Thermal properties of sawdust reinforced vinyl ester composites post-cured in microwaves: pilot study

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Abstract: The mechanical properties of sawdust reinforced vinyl ester resin composites post-cured in microwaves have been measured and evaluated in earlier studies. This basic but critical and important data have caused interests in the relevant industry in Australia. This study is therefore carried out to measure and evaluate the thermal properties of the composites with a view to benefit the civil and construction industry as the materials are used in the industry. The original contributions of this paper are that samples post-cured in microwaves, irrespective of the percentage by weight and particle size of sawdust, have higher glass transition temperatures than their counterparts post-cured in an oven; these imply that the stiffness of the samples post-cured in microwaves are higher than their peers. From previous study, it was discovered that the fracture toughness increased with increasing particulate loading. These properties are vital in civil engineering applications because civil structures need composites with high rigidity and fracture toughness. It is hoped that the discussions and results in this work would not only contribute towards the development of sawdust reinforced vinyl ester composites with better material properties, but also useful for the investigations of thermal and mechanical properties in other composites.

Introduction

The Centre for Excellence in Engineered Fibre Composites (CEEFC) at the University of Southern Queensland (USQ) seeks to facilitate the development and introduction of lightweight composite materials into engineering commercial applications. The most commonly used thermosets as composite matrices are unsaturated polyesters, epoxies and vinyl esters. Unsaturated polyesters dominate the market, whereas epoxies are preferred in high-performance applications. Unsaturated polyester offers an attractive combination of low price, reasonably good properties, and simple processing. However, basic unsaturated polyester formulations have drawbacks in terms of poor temperature and ultra-violet tolerance. Additives may significantly reduce these disadvantages to suit most applications. Where mechanical properties and temperature tolerance of unsaturated polyesters no longer suffice, epoxies are often used due to their significant superiority in these respects. These improved properties come at a higher price and epoxies are most commonly used in areas where cost tolerance is the highest [1]. Epoxy vinyl ester range of resins (vinyl ester resins) was developed in the 1960s [2]. Vinyl esters (VE), as they are usually called, are closely chemically related to both unsaturated polyesters and epoxies and in most respects represent a compromise between the two. They were developed in an attempt to combine the fast and simple crosslinking of unsaturated polyesters with the mechanical and thermal properties of epoxies [1].

The pure vinyl ester resin is brittle and one approach to increase the performance and minimize the costs of the resin is to reinforce it with fillers. As the structural products are cast to shape, the best option to reinforce the vinyl ester resin is to mix it with particulate fillers. In this study, thermal properties of the prepared composites were investigated with

the percentage by weight and particle size of sawdust varied. The composites were cured in conventional oven and in microwaves.

The sawdust content in the resin was varied from 5% w/t to 15% w/t. Above this percentage, it became very difficult to mix. The sawdust was mixed with the resin without any treatment. MEKP (methyl ethyl ketone perioxide) was the hardener used for curing. Before subjecting the samples for short bar tests, they were cured under ambient conditions for 24 hours and then post-cured in microwaves. The MTS 810 universal tensile testing machine was used for the testing.

The Materials

The vinyl ester resin used is Hetron 922 PAS in summer and Hetron 922 PAW in winter. The vinyl ester is dissolved in 50% by weight of styrene. In this study, Hetron 922 PAW was used. The resin hardener (methyl ethyl ketone peroxide, MEKP) ratio used in this study was 98% resin by volume and 2% hardener by volume [3].

The sawdust used was pine waste from sawmills. It has a variety of practical uses, including fuel and manufacturing of the particle board. Until the advent of refrigeration, it was often used in icehouses to keep ice frozen during summer. In terms of hazards it is flammable when in contact with fire [4]. It was sieved with three sieves different sizes, <300 μm, 300-425 μm and 425-1180 μm. The sawdust particles reduce the weight of the composites, lowering its cost and improving its performance.

The Composite Samples

The reinforcer was glass powder (glass hollow spheres) particulates and they were made 5 % to 15% by weight in the cured vinyl ester composite, VE/GP (X %), where X is the percentage by weight of the filler. As the raw materials of the composites are liquid and glass hollow spheres, the specimens of 60 mm x 4 mm x 10 mm were cast to shape. The resin is first mixed with the hardener. After that the sawdust was added to the mixture, they were then mixed to give the uncured composite. The mixture of sawdust, resin and hardener was blended with mechanical blender to ensure a more homogenous mixture. 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 releasing agent (wax) to enable easy release of the samples after curing. The uncured composite was then cast into the moulds curing in ambient conditions. Table 1 shows the mass in grams of resin, hardener and sawdust required respectively to make 1000 grams of uncured composite of 10 % by weight of sawdust.

After initial 24-hour curing, half of the test pieces were removed from the mould and had their thermal properties were measured using dynamic mechanical thermal analysis (DMTA) technique.

The other half of the samples was post-cured in microwaves. The specimens (6 pieces) were placed on the oven plate evenly. The samples were post-cured in microwaves for 10 minutes using a power level of 480 W and the temperature reached would be 100 ^{o}C. The temperature was measured using an Oakton Temp Testr Infra Red handheld thermometer.

Allow the samples to cool in the oven cavity to room temperature [5]. The thermal properties of the specimens were then measured.

Dynamic Mechanical Thermal Analysis (DMTA)

DMTA is a technique used to study and characterize materials. It is most useful for observing the visco-elastic nature of polymers. Two methods are currently used. One is the decay of free oscillations and the other is forced oscillation. Free oscillation techniques involve applying a force to a sample and allowing it to oscillate after the force is removed. In this project, forced oscillation was employed. Forced oscillations involve the continued application of a force to the sample. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. This method is the most commonly used one today. Samples can be either solids or melts. Most solids are tested by linearly applying strains, and melts or liquids are normally tested in shear. The sample deforms under the load. From this, the stiffness of the sample can be determined, and the sample modulus can be calculated. Two quantities are obtained from the measurement, one is storage modulus, E', a measure of the energy stored during a cycle, and the other is loss modulus, E'', a measure of the energy lost and converted into heat. The quantity E'' has a maximum at the glass transition temperature of the polymer, where it softens from a glassy to a rubbery polymer. The quantity tan δ is the ratio of E'' to E'."

