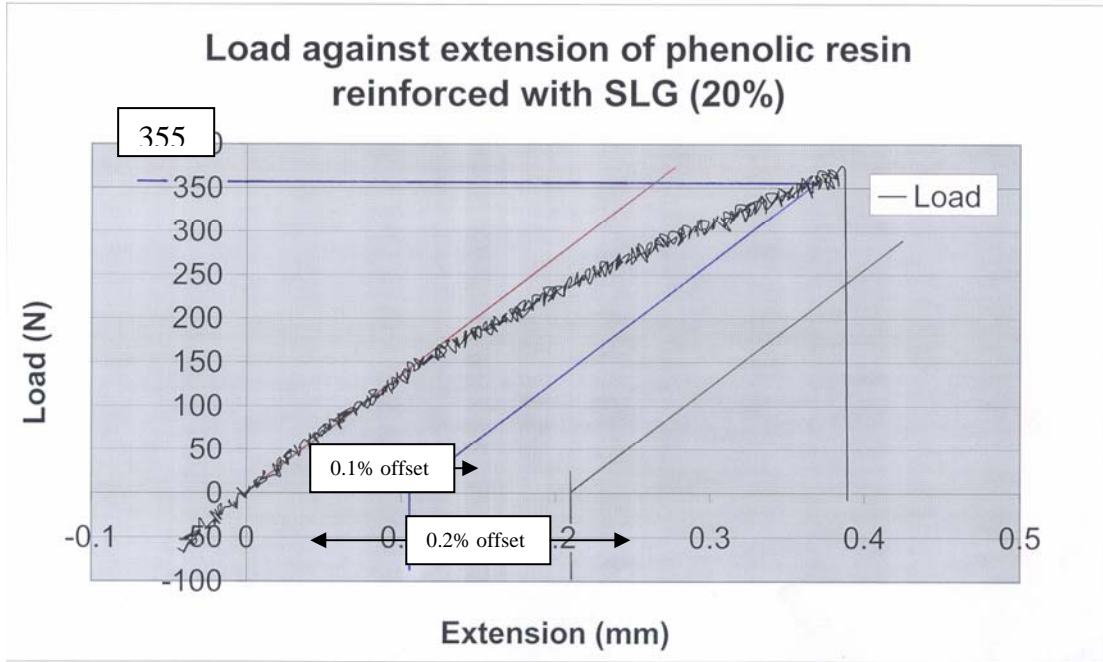


Figure 1: Load against extension of a sample showing the 0.1% proof load

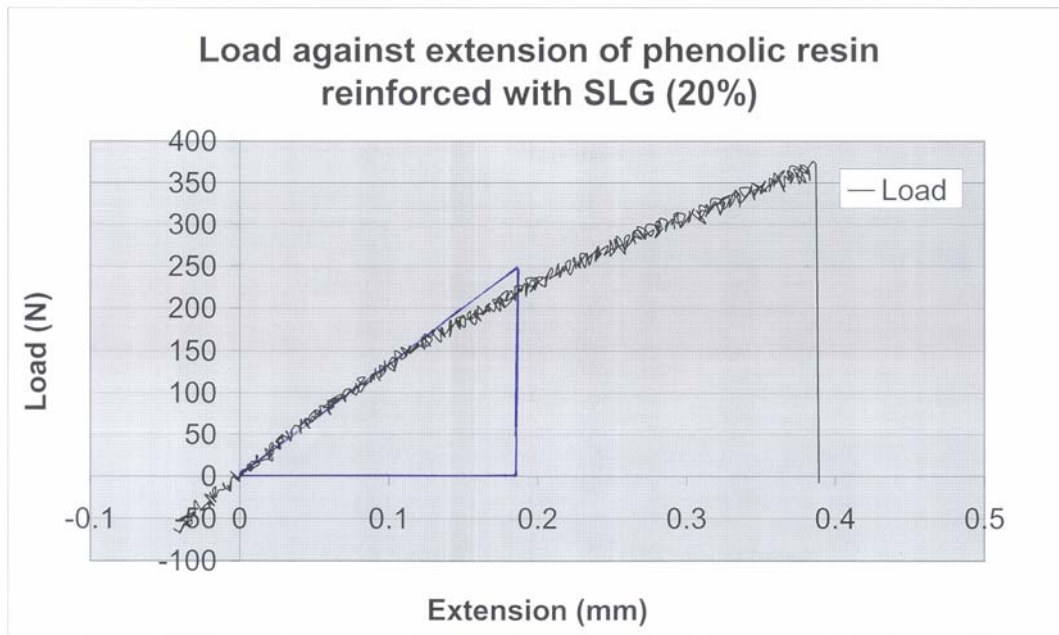


Figure 2: Graph showing how to get data for calculating Young's modulus in phenolic composite

