Flexural properties of sawdust reinforced phenolic composites: Pilot Study

H Ku[*], F Cardona[*], M Trada* and G Vigier[*]

[*]Faculty of Engineering and Surveying,
Centre of Excellence in Engineered Fibre Composite,
University of Southern Queensland

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 :   The advantageous properties of sawdust and phenolic resins were combined by making sawdust reinforced phenolic composites with different percentages by weight of sawdust. The sawdust was divided into three grades in accordance with its particulate size. Garamite and propylene glycol were added individually and together to enhance the flexural properties of the composites obtained. Without any garamite and propylene glycol, it was discovered that the best flexural properties of the composites were obtained when the percentage by weight of sawdust ($< 300\mu$ m) is up to 15%. Beyond this, the flexural properties dropped significantly; in addition, the fluidity of the composite was very low and the mixture was not suitable for casting. In general, the flexural modulus of the composites decreases with an increase in sawdust content, i.e. they are more elastic but their maximum flexural strain does not improve. Garamite was therefore added to improve the maximum flexural strains of the composites and this was successful. The addition of propylene glycol makes the composite more plastic.

1. Introduction

Natural fillers have attracted the attention of the composite industries because they give advantages over conventional fillers e.g. carbon fibre and glass fibre. Sawdust and other low cost agricultural-based flour can be considered as particulate fillers that enhance the flexural properties of the composite, with little effect on the composite strength. Natural fillers can also be incinerated after the composite component has served its useful life. Sawdust is one of the most common natural fillers used in the thermoplastic industry. One of the variables used to differentiate sawdust is particle size. When sawdust is used as fillers for plastics, it tends to increase its stiffness of the composite, but does not improve its strength [1].

Aggression of particles refers to particles coming together to form a mass. Aggression of particles, especially finer particles, is another factor that can influence the final properties of the composite [2]. In most cases, aggression occurs at higher filler contents (20 and 30 wt %); higher filler contents will also make the composite sticky and cannot be mixed properly and cast to the moulds [1, 3]. Salemane and Luyt claimed that very fine filler particles are also difficult to disperse, and the agglomerates then behave as large single particles [1]. On the other hand, finer or small particles are found to improve the mechanical properties of polymer composites better than the larger ones. Most wood powder-plastic composites result in materials with a weak interfacial region, which is found to reduce the efficiency of stress transfer from the matrix to the reinforcement component. In natural filler composites, weak adhesion may result from poor dispersion and incompatibility between the natural filler and the polymer. Salemane and Luyt added maleated polypropylene (MAPP) to polypropylene/sawdust composites and found that composites with higher than 20 wt % of MAPP have better tensile properties [1]. This is due to the fact that interactions between the anhydrite groups of the maleated coupling agents and the hydroxyl groups of the natural fillers can overcome the incompatibility problems; thus increasing the flexural and tensile strength of the composites.

Phenolic resins are thermosetting polymers with high chemical resistance and thermal stability but low toughness and mechanical resistance. Moreover, phenolic resoles have intrinsic resistance to ignition, low generation of smoke and relatively low cost. On the other hand, they are characterized by a complex process of polymerization with release of water and formaldehyde and 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.

Phenolic resin is resistant to ignition; sawdust increases the stiffness of resins. Sawdust filled phenolic composites were therefore manufactured to serve heat resistant environments in civil and structural engineering, e.g. internal compartments of mass transit system; these composites are also more environmental friendly because the filler is a natural one. Different percentage by weight of sawdust is added to phenolic resin to produce different composites and one of the aims of this research is to find out the optimum percentage by weight of sawdust in the resin to give the best flexural properties. Propylene glycol and garamite will also be added to the composites to further enhance their flexural properties.

2. Materials

The composites were made by mixing different percentages by weight of sawdust and phenolic (resole) resins with a catalyst, Phencat 15. Other additions included garamite and propylene glycol.

2.1 Phenolic resin and its catalyst

A resol commercial resin called Cellobond® J2027L phenolic resin, a classic resin was used in this study. It is a brown prepolymer with a phenolic odour. The viscosity is around 2800 cP at 25 °C and is a gas noxious. Its composition consists of phenol/formaldehyde resin, 30 to 60%, phenol, 1 to 10%, formaldehyde, 1 to 5% and water, 30 to 60%. The polymer based on phenolic resin is Phenol-formaldehyde (PF). PF resins are the major adhesives used for bonding wood panels for exterior applications. The PF adhesive resins are used primarily in the production of softwood plywood, oriented strand board, and wafer board. One recent application of phenolic resins is for inner lining of multilayered composite in fire critical applications [4, 5]. By varying the reaction time, reaction temperature, catalyst type, and the

ratio of formaldehyde to phenol, a number of adhesive systems with different properties can be produced [5]. The basic reaction between formaldehyde and phenol is shown in Figure 1.

In general, there are three catalysts for phenolic resin: Phencat 15, Phencat 382 and UH. Phencat 15 is used in this study and is a fast action acid 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. The reaction with phenolic resins is strongly exothermic. It is toxic and causes burns with body contact. Its composition consists of xylenesulfonic acid, 70 to 90%, phosphoric acid, 10 to 20% and water, 1 to 10%.

2.2 Sawdust

The sawdust used was pine waste from the sawmills. It was sifted with three sieves of different sizes (<300 μm; 300-600 μm; 600-1650μm). The sawdust content in the resin varied from 5 to 25% by weight. Above this percentage by weight, it became very hard to mix. The sawdust will be mixed with the resin and other additives without any treatment.

2.3 Garamite®

Garamite®, a white powder, is a mixed mineral thixotrepe (MMT) specifically designed to enhance rheology at low viscosity in thin film applications, such as crosslinked thermoset systems. MTT technology involves the blending of acicular and platey minerals that are then surface modified for resin compatibility. Garamite® additives are the first additives available to formulators of composites and coatings that allow for improvements in sag resistance, anti-settling, syneresis, orientation of metallic particles, and spray atomization while having a

minimal impact on viscosity. Garamite® additives control settling/floating of particles and lightweight materials and prevent phase separation and/or syneresis in formulated products because they penetrate into the resin network. Garamite® additives employ the concept of focused performance to deliver desired performance with fewer unwanted negative side effects [7]. The percentage by weight of garamite added was around 1 percent.

2.4 Propylene glycol

This is a fluid plasticizer and is added to the composites to improve its plasticity and maintain its fluidity. Research has shown that ethylene glycol improved flexural properties of phenolic resin significantly [5]. In this study, propylene glycol is used in place of ethylene glycol because the two additives come from the same family and will have the same effect on phenolic resin besides the former is readily available in our laboratory.

2.5 The samples

The samples were cast into a rectangular plastic container and then cut to size. The dimensions of the specimens of resins were 64mm x 13mm x 7mm. Samples were made with percentages by weight of sawdust varied from 0 to 25 % [8, 9].

3. Flexural tests

The flexural test measures behaviour of materials when subjected to simple beam loading. It is also called a transverse beam test with some materials. Maximum fibre stress and maximum strain are calculated for increments of load. Flexural modulus is a measure of the stiffness of a material in bending. Flexural modulus is calculated from the slope of the stress

against deflection curve. Flexural test is often done on relatively flexible materials such as polymers, wood and composites [10]. There are two types of the test: 3 point flexural test and 4 point flexural test. Three point bending test will be used in this project. In this test, the area of uniform stress is quite small and concentrated on the centre loading point. Consider a rectangular beam, on which a simple flexural force is exercised in the centre of the beam with a load as depicted in Figure 2. The standard used is ISO 14125:1998(E) because the results can then be compared with the work of others [11]. A MTS Alliance RT/10 at 10kN couple with the software TESTWORK 4 was used in the tests. The specimens were tested at a crosshead speed of 4 mm/min.