By measuring the time lag in the displacement compared to the applied force it is possible to determine the damping properties of the material. The time lag is reported as a phase lag, which is an angle. The damping is called tan δ, as it is reported as the tangent of the phase lag. Visco-elastic materials such as polymers typically exist in two distinct states. They

exhibit the properties of a glass (high modulus) at low temperatures and those of a rubber (low modulus) at higher temperatures. By scanning the temperature during a DMA experiment change of state, the glass transition or alpha relaxation can be observed. The glass transition temperature (T_g) is often measured by DSC (Differential Scanning Calorimetry), but the DMA technique is more sensitive and yields more easily interpreted data. DMA can also be used to investigate the frequency (and therefore time) dependent nature of the transition. This is useful as the degree of dependence is specific to the transition type. T_g has a strong dependence on frequency but melting is frequency independent; DMA can also resolve sub-T_g transitions, like beta, gamma, and delta transitions as the DSC technique is not sensitive enough to pick them up in many materials that. In addition, DMA gives modulus values. Frequency is constant and the temperature is varied [6].

In the test, an oscillating force is applied to a sample while the temperature is varied the resulting displacement of the sample is measured. The sample dimension used in the test was 60 mm x 10 mm x 4 mm; the frequency of oscillation was 1 Hz. UNIVERSAL ANALYSIS 2000, the software used, carries out the calculations. From these experiments, graphs of tangent delta loss and storage modulus were produced.

Results and discussions

Figures 1 and 2 (for 5 % w/t of sawdust, particle size is 425-1180 µm) show that the glass transition temperatures of, samples cured in an ambient conditions and microwaves were 119.97 ^{o}C and 122.14 ^{o}C respectively. This means that the sample post-cured in microwaves was stiffer than its counterpart. They also illustrate that the mechanical loss tangent (tangent delta) of the sample cured in ambient (1.13 at T_g) conditions was also higher than its peer

(1.00 at T_g). Samples post-cured in microwaves would have most of their water content in the composites expelled and vaporized by the microwave irradiation. This phenomenon has been supported by the fact that the mechanical loss tangents of the specimens post-cured in microwaves were lower than their counterparts. As a result of the above characteristics, the composites became stiffer and this was also reflected by the higher glass transition temperatures of samples post-cured by microwave irradiation. This is in line with the glass transition temperature implication higher mechanical loss tangent means more energy can be converted into heat during deformation and the material is softer. This does match the phenomenon for most materials. Moreover, the highest storage moduli for ambient cured and microwave post-cured samples were 1,836 MPa and 1,784 MPa respectively; in general, for the range of temperature measured, the storage modulus of sample cured in ambient conditions was higher than its counterpart.   This is in line with the glass transition temperature implication because higher storage modulus means more energy can be stored in the material during deformation.   The results are in line with those obtained in previous studies [7, 8].

Figures 3 and 4 (for 10 % w/t of sawdust, particle size is 425-1180 µm) show that the glass transition temperatures of sample cured in an ambient conditions and microwaves were 119.00 ^{o}C and 126.28 ^{o}C respectively. This means that the sample post-cured in microwaves was stiffer than its counterpart. They also illustrate that the mechanical loss tangent (tangent delta) of the sample cured in ambient (1.02 at $T_{g)}$ conditions was also higher than its peer (0.86 at T_g). This is in line with the glass transition temperature implication as higher mechanical loss tangent means more energy can be converted into heat during deformation and the material is softer. This does match the phenomenon for most materials. The reasons are the same with samples with 5 % wt of sawdust. Moreover, the highest storage moduli for

ambient cured and microwave post-cured samples were 1,735 MPa and 1,692 MPa respectively; in general, for the range of temperature measured, the storage modulus of sample the cured in ambient conditions was higher than its counterpart.   This is in line with the glass transition temperature implication because higher storage modulus means more energy can be stored in the material during deformation.   The results are in line with those obtained in previous studies [7, 8].

The results for 15 % w/t with the same particle size were the same as above and the reasons are also the same. By viewing at Figures 2 and 4, it can be found that for the samples post-cured in microwaves; higher particulate loadings resulted in higher glass transition temperature. The stiffness of the samples can be argued to increase with increasing wt % of sawdust. On the other hand, the storage modulus decreased with increasing sawdust by weight of the composites. This was matched by the mechanical loss tangent for the range of temperature measured. Both, the storage modulus and mechanical loss tangent confirmed the above argument that the stiffness of the samples increased with increasing wt % of sawdust. The trend is the same with that of the fracture toughness, a critical value of the stress-intensity factor at a crack tip necessary to produce catastrophic failure under simple axial loading, of the three types of composites (5% w/t %, 10 % w/t and 15 % w/t of sawdust) as depicted in Figure 5 [5, 9]. The fracture toughness of VE/sawdust increased with sawdust content. The values of the fracture toughness and their standard deviations of VE/sawdust with varying particle sizes and percentage by weight were tabled in Table 2. As the values of the standard deviation were not large, it can be argued that the values of the fracture toughness were correct and reliable.

Ray et al. prepared vinyl ester resin matrix composites with a fly ash loading of 30, 40, 50 and 60 w/t %. It was found in their study that the flexural modulus values showed a steep rise up to 50 w/t-% filler loading, and the increase was 9.5, 56.74 and 112.24%, respectively, in case of 30, 40 and 50 w/t % filler loaded composites, compared to the neat resin (Figure 6). It indicated that at 50 w/t % loading, the rigidity of the composites were highest [10]. Similar increase in flexural modulus was observed by Bose et al. [11] as depicted in Figure 7. Ku et al. also found the same trend in flexural modulus behaviour in their study in glass powder reinforced phenolic composites as shown in Figure 8 [12].   Again, in Ray et al.'s case, there was a fall in the flexural modulus values in the 60 w/t % loaded composites due to insufficient penetration of the resin into the filler particles. With the addition of fly ash particles, the composites became brittle as evident from their strain vs. fly ash loading [10]. The same explanations can be applied to the cases of Ku et al. and Bose et al.

Karger-Kocsis et al. produced hybrid thermosets from polymeric diphenyl isocyanate (PMDI), styrene cross-linkable vinyl ester (VE) and water glass (WG) using melamine formaldehyde (MF) resin as additional reactive emulsifier.   VE was added to PMDI/MF mixture in which WG was dispersed next. The content of MF in the resin formulation was varied between 0.5 and 15 w/t %. The resulting thermosets were cured at room temperature for 24 hours and then post-cured at 100 ^{o}C for 4 hours.   The DMTA properties of the resin were then assessed [13].   Table 3 shows the composition and designation of 3P/VE/MF hybrid systems. The flexural modulus increased with increasing MF content as depicted in Table 4 [13].   On the other hand, flexural strength increased with MF loading as shown in Table 4. These are in line with the results obtained by Ray et al. [9].   The stiffness and strength of the hybrids were higher markedly higher than those of the 3P resin, but lower than those of 3P/VE hybrids as depicted in Table 4 [13]. However, unlike the case of this studies,

the fracture toughness, unexpectedly s decreased with increasing MF as illustrated in Table 4[13].