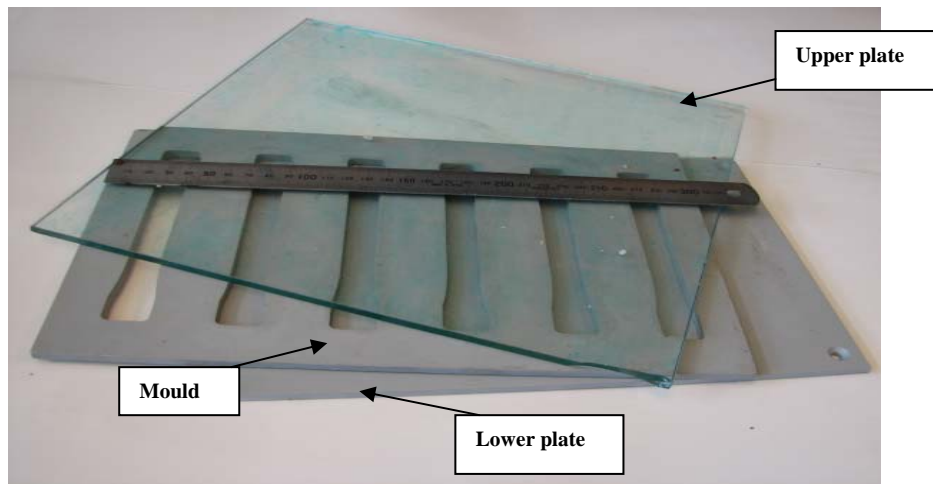


Figure 3: Moulds for the specimens

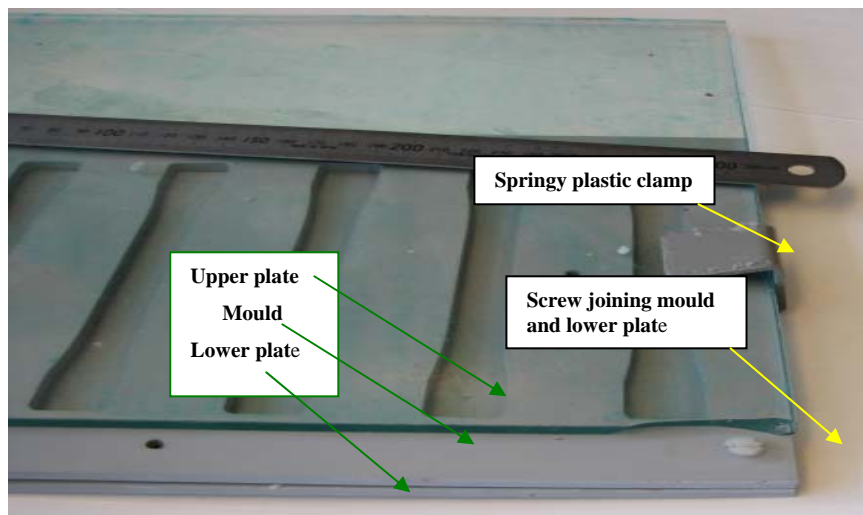


Figure 4: Screwing and clamping of mould, upper and lower plates

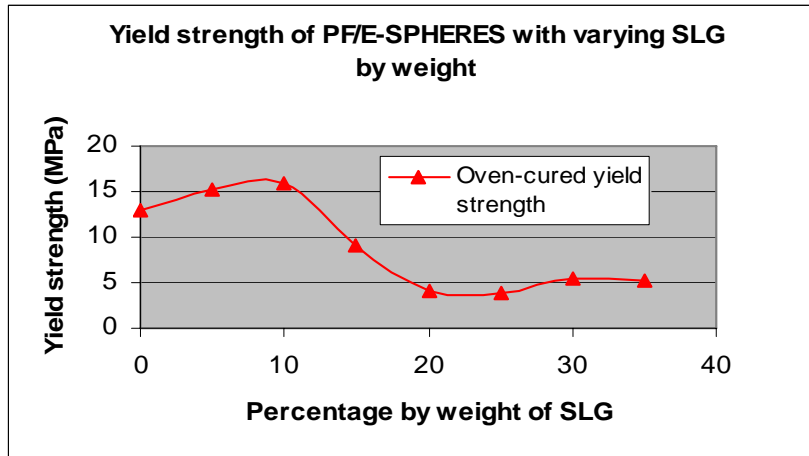


Figure 5: Yield strength of phenolic composite reinforced with varying SLG by weight

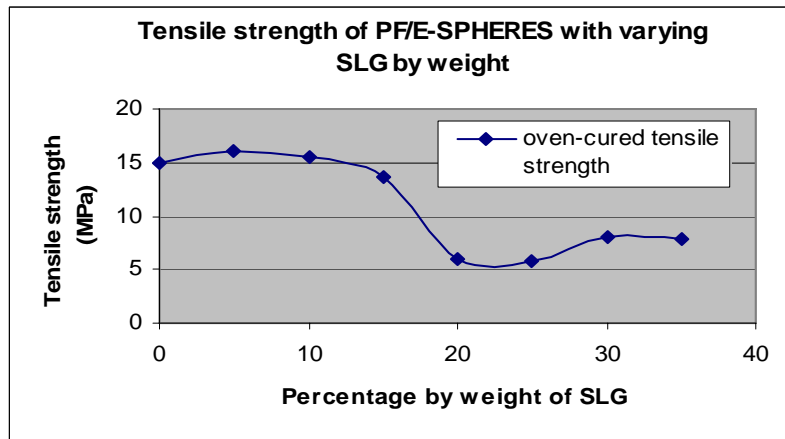


Figure 6: Tensile strength of phenolic composite reinforced with varying SLG by weight