4. Results and discussions

The densities of sawdust of different sizes and phenolic resin were measure using picnometry before sample preparation and are shown in Table 1 from which it can be found that phenolic resin has the lowest density value, and the density of sawdust increases with increasing particles size. Composites were made from three different ranges of particle size of sawdust: <300μm, 300-600 μm, 600-1650 μm.

Figure 3 shows the flexural curve (stress vs. strain). Points B and M are the start and end points of a straight line selected for calculating the slope of the graph. In this case, the line joining the origin, points B and M is a straight line and it seems that points B and M are unnecessary. However, in some stress vs. strain curves, the line joining the origin and point B is not a straight line; it is therefore necessary to find two points, points B and M, so that the line joining them is a straight line, from which Young's modulus can be calculated. Point P is the point of peak load. The composite displays purely elastic behaviour i.e. the material is brittle. It has the same behaviour as ceramics with a high modulus and only elastic stress.

Figure 4 illustrates the flexural modulus of different percentages by weight of sawdust reinforced phenolic composites. From the curve, it can be observed that the addition of sawdust decreases the flexural modulus of the composite; its flexural modulus decreases steadily from 5 to 20% by weight of sawdust; the reduction became stable from 20 to 25%. It can, as far as flexural modulus and cost are concerned, be argued that when particle loading of sawdust is 20%, the composite obtained was the best one. It was observed that there was an increase in the number of pores in the samples with increasing percentage of sawdust and this may be due to the presence of moisture; the number of pores with over 15% by weight of sawdust was particularly obvious and the pores could make the samples more brittle.

Figure 5 shows the flexural modulus of different percentages by weight and particle sizes of sawdust reinforced phenolic resin. Generally speaking, sawdust reduces the flexural modulus of the composites. It can be observed that when the particle size of sawdust was smaller, the dispersion of the particles was better, resulting in a higher flexural modulus. This is due to the easier penetration of smaller particles to the resin network and form composites with better mechanical properties. With sawdust of particle sizes of 600-1650 μm, a large amount of air bubbles were found in the composite and the sawdust tended to stay at the surface of the sample as depicted in Figures 6(a) and 6(b). This means sawdust with this range of particle sizes did not disperse very well and floated to the surface of the composite. The values of flexural modulus of the other two composites with different particulate sizes were lower than their counterpart. However, the trend of the curves was the same.

Figure 7 illustrates the maximum flexural strain of different percentages by weight and particle sizes of sawdust reinforced phenolic resin. The maximum flexural strains (%) of composites with sawdust particulate size of '<300' microns were higher than its counter

parts. However, the maximum flexural strains did not vary much with the percentage of sawdust by weight. Composites with sawdust particulate sizes of 300-600 µm came second. The maximum flexural strains decreased with the increase of percentage of sawdust by weight. As the maximum flexural strain of composite is elastic, it is logical to write

$$\sigma = E.\varepsilon \Leftrightarrow \frac{\sigma}{\varepsilon} = E \qquad (1)$$

Therefore, if E increases then either σ increases or ε decreases.

From the curves of Figure 5, flexural modulus generally went down with an increase in sawdust content. The composite was made more elastic but the sawdust did not improve its maximum flexural strain. Something has to be added to give some plasticity to the composites and garamite and propylene glycol were therefore added.

Figures 8(a) and 8(b) show the cross-sections of samples with [8(a)] and without [8(b)] garamite. With garamite, the colour changed entirely to yellow, so it meant the sawdust was well dispersed in the resin. Garamite combined different mineral morphologies promoted particle spacing creating a product that disperses very easily [12]. This is due to the fact that garamite penetrated the resin network. On the sample without garamite, a second phase could be observed. The second phase is the sawdust. Furthermore, the colour was pink which more like a sample without sawdust looked. With garamite, the colour changed to entirely yellow, so it meant the sawdust was well dispersed in the resin.

Figure 9 illustrates that the flexural modulus of different percentages by weight and particle sizes of sawdust reinforced phenolic resin with and without garamite. It was observed that the samples with garamite have a lower value of flexural modulus. The flexural modulus of these

samples had the same behaviour as those without garamite when the sawdust content increased; the larger the percentage by weight of garamite, the lower the flexural modulus would be but the plasticity moved in the opposite direction as shown in Figure 10, which shows the maximum flexural strain of different percentages by weight and particle sizes of sawdust reinforced phenolic resin with and without garamite. It can be found that samples with garamite have a higher value of maximum flexural strain because they are more plastic and this is in agreement with the curves in Figure 9.

Figure 11 shows the flexural modulus of different percentages by weight of sawdust (<300 μm) reinforced phenolic resin with and without propylene glycol (PG) which was added to give some plasticity to the composite, i.e. to increase the maximum flexural strain. PG penetrated the resin network, but would not create a new network because the temperature of curing is not high enough to polymerize it [1]. It can be argued that the best properties of the composite are when the content of reinforcement is 20% of sawdust and this is in line with the results depicted in Figure 4. Propylene glycol has significant influence on flexural properties of the composites. If the curve with PG (of Figure 11) were divided into two regions, one from 0 to 15% and the other 15 to 25%, a linear dropping in value of flexural modulus is observed between 0 to 15% of sawdust, i.e. propylene glycol and sawdust are miscible and there is no interfacial problem. After 15%, the modulus is more stable at about 750MPa.

The stress-strain curve of the flexural test (Figure 12) shows a plastic (non linear) strain. It means that the composite is less brittle. However, one will never obtain a composite with thermoplastic behaviour i.e. a large plastic strain.

Figure 13 illustrates the maximum flexural strain of different percentages by weight of sawdust reinforced phenolic resin with and without propylene glycol; the values with PG are slightly higher than those without it. It is in accordance with the stress-strain curve in Figure 12. Sawdust does not have a real effect on maximum flexural strain of the composites.

Figure 14 shows the flexural modulus of different percentages by weight of propylene glycol plus 1% garamite reinforced phenolic resin with and without sawdust. Samples with sawdust were made with 15% by weight of sawdust and 1% by weight of garamite. It can be found that the flexural modulus of specimens with sawdust were higher than their counterparts. For both types of composites, the flexural modulus decreased with increasing percentage by weight of propylene glycol. If trend lines were added to the curves in Figure 14, they are found to be parallel; it can be argued that there is a good interface adhesion between resin, sawdust and PG.

Figure 15 illustrates the maximum flexural strain of different percentages by weight of propylene glycol plus 1% garamite reinforced phenolic resin with and without sawdust. It can be found that propylene glycol increases the maximum flexural strain of the composites without or with 15 % by weight of sawdust (< 300 micron). The values of maximum flexural strain with 15 % by weight of sawdust (< 300 micron) were higher than their counterparts and the composites are more plastic.