Consider Figures 1, 3 and 9, it can be found that the stiffness of samples cured in ambient conditions also decreased with increasing particulate loading as indicated by their glass transition temperatures and mechanical loss tangents. The increase in the particulate content increased the brittleness of the composites as indicated by Ray et al. [10].

With reference to Figures 1 and 3, and 2 and 4, it can be found that the samples cured in ambient conditions had lower glass transition temperatures than those of their counterparts. This is matched by their higher delta tangent values. The samples were therefore stiffer than their peers. It can therefore be argued that samples post-cured in microwaves had higher fracture toughness than their counterparts, particularly at higher particulate loading.

Figures 10 and 11 (for 10 % w/t of sawdust, particle size is ≤ 300 µm) show the DMA results of the composites cured under ambient conditions and post-cured in microwaves. They show that the sample post-cured in microwaves was stiffer than its counterpart cured under ambient conditions. The situation is exactly the same to that show by Figures 3 and 4, in which the w/t % of the sawdust was the same except the sawdust particle size was 425-1180 µm. The reasons were the same as those mentioned for samples with particle size ranging from 425-1180 µm. The results are in line with those obtained in previous studies [7, 8]. Similar results were obtained for the 5 % w/t and 15 % w/t composites.

Figures 12 and 13 (for 15 % w/t of sawdust, particle size is 300 - 425 µm) show the DMA results of the composites cured under ambient conditions and post-cured in microwaves.

They show that the sample post-cured in microwaves was stiffer than its counterpart cured under ambient conditions. The situation is exactly the same to that show by Figures 10 and 11, in which the w/t % of the sawdust was the same except the sawdust particle size was ≤ 300 μm. The reasons were the same as those mentioned for samples with particle size ≤ 300 μm. The reasons are the same with samples with sawdust with particle size ≤ 300 μm and ranging between 425-1180 µm. mentioned above. The results are in line with those obtained in previous studies [7, 8]. Similar results were obtained for the 5 % w/t and 10 % w/t composites. The trend is again the same with that of the fracture toughness, a critical value of the stress-intensity factor at a crack tip necessary to produce catastrophic failure under simple axial loading, of the three types of composites (5% w/t %, 10 % w/t and 15 % w/t of sawdust) as depicted in Figure 14 [5, 9].

Conclusions

This study evaluated the relationship between the glass transition temperature, storage modulus and loss modulus, of sawdust filled vinyl ester composites cured in ambient conditions and post-cured in microwaves. It was discovered that the stiffness of samples post-cured in microwaves were higher than their ambient cured only counterparts. It was discovered that the stiffness of the samples increased with increasing wt % of sawdust. Furthermore, the trend the fracture toughness of the composites was the same. The results of this study matched those of other studies made by Ku et al. [14].

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Sample: 1.180-mm Sawdust -5% VE
Size: 35.0000 x 9.6100 x 5.5300 mm
Method: Temperature Ramp
Comment: 1.18mm Sawdust -5% VE Ambient curing

DMA

File: C:...\MALAY-2009\Sample-1 ambient.001
Operator: Francisco Cardona
Run Date: 03-Jul-09 13:08
Instrument: DMA Q800 V5.1 Build 92
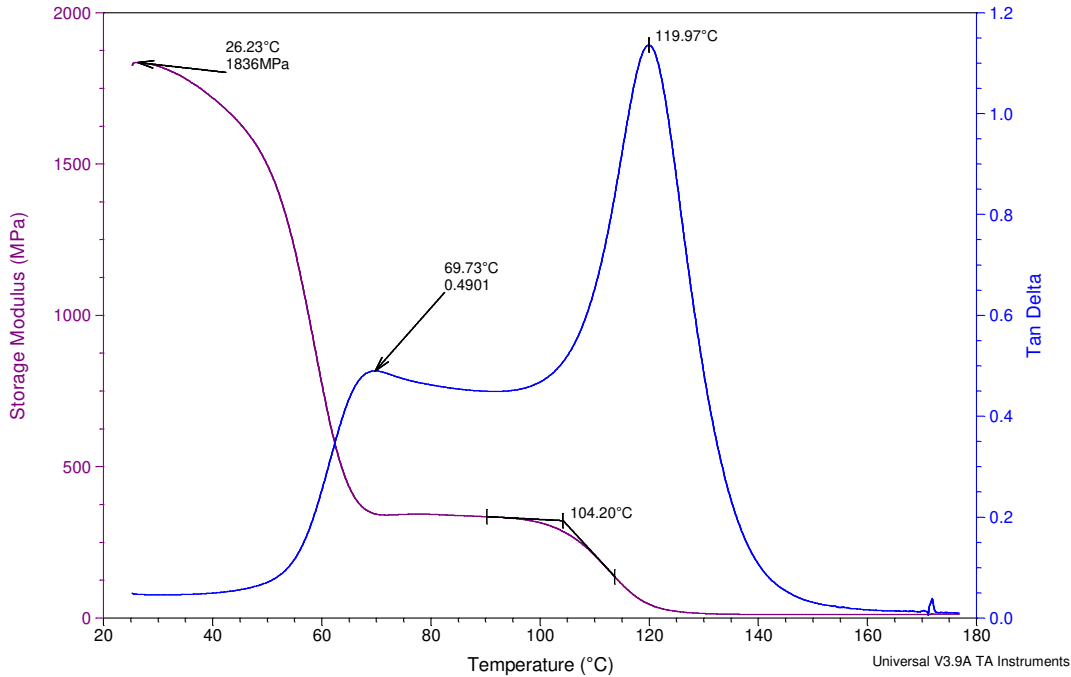
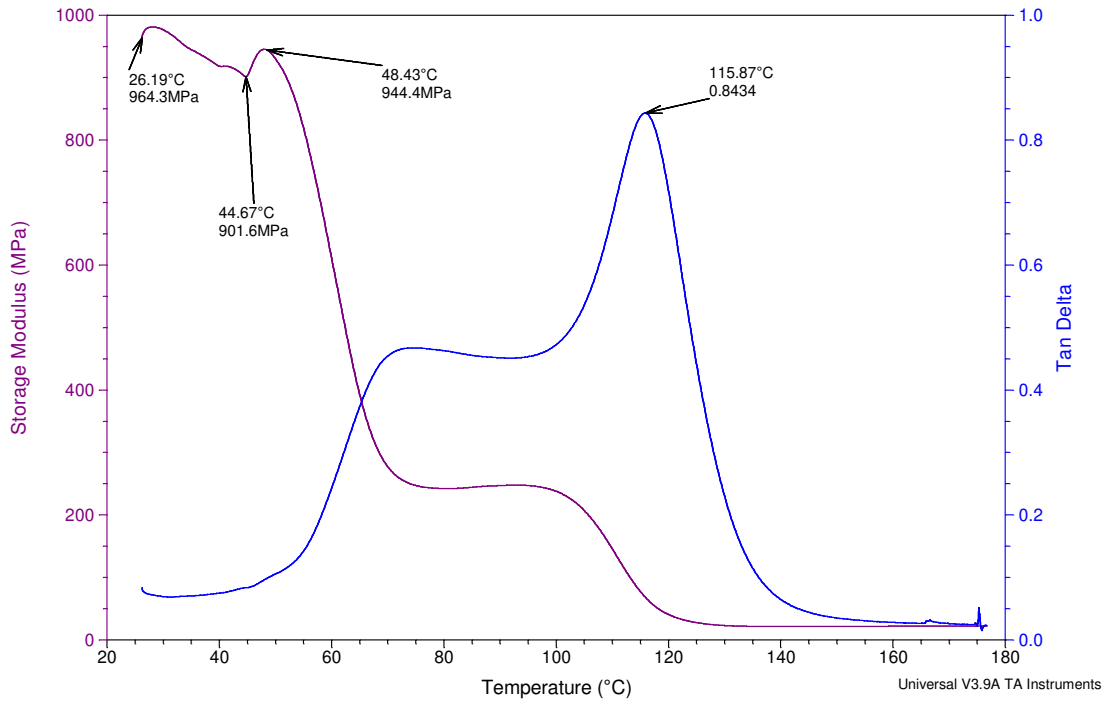**Figure 1: DMA results of 5% sawdust (425 - 1180 μm) reinforced vinyl ester resin cured at ambient conditions for 24hours**