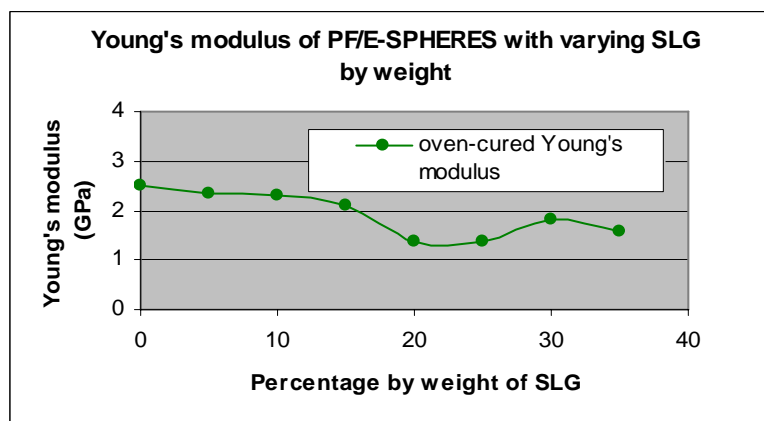


Figure 7: Young's modulus of phenolic composite reinforced with varying SLG by weight

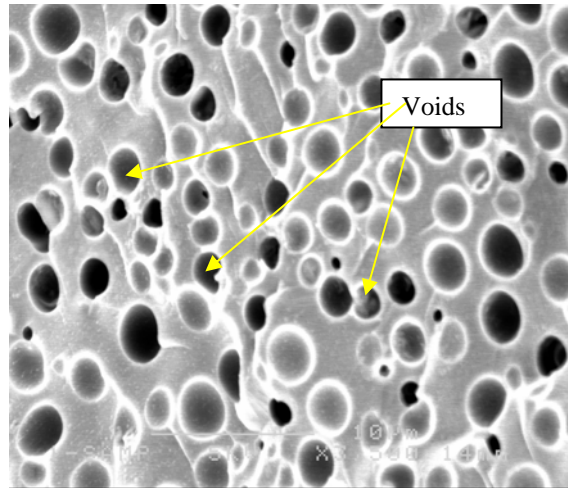


Figure 8: Phenolic resin post-cured for 4 hours at 80 °C at a magnification of 3,500 times

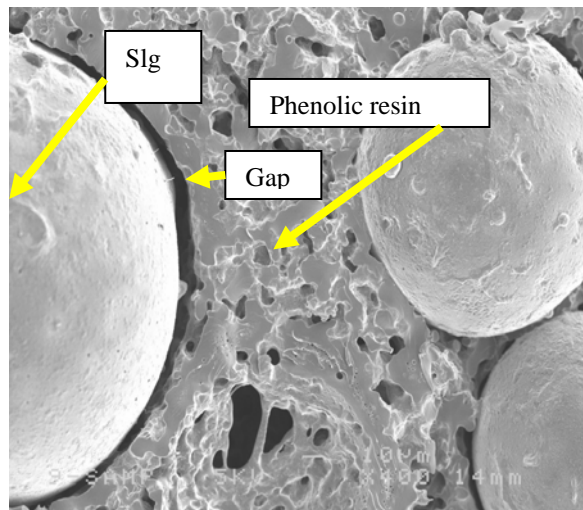


Figure 9: PF/E-SPHERE (20%) post-cured for 4 hours at 80 °C at a magnification of 25,000 times

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

Parameters	Materials	Resin (R)	Catalyst (C)	R + C	Slg	Composite
Percentage by weight		20	1	---	---	---
Percentage by weight		---	---	7	3	---
Weight of materials in 300 g of PF/SLG (10%)		686(g)	14 (g)	700 (g)	300 (g)	1000 (g)

Table 2: Yield strength, tensile strength and Young's modulus of phenolic composite reinforced with SLG

Mechanical properties	Percent weight of SLG	0	5	10	15	20	25	30	35
0.1 % Yield strength (MPa)		13.00	15.25 (2.02) [#]	15.80 (1.16)	9.05 (0.54)	4.01 (0.302)	3.85 (0.89)	5.49 (0.39)	5.24 (0.44)
Tensile strength (MPa)		15.00	16.08 (3.84) [#]	15.50 (1.34)	13.57 (1.27)	6.07 (0.55)	5.84 (1.45)	7.95 (0.71)	7.94 (0.97)
Young's modulus (GPa)		2.27 (0.08) [#]	2.97 (0.27)	2.77 (0.05)	2.52 (0.12)	1.69 (0.14)	1.63 (0.23)	2.10 (0.21)	2.19 (0.87)

[#] standard deviation