Nassar discovered the superior reinforcing characteristics of phenol-formaldehyde resin by viewing the samples under scanning electron microscope (SEM). The composites, produced by incorporating phenolic resin into sawdust-rice husk ethylene vinyl acetate mixture, had the best mechanical properties [13]. By viewing fractured samples of the flexural tests under

SEM as depicted in Figure 16, this study reinforced his discovery to be correct, which shows the fractured surface of 15 % by weight of sawdust (<300 μm) reinforced phenolic composite, 100X. It can be found that the sawdust particles were distributed quite evenly and the resin network was well penetrated by the sawdust particles. On the other hand, air bubbles and micro porosities were also found. Figure 17 illustrates a closer look of the bottom left hand corner of Figure 16, 400 X. This further proved that the sawdust particles penetrated the resin network and dispersed evenly [14].

Miyano et al. found that the flexural static and fatigue behaviour was remarkably dependent on time and temperature, in a manner termed as viscoelastic behaviour. On account of the usage of the phenolic composites, e.g. internal compartment for mass transit system, the flexural properties of composites studied here will not be dependent too much on time and temperature [15].

Polymer matrix fibre reinforced composites are usually cured at an elevated temperature and then cooled to ambient conditions. On account of their heterogeneous nature and the very dissimilar expansion or contraction behaviour and mechanical properties of the two components, thermal stresses are generated with ease and will bring about premature failure. The effects are exacerbated by thermal cycling, which involves repeatedly cycling a material between two temperatures with sufficient dwell time at either extreme to allow thermal equilibrium to be attained. Often flexural and traverse tensile properties are reduced and matrix cracking is frequently reported [16].

In this study, the preliminarily ambient cured composite samples were post-cured in conventional oven as mentioned earlier. At each cycle, the specimens were cooled slowly

inside the furnace. It can be argued that the thermal residual stresses due to the manufacturing processes of the composites were minimal due to the slow cooling process. The flexural properties of the composites would not only be affected by the dispersion of the sawdust particles in the phenolic resin but also with the thermal effects. The flexural properties of composites with sawdust particle sizes of < 300 µm would have fewer effects by residual thermal stresses because the sawdust particles would be more evenly dispersed as mentioned earlier and shown in Figures 16 and 17. However, those of specimens with larger sawdust particles would be affected more by residual thermal stresses; aggression of sawdust particles would cause certain part of the composites expand or contract more than the other part of the composites during the manufacturing processes and subsequent service conditions. The extent of effect by the thermal residual stresses on the flexural properties of the composites would be best studied by numerical methods; one such similar study had been carried out by Bouchikhi and Megueni [17]. Similar study will be carried out as an extension of this paper and could be published in another submission. By and large, the flexural properties of the composites, e.g. flexural modulus would be reduced during service due to thermal cycling; fortunately phenolic composites were not usually used in environment that would bring about the above thermal effect.

Hancox also claimed that when thermal degradation occurred it is better to assess damage by measuring a critical property, e.g. flexural modulus rather than trying to predict behaviour on the basis of loss weight. It is concluded that thee is no simple way of predicting the performance of a particular system under prolonged exposure at elevated temperature [18]. However, finite element method will have a position is solving this problem.

Conclusions

In general, the main drawback of phenolic resin or resins is its brittleness, therefore, sawdust was added to the resin. Sawdust decreases the flexural modulus of the composites, i.e. the elasticity of the composite is increased. However, sawdust has no effect on the maximum flexural strain. The best composite properties were obtained with sawdust of particle sizes of <300μm but there were always a lot of pores. Garamite improves the dispersion of the sawdust, which improves the elasticity of the composites but has no effect on the maximum flexural strain. Excellent composite properties were obtained with a suitable combination of garamite and propylene glycol. On the flexural curve of Figure 12, one can observe that there is plastic strain; this means propylene glycol is a plasticizer. Finite element method will be used to compute and analyse the residual stresses, particularly near the sawdust/phenolic interface.

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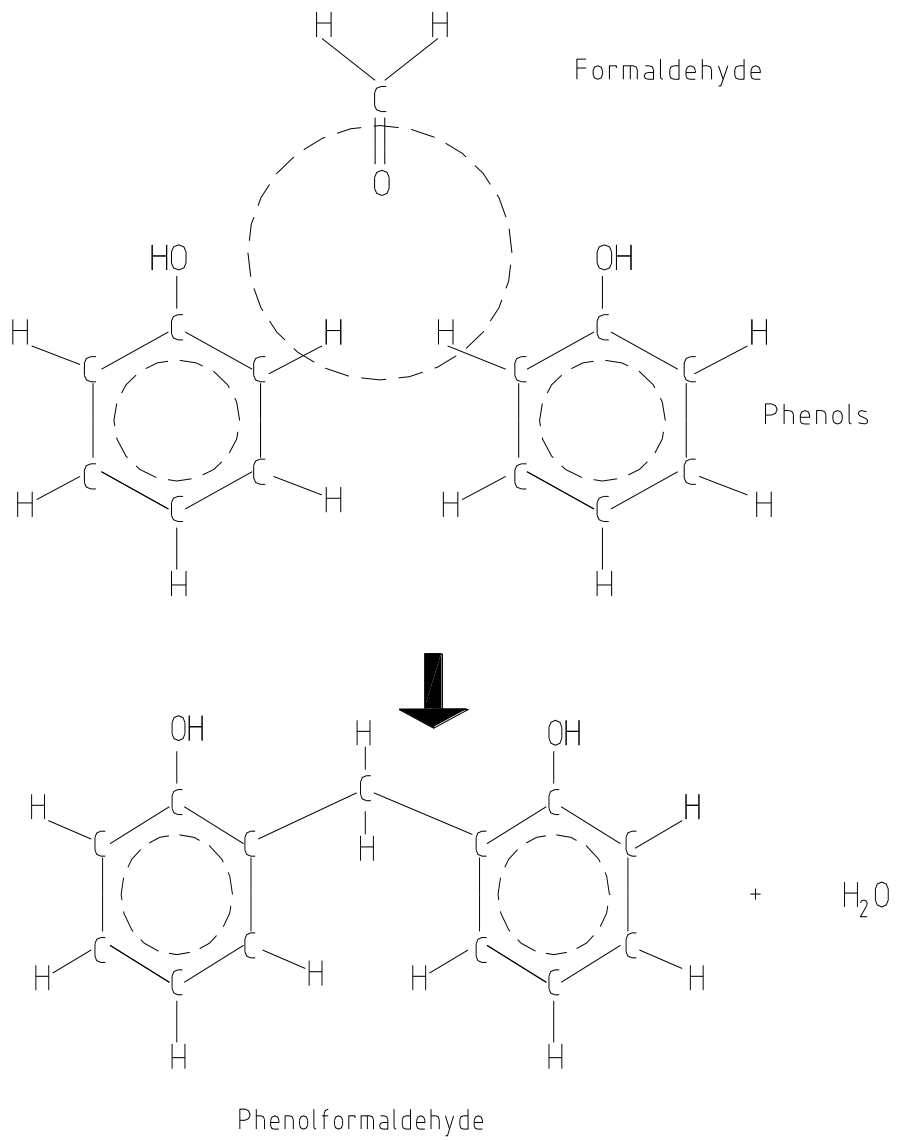
Figure 1: Formation of Phenol formaldehyde