Sample: Sampl-17 1180micr-5 VE microwav
Size: 35.0000 x 9.8300 x 6.2000 mm
Method: Temperature Ramp
Comment: Sample-17 1180microns-5% VE microwave

DMA

File: C:...\MALAY-2009\Sample-17 microwave.001
Operator: Francisco Cardona
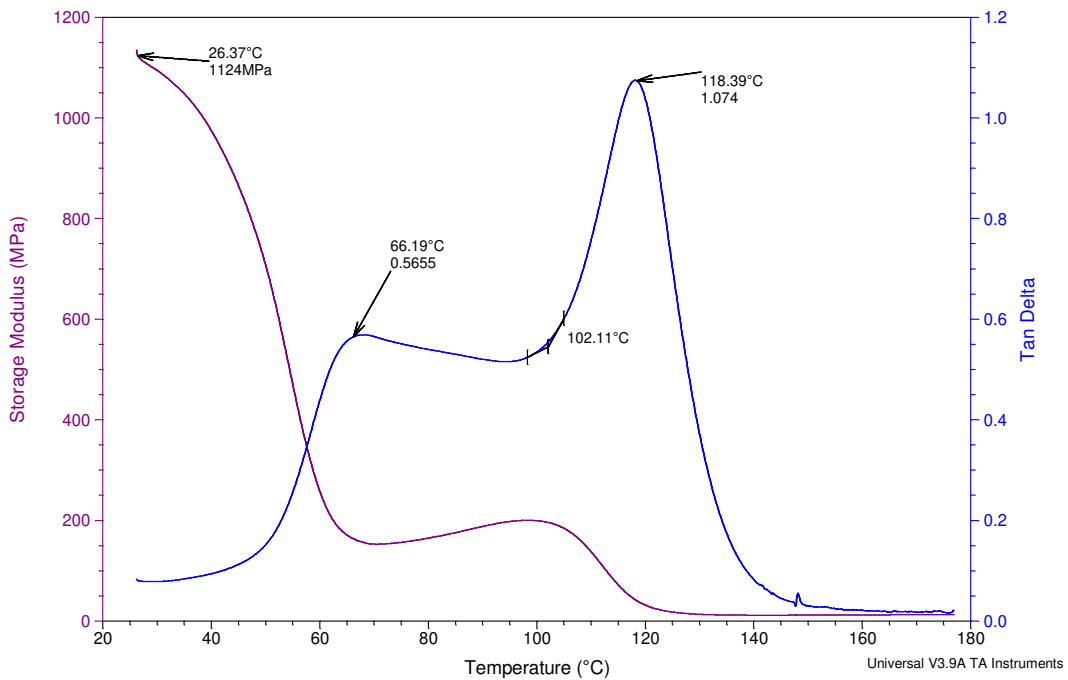Run Date: 03-Jul-09 13:08
Instrument: DMA Q800 V5.1 Build 92
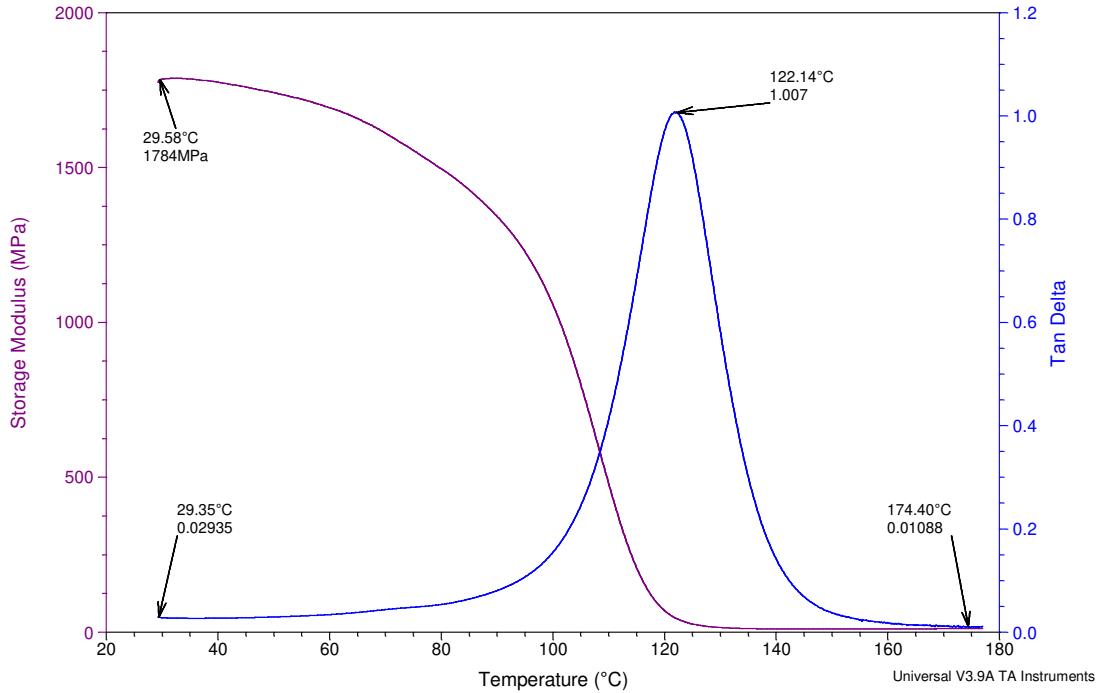
Figure 2: DMA results of 5% sawdust (425 - 1180 μm) reinforced vinyl ester resin post-cured in microwaves

Figure 3: DMA results of 10% sawdust (425 - 1180 μm) reinforced vinyl ester resin cured at ambient conditions for 24hours
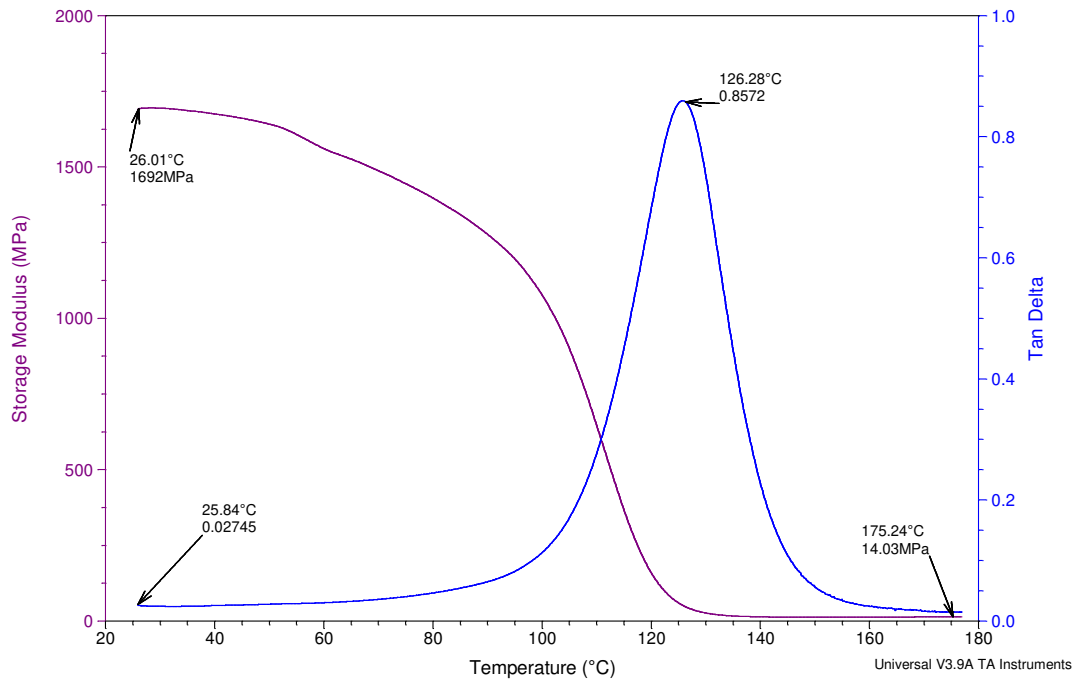
Figure 4: DMA results of 10% sawdust (425 - 1180 μm) reinforced vinyl ester resin post-cured in microwaves
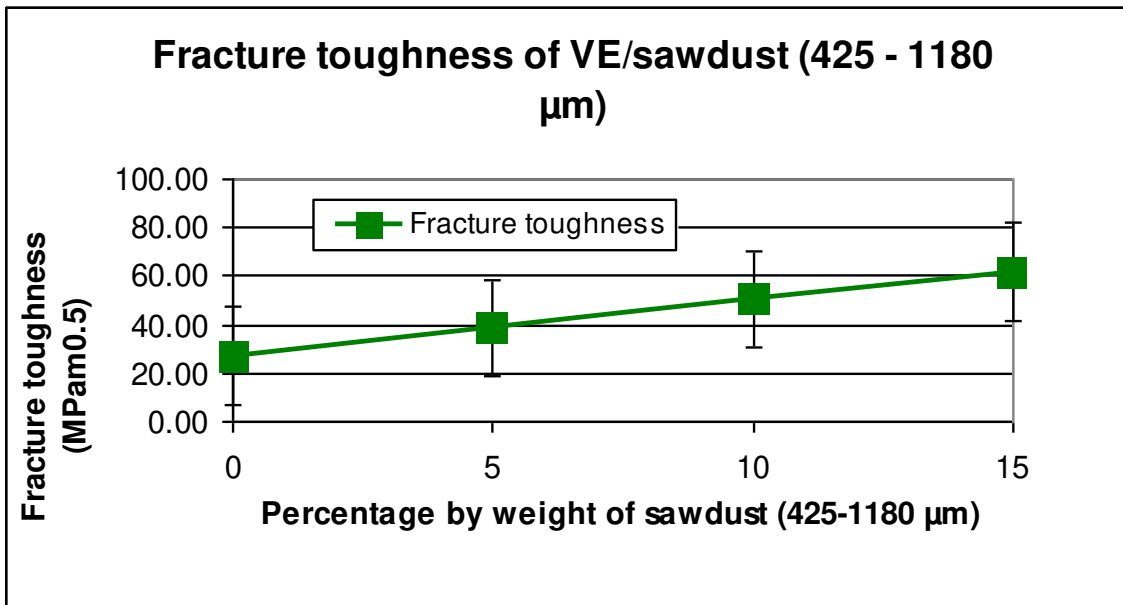
Figure 5: Fracture toughness of vinyl ester composites reinfoprced with sawdust with diameters of 425 - 1180 μm
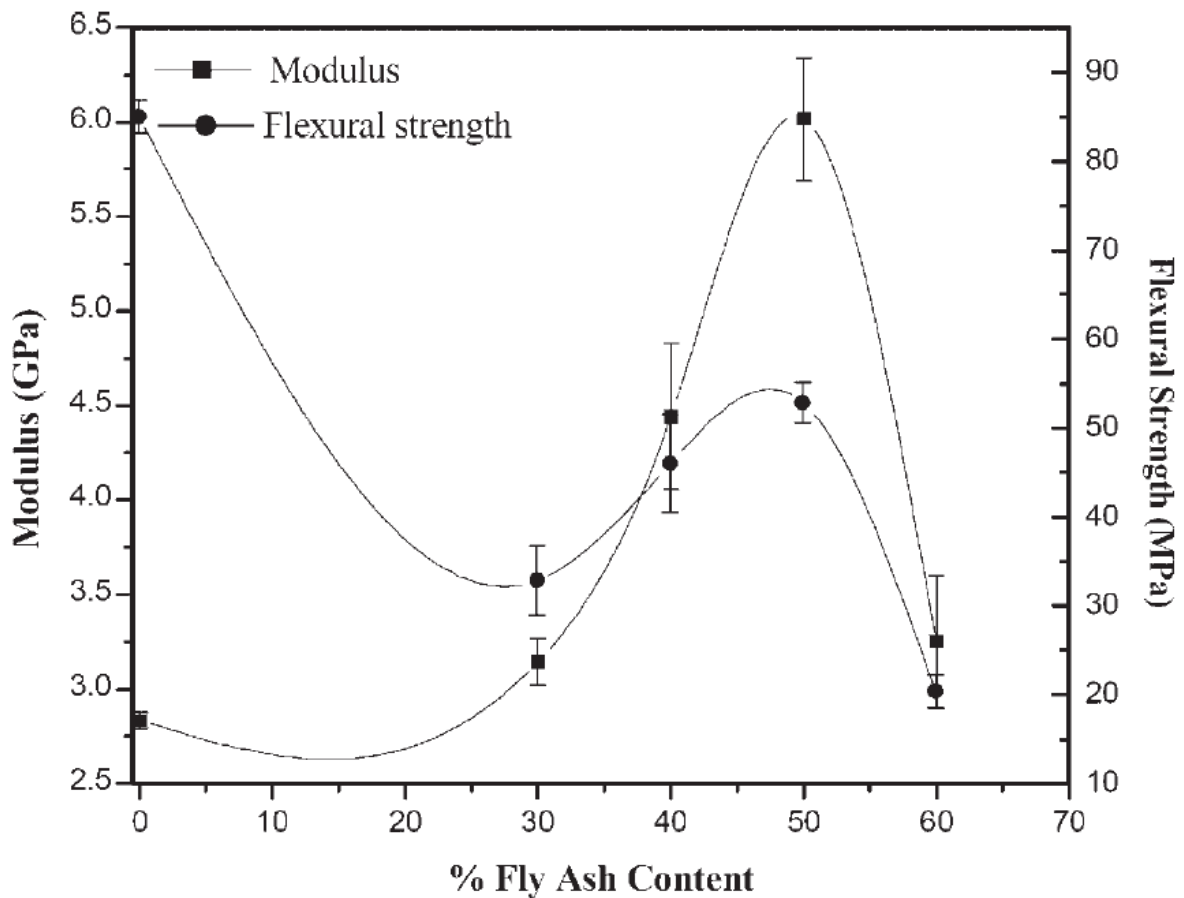