Figure 2: Three-point bending test on flexural specimen
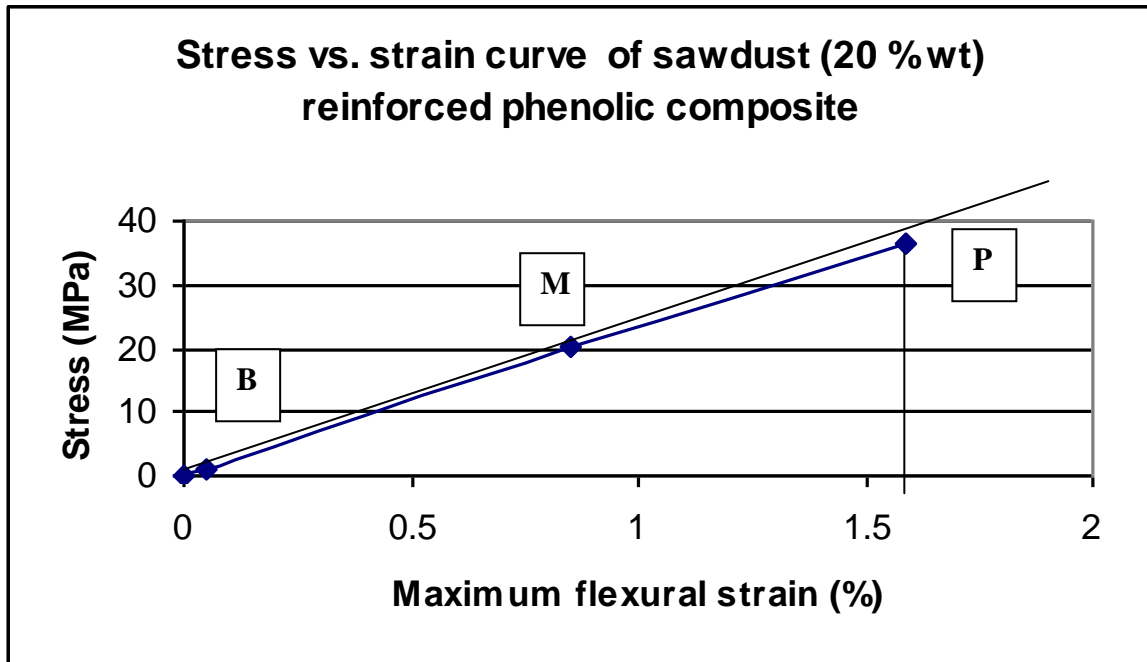
Figure 3: The stress vs. strain curve of sawdust (20% wt) reinforced phenolic composite
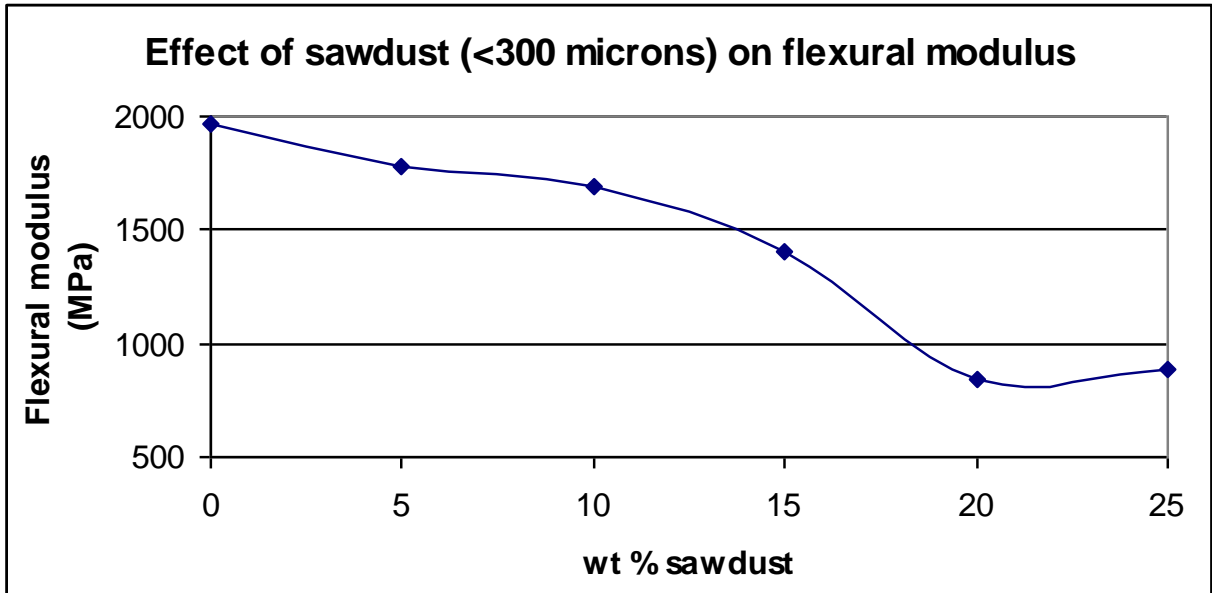
Figure 4: Flexural modulus of different percentage by weight of sawdust reinforced phenolic resin
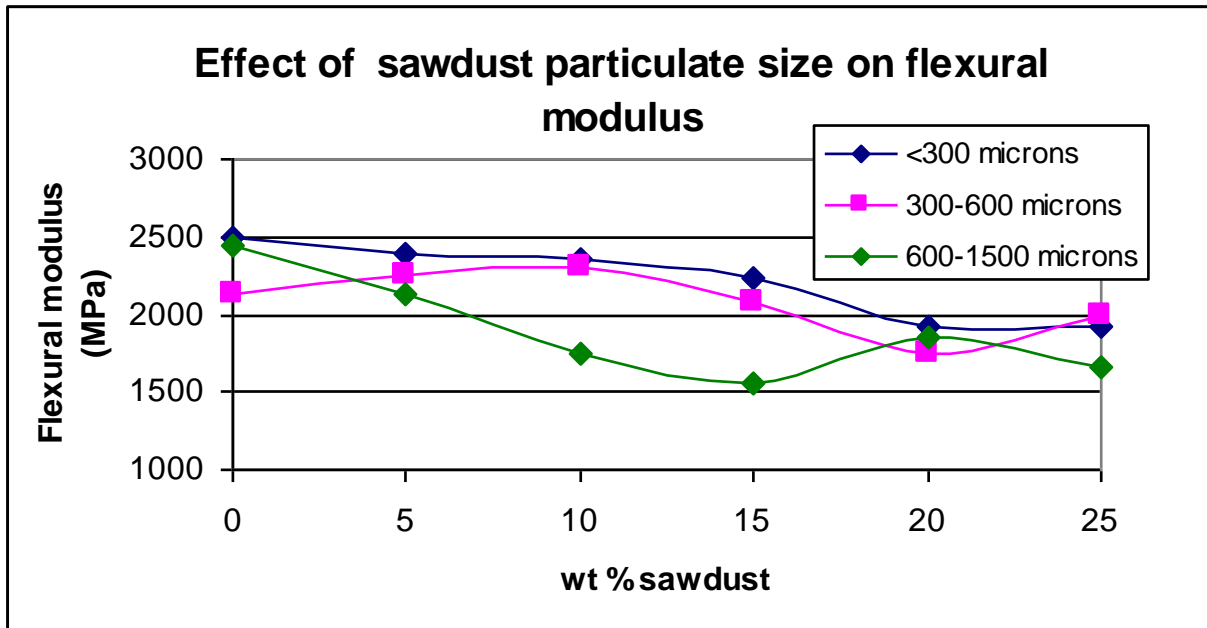
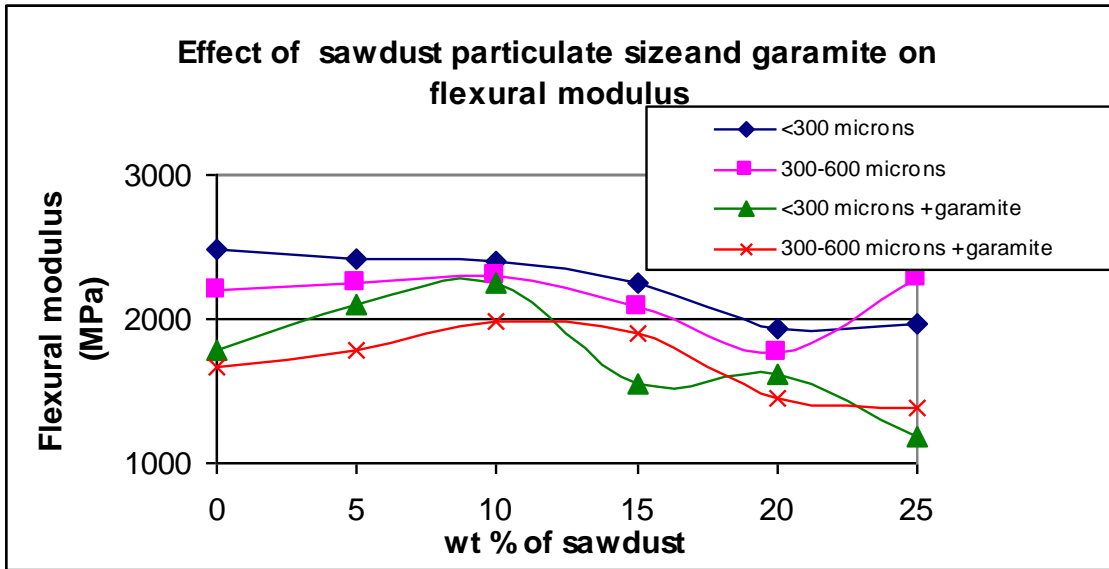**Figure 5: Flexural modulus of different percentages by weight and particule sizes of sawdust reinforced phenolic resin**
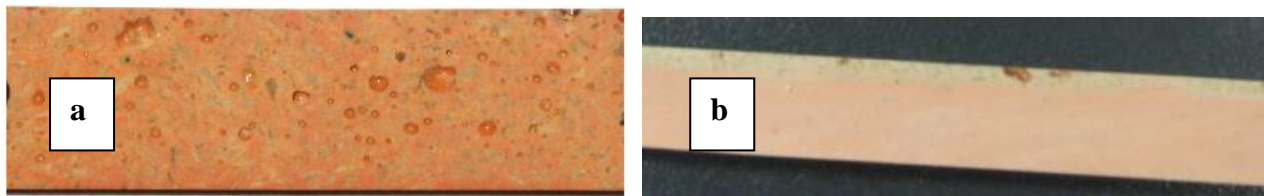

Figure 6: (a) Air bubbles and (b) 2 phases on samples with sawdust of particle size of 600 -1650 μm
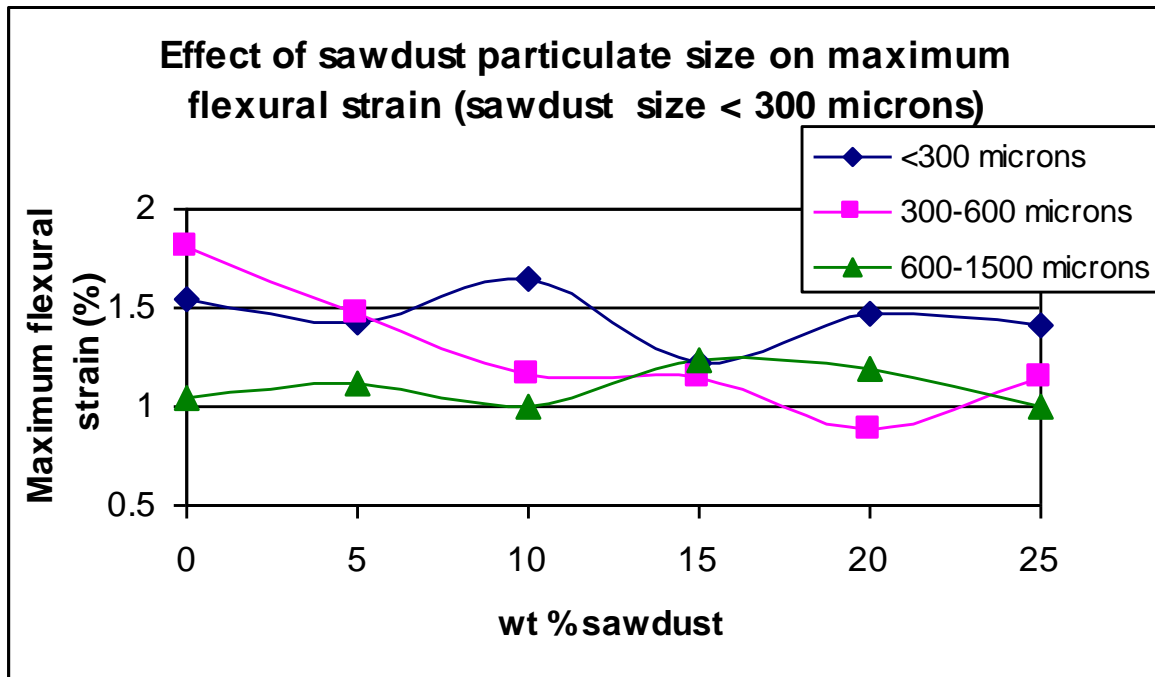
Figure 7: Strain of different percentages by weight of and particle size of sawdust reinforced with phenolic resin
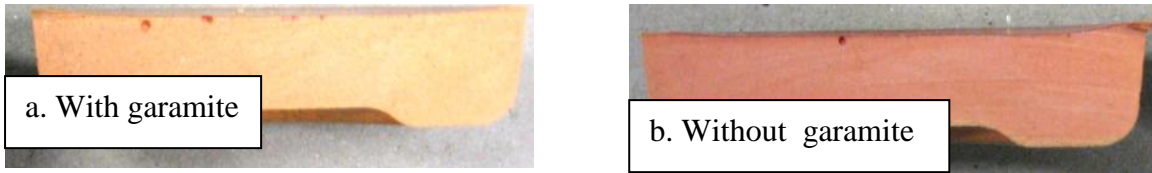
Figure 8: (a) With garamite colour totally changed to yellow, (b) without garamite, presence of second phase and brown in colour