Figure 6: Variation in flexural strength and flexural modulus of the vinyl ester resin matrix composites containing different w/t % of fly ash [9]
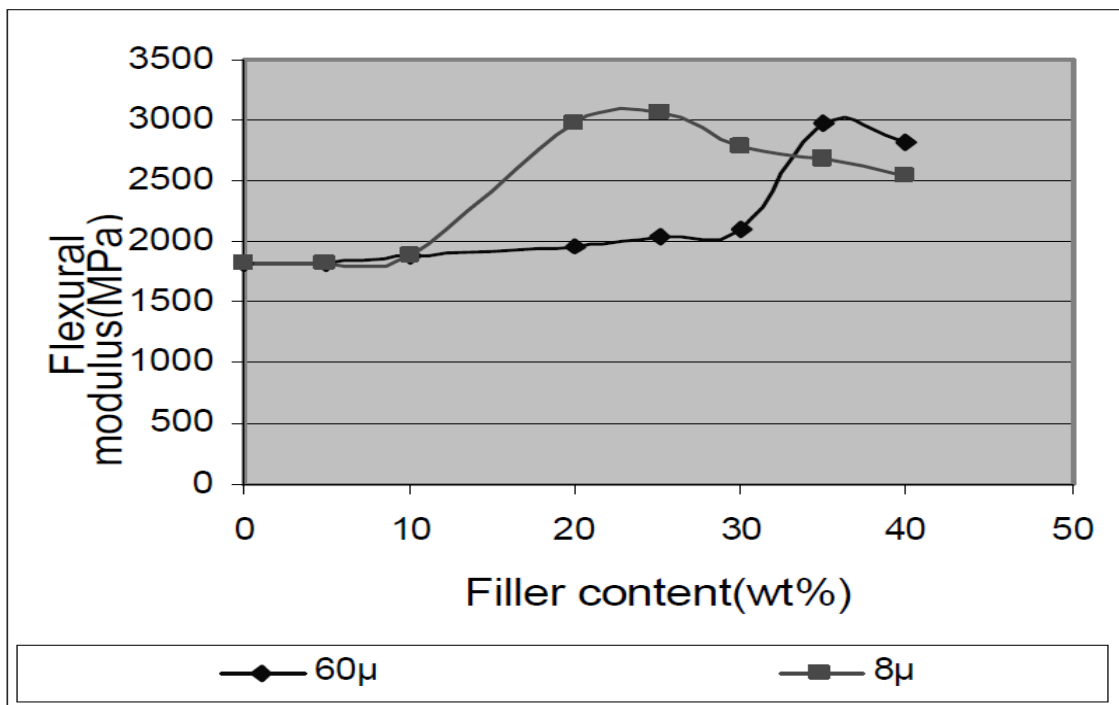
Figure 7: Variation in flexural modulus of different particle size fly ash with varying concentration [10]
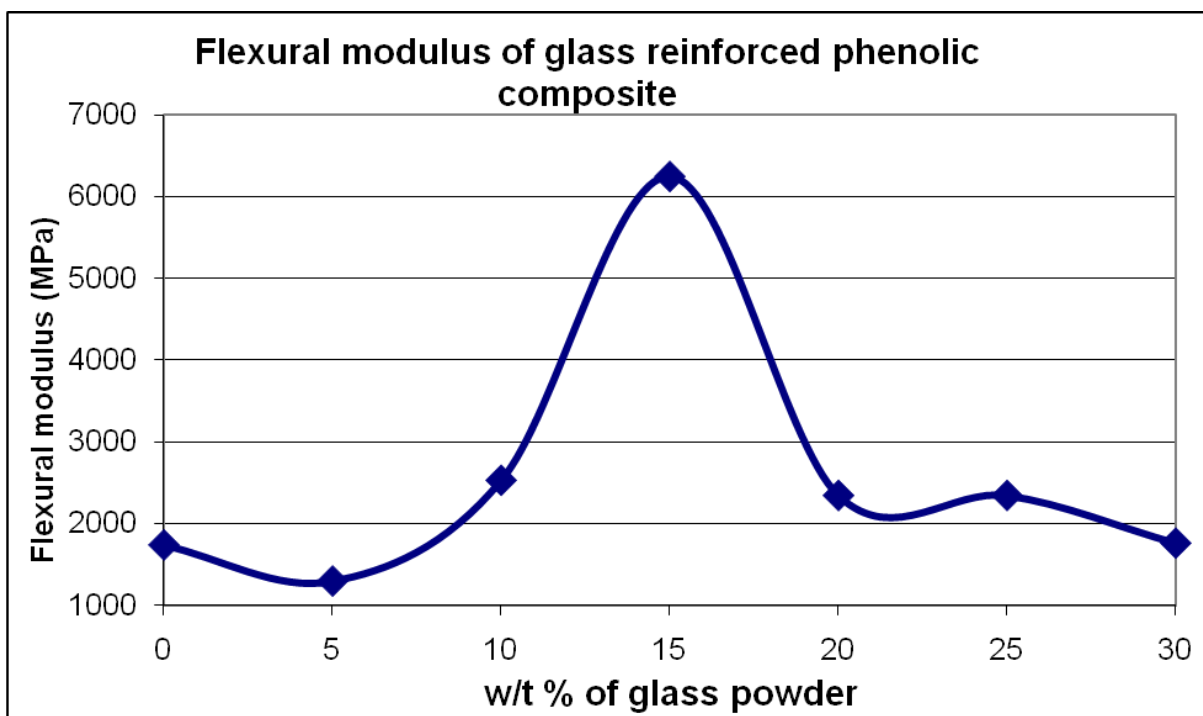
Figure 8: Flexural modulus of varying percentage by weight of glass powder reinforced phenolic resin