Figure 9: Flexural modulus of different percentages by weight and particle sizes of sawdust reinforced with phenolic resin with and without garamite
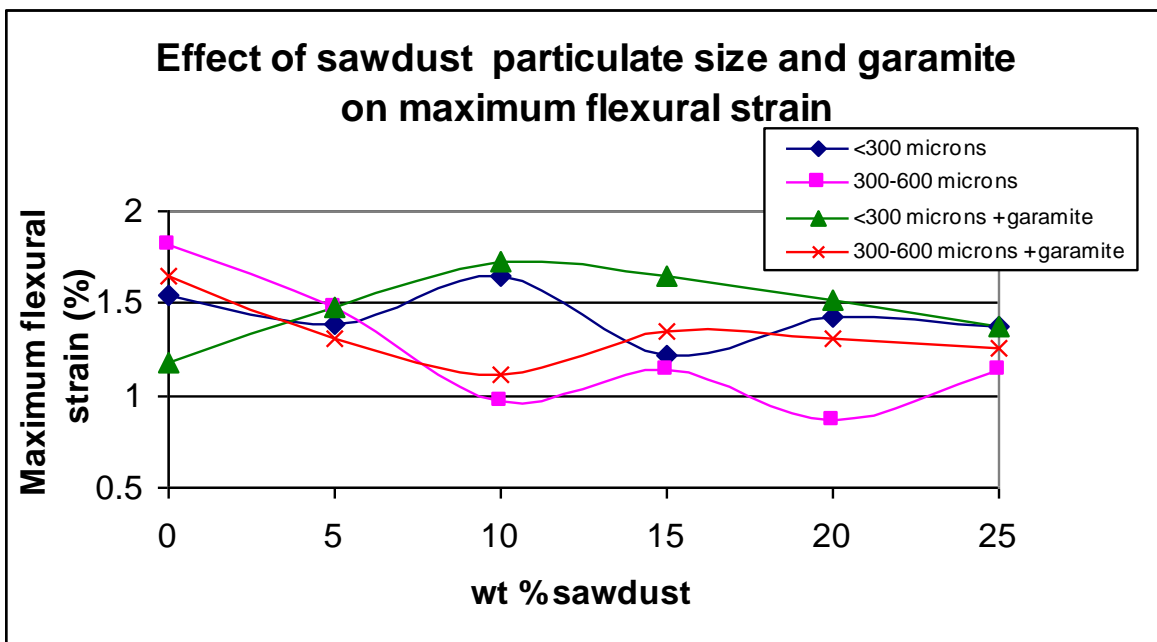
Figure 10: Maximum flexural strain of different percentages by weight and particle size of sawdust reinforced with phenolic resin with and without garamite
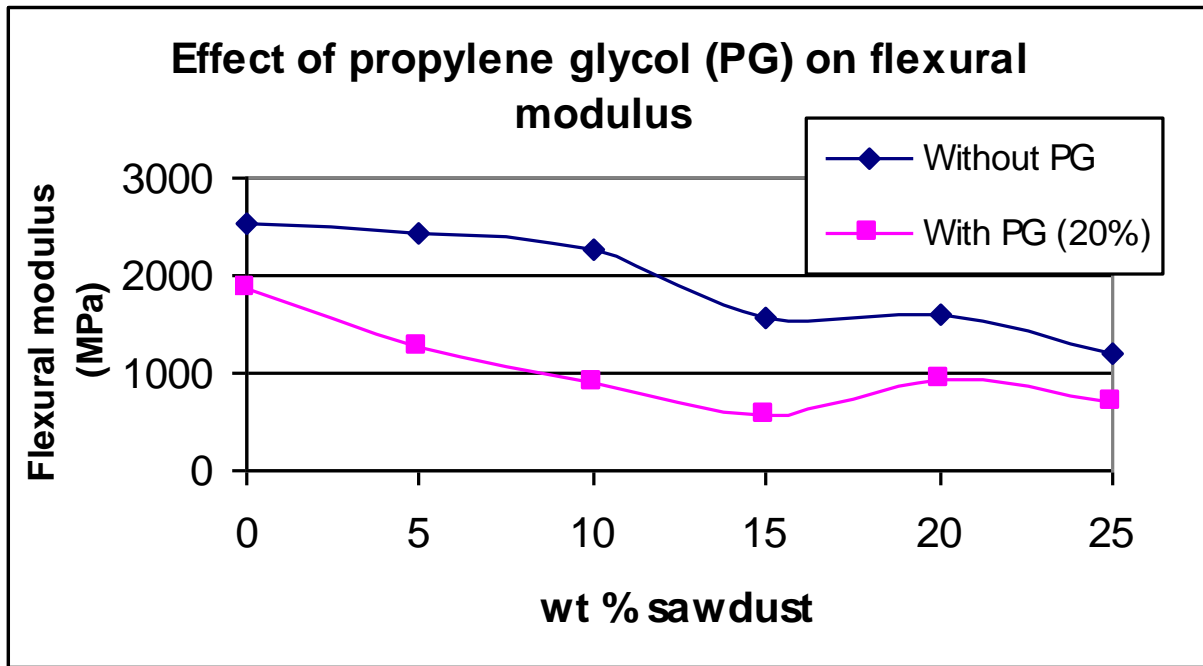
Figure 11: Flexural modulus of different percentages by weight of sawdust reinforced with phenolic resin with and without propylene glycol (PG)
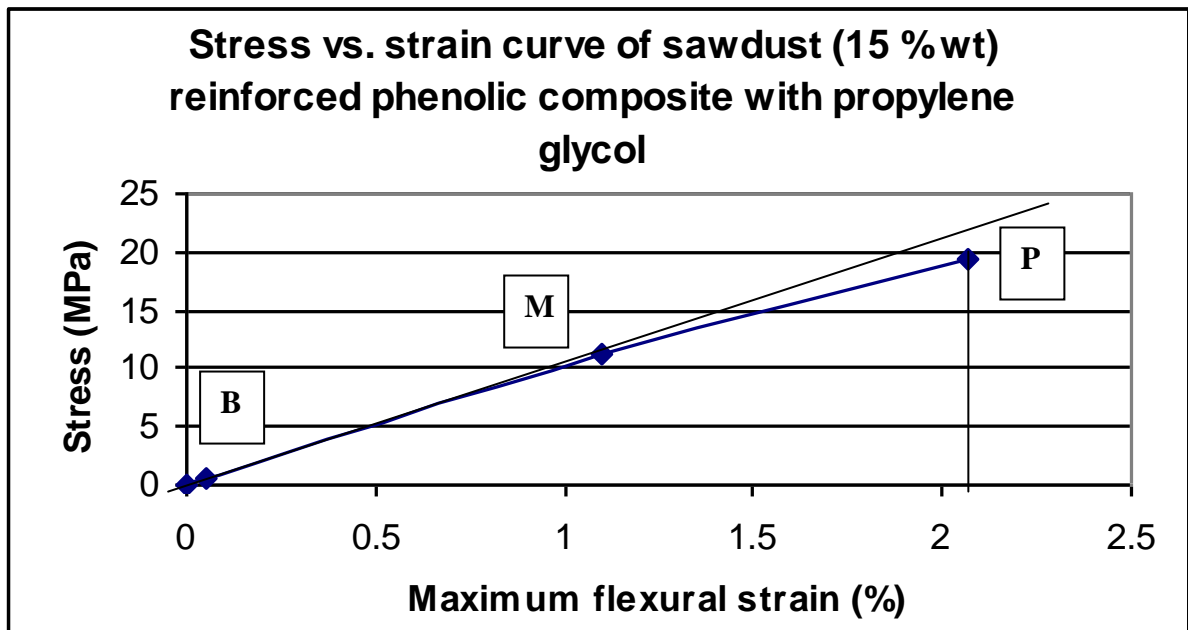
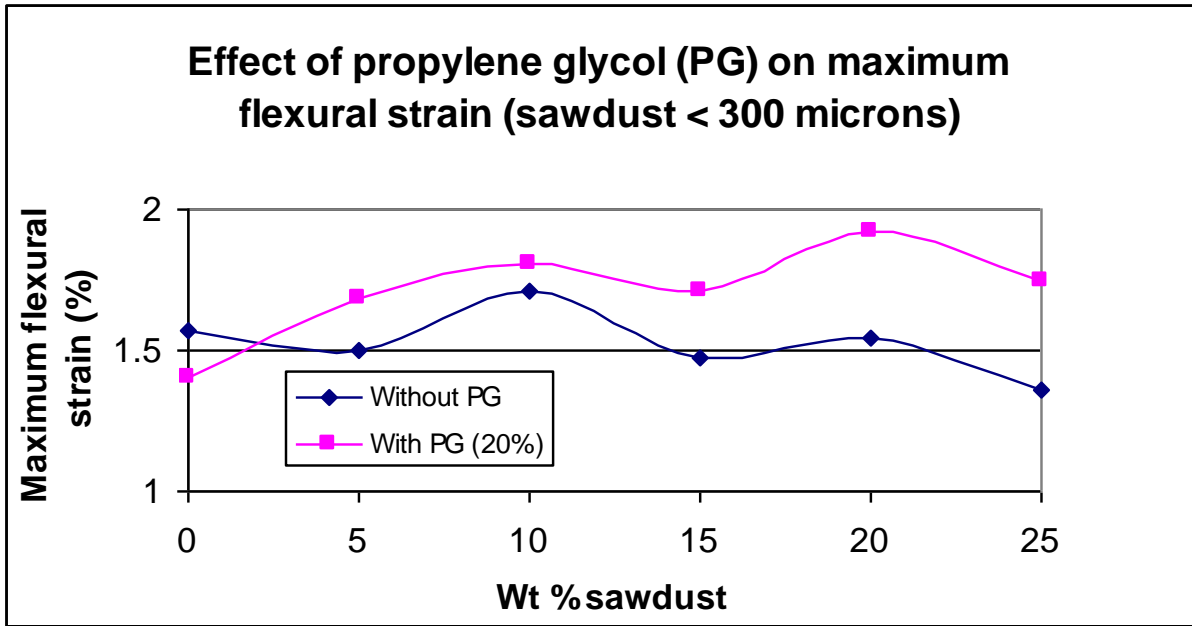**Figure 12: the stress vs. strain curve of sawdust (15% wt) reinforced phenolic composite with propylene glycol**