Figure 9: DMA results of 15% sawdust (425 - 1180 μm) reinforced vinyl ester resin cured at ambient conditions for 24hours

Figure 10: DMA results of 10% sawdust (≤ 300 μm) reinforced vinyl ester resin cured at ambient conditions for 24hours

Figure 11: DMA results of 10% sawdust (≤ 300 μm) reinforced vinyl ester resin post-cured in microwaves

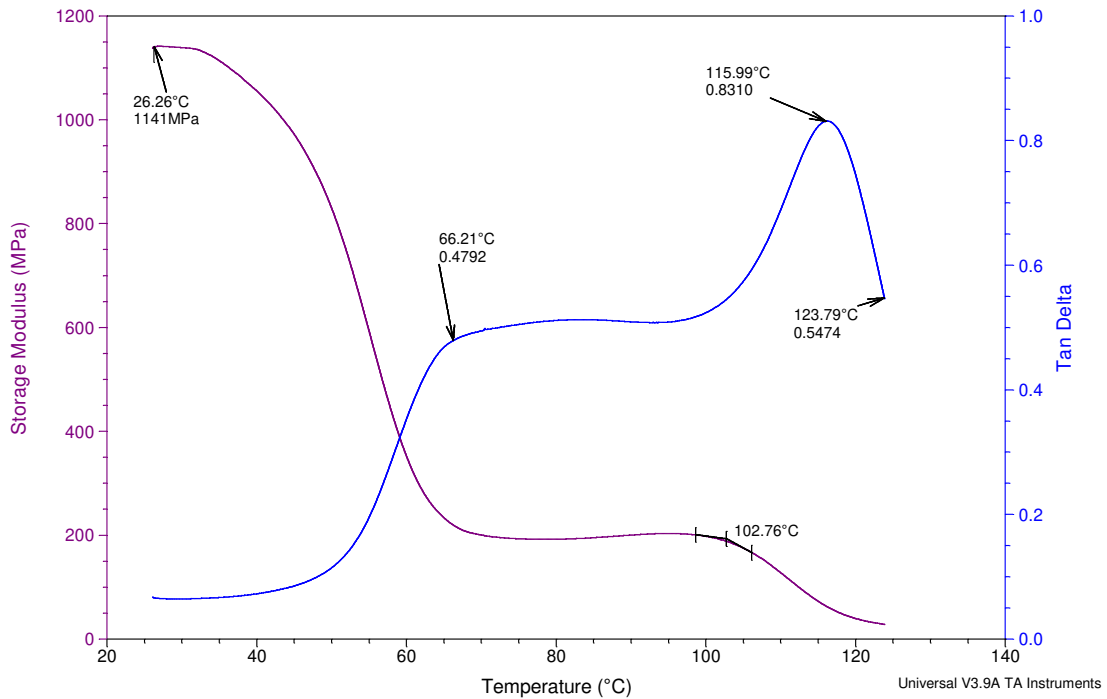**Figure 12: DMA results of 15% sawdust (300 - 425 μm) reinforced vinyl ester resin cured at ambient conditions for 24hours**
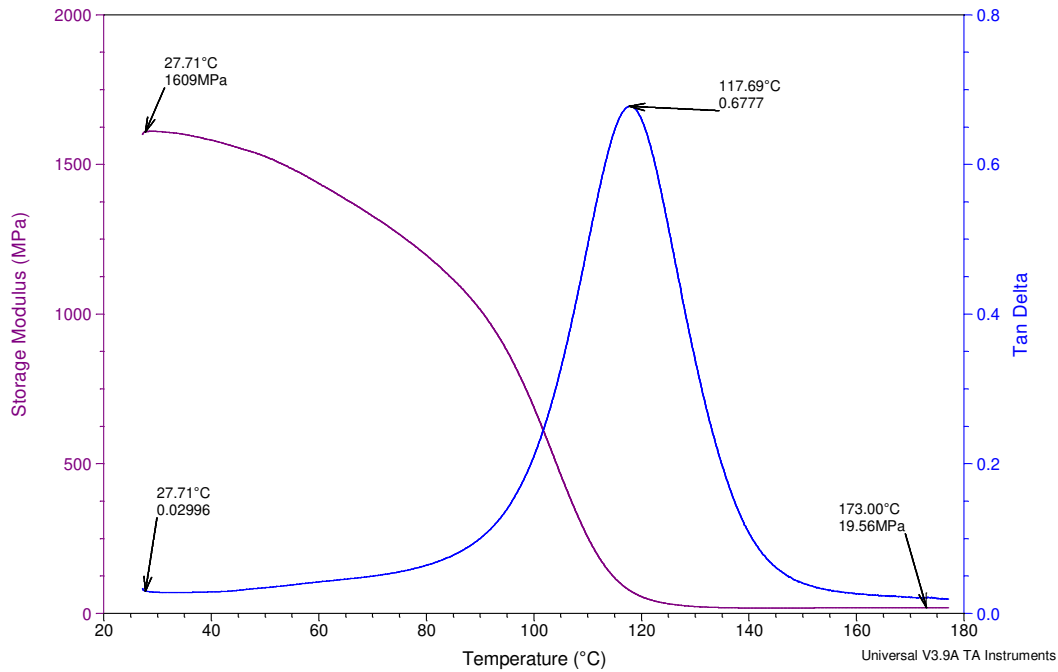
Figure 13: DMA results of 15% sawdust (300 - 425 μm) reinforced vinyl ester resin post-cured in microwaves
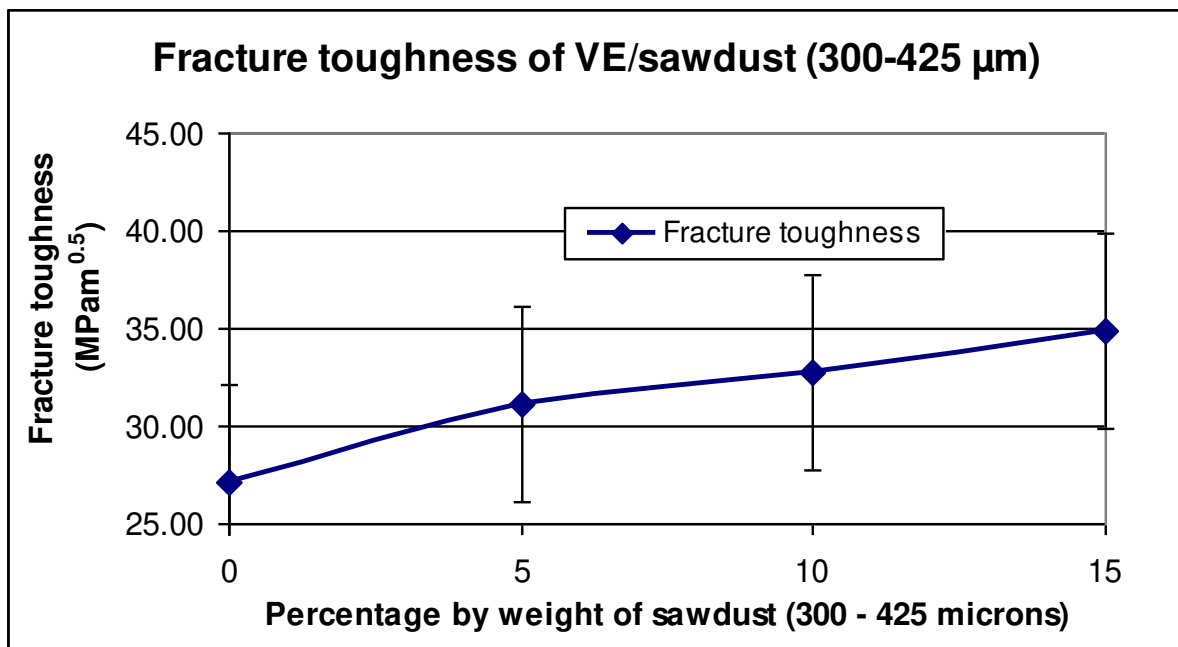

Figure 14: Fracture toughness of phenolic composites reinfoprced with sawdust with diameters of   300 - 425 μm

Table 1: Weight of materials required to make 1000 g of VE/Sawdust (15%)

Parameters / Materials	Materials	Resin (R)	Hardener	R+ H	Sawdust	Composite
Percentage by weight		40	1	---	---	---
Percentage by weight		---	---	17	3	---
Weight of materials in 1000 g of PF/Sawdust (15%)		809.5 (g)	40.5 (g)	850 (g)	150 (g)	1000 (g)

Table 2: Fracture toughness of VE/Sawdust with varying particle sizes and percentage by weight