Figure 13: Maximum flexural strain of different percentages by weight of sawdust reinforced phenolic resin with and without propylene glycol (PG)
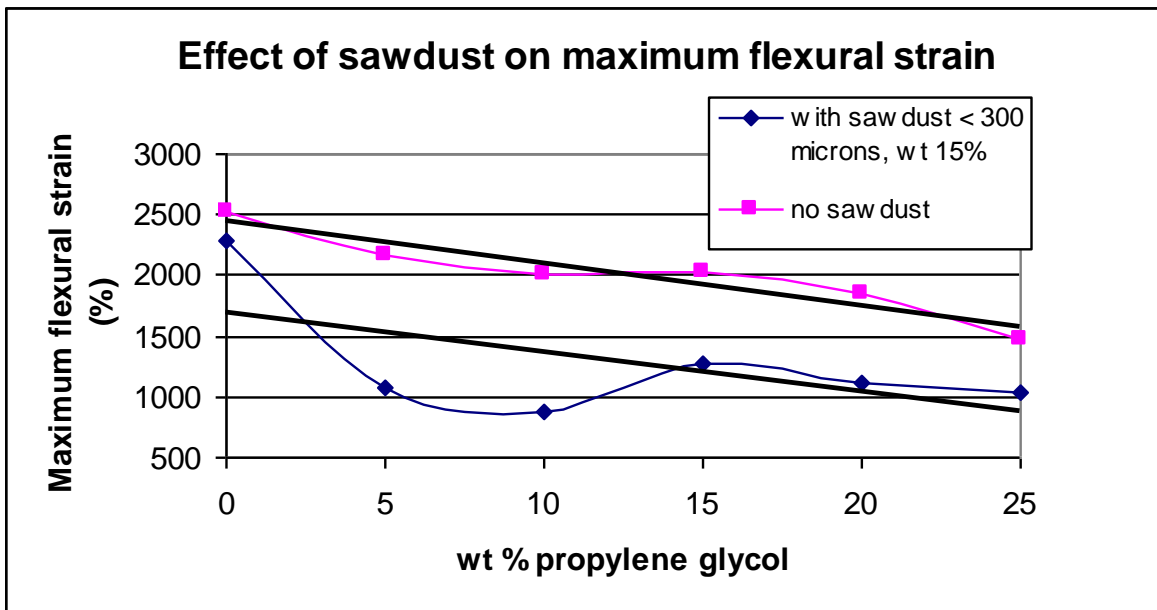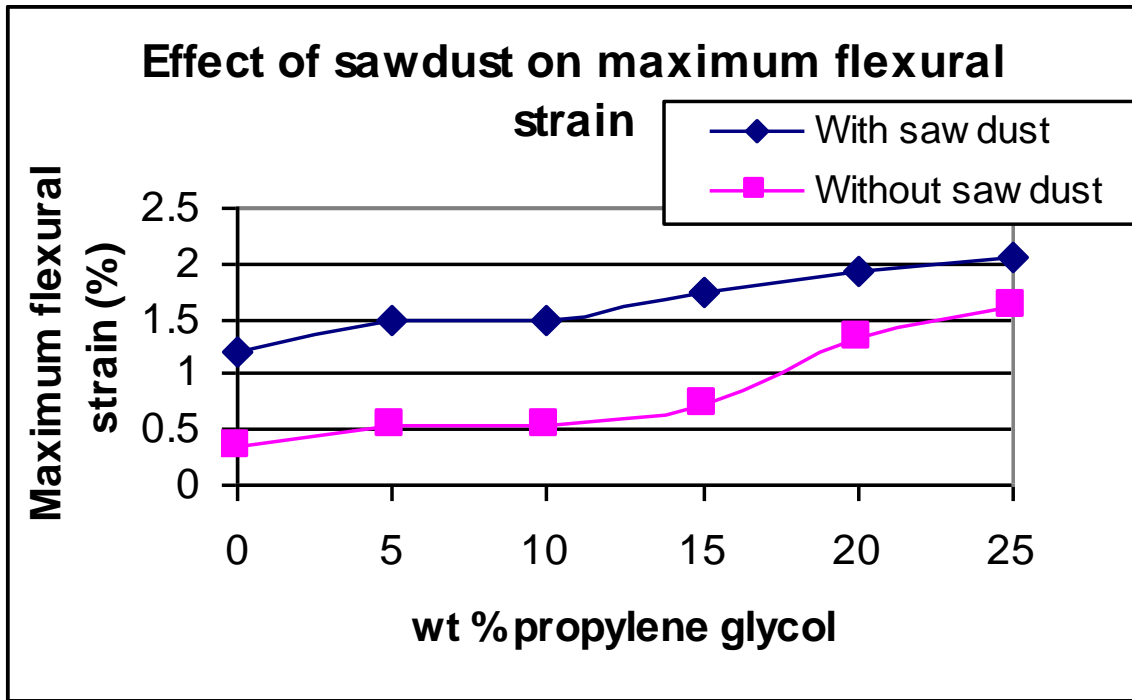

Figure 14: Maximum flexural strain of different percentages by weight of propylene glycol plus 1% garamite reinforced phenolic resin with and without sawdust

Figure 15: Maximum flexural strain of different percentages by weight of propylene glycol plus 1% garamite reinforced phenolic resin with and without sawdust
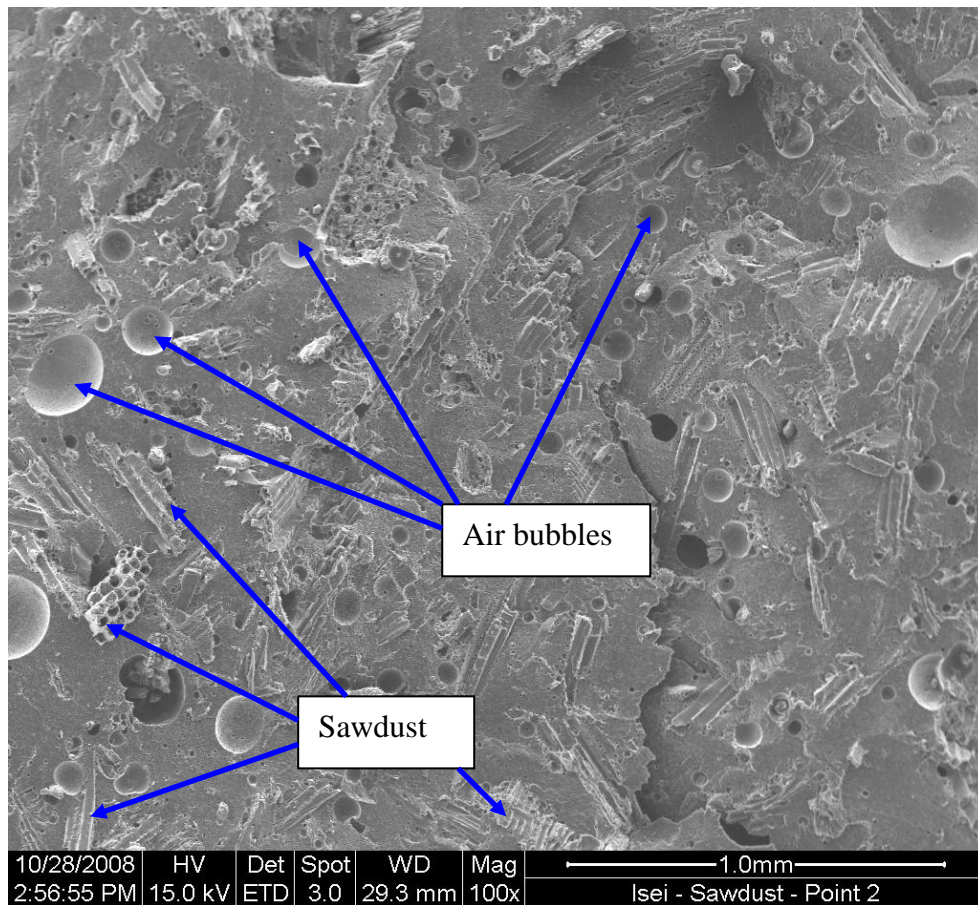

Figure 16: Fractured surface of 15 % by weight of sawdust (< 300 μm) reinforced phenolic composite, 100 X
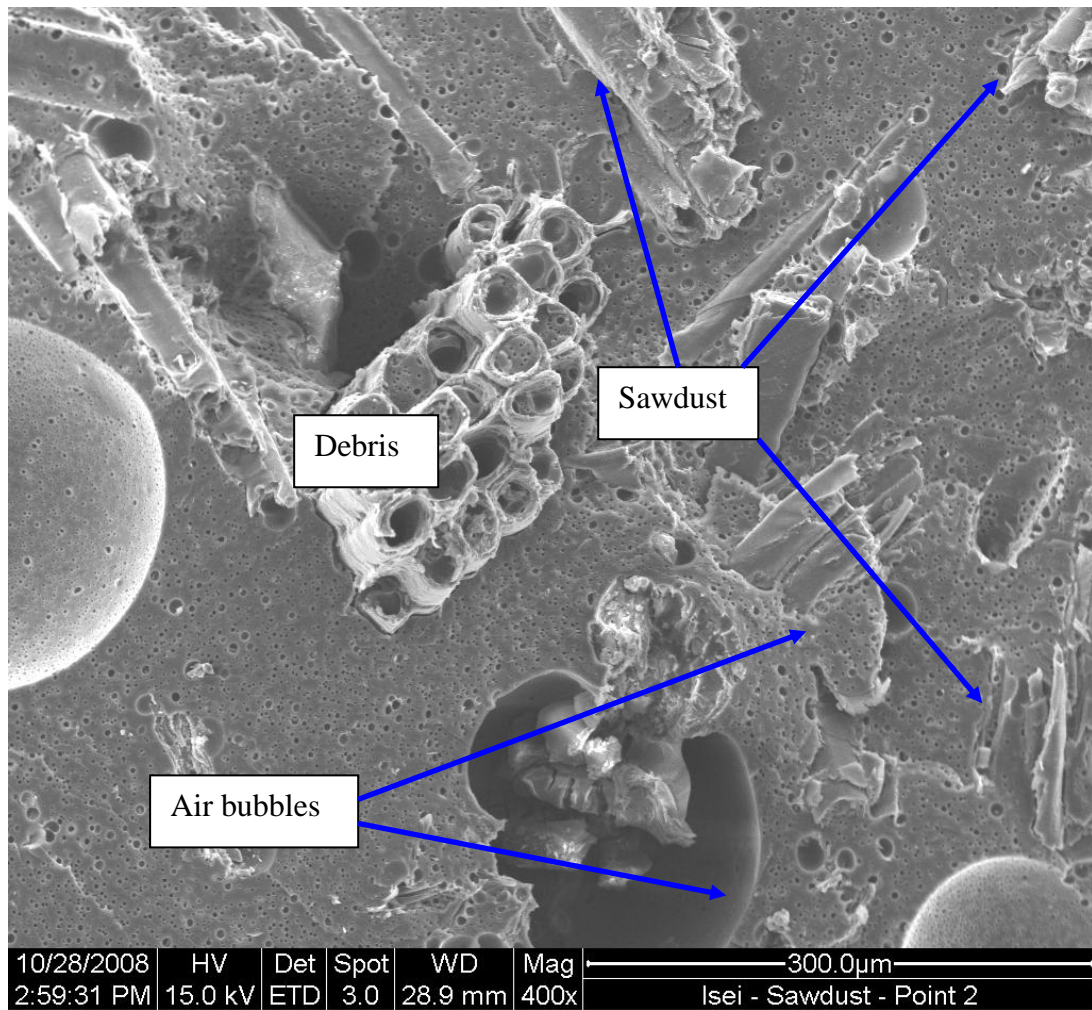
Figure 17: A closer look of the bottom left hand corner of Figure 16, 400 X

Table 1: Densities of the sawdust of different particle sizes.

Particles size of sawdust	<300µm	300-600 µm	600-1650 µm	Phenolic resin
Density (g/cm^3)	0.29	0.31	0.36	1.2353