w/t %	0%	5%	10%	15%
Fracture toughness (MPa $\sqrt{m}$), Sawdust (425-1180 microns)	27.15 (1.53)	38.45 (4.12)	50.65 (3.30)	61.79 (1.90)

#Standard deviation

Table 3: Composition and designation of 3P/VE/MF hybrids systems [adapted from 13]

3P (50 w/t %)				
Material code	VE content, w/t %	PMDI content, w/t %	WG content, w/t %	MF content, w/t %
3P*/VE/MF-0.5 w/t %	50	25.4	24.1	0.5
3P/VE/MF-1 w/t %	50	25.1	23.9	1.0
3P/VE/MF-2.5 w/t %	50	24.3	23.2	2.5
3P/VE/MF-5 w/t %	50	23.0	22.0	5.0
3P/VE/MF-10 w/t %	50	20.5	19.5	10
3P/VE/MF-15 w/t %	50	17.9	17.1	15

*3P is the designation of polyisocyanate, phosphate and polysilicate.

Table 4: Flexural modulus, flexural strength and fracture toughness of 3P/VE/MF hybrids systems [adapted from 13]

Material code	Flexural modulus (MPa)	Flexural strength (MPa)	K_{CI} MPam$^{\frac{1}{2}}$
3P/VE/MF-0.5 w/t %	2225.2 ± 13.4	71.3 ± 13.3	0.81 ±0.05
3P/VE/MF-1 w/t %	2241.9 ± 269.7	74.1 ± 7.9	0.73 ± 0.04
3P/VE/MF-2.5 w/t %	2143.0 ± 152.7	66.6 ± 3.4	0.69 ± 0.02
3P/VE/MF-5 w/t %	2334.9 ± 104.2	60.8 ± 4.0	0.66 ± 0.07
3P/VE/MF-10 w/t %	2506.9 ± 92.9	53.9 ± 5.1	0.73 ± 0.04
3P/VE/MF-15 w/t %	2509.6 ± 79.2	42.8 ± 2.4	0.60 ± 0.12