THE INFLUENCE OF RUBBER PARTICLE CONCENTRATION ON FRACTURE TOUGHNESS OF INTERLAYER-TOUGHENED VINYL-ESTER/GLASS FIBRE COMPOSITE

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SUMMARY: An investigation into the influence of rubber particle concentration on Mode I and Mode II fracture toughness of an interlayer toughened vinylester/glass composite has been undertaken. Fracture toughness in both modes were found to be highly influenced by the particle concentration in the interlayer region. Optimum particle concentration was around 7% and 3.5% for Mode I and Mode II respectively, that resulted the increase of fracture toughness around 85% in comparison with the base composite material without an interlayer. It was found that the physical presence of rubber particles in the interlayer and chemical modification of the interlayer resin were responsible for the toughness increase. Mode I crack propagation ranged from highly unstable to completely stable, as the particle concentration increased. Mode II crack propagation was stable for all studied rubber concentrations. The study established the basic toughening mechanisms for the interlayer-toughened vinylester/glass fiber composite.

KEYWORDS: interlayer toughening, interlaminar fracture toughness, crack propagation, mode I, mode II

INTRODUCTION

Various applications of composite materials in primary and secondary load-bearing structures, over the past several decades, have established them as a good substitute for metallic materials. However, features such as specific strength and modulus are diminished by the composites' tendency to delaminate under repeated loading, low-velocity impact or both. This is due the inherent brittleness of the composite's matrix resin.

In the last two decades various attempts have been made to improve fracture and impact resistance of composite materials. Matrix toughening has been proposed by several researchers. However, good resin fracture toughness does not always give a significant improvement in the composite toughness. Another approach, named interleaving or interlaminar toughening [1, 2], has been introduced, showing promising results in improvement of the composites fracture resistance. The major obstacle for the approach is a weight penalty, associated with the thermoplastic or thermosetting interleaf film. Further development in the last five years has led to the use of the rubber and thermoplastic particles for interlayer toughening. In this type of composite system interleaves are not homogeneous thermoplastic or thermoset resin but resin mixed with thermoplastic particles of 10-50μm in diameter. Woo and Mao [3] and Sue et al. [4], have presented composite systems with different toughening particles, and obtained similar enhancement for mode II fracture toughness and impact resistance. It should be noted that Woo and Mao found excellent improvement in the mode I fracture toughness (from 165 to 540 J/m^2) but Sue et al. reported only moderate fracture toughness improvement (from 343 to 492 J/m^2).

The aim of this work is to investigate the influence of interlayer particle concentration on mode I and mode II fracture toughness of a vinyl-ester/glass fiber composite material.

MATERIALS AND SPECIMEN PREPARATION

Materials used in this study were Dow Chemicals Derakane 8084 vinyl-ester resin and unidirectional E-glass fibers with a silane sizing (Vetrotex P177). The interlayer toughening is through the addition of (polyacrylonitrile-butadiene-styrene) particles (ABS), of 100μm in size, provided by DENKA Co. of Japan. The ABS was applied only between the two mid layers to keep the specimen compliance close to the compliance of specimens without the interlayer, in order to satisfy the stiffness requirements of the standard tests for the mode I and mode II interlaminar fracture toughness.

The toughened resin was prepared prior to the laminate fabrication. Three different particle weight concentrations were used: 3.5%, 7% and 15%. The ABS powder was mixed with the resin using a high-speed shear blender SILVERSON L4RT. The ABS powder was dried in a vacuum oven for 5 hours on 50°C before the mixing. An optimum mixing procedure was obtained with three different mixing heads using mixing speeds in the range of 7000 and 7500 cycles/min.

Each laminate was fabricated by hand in a wet lay-up process. Alternate layers of liquid resin and fiber plies were placed inside the dam on a flat mould plate. The toughened resin was poured between two mid-layers of fiber. Thickness of the layer was controlled by the amount of used toughened resin. The optimum interlayer thickness is believed to be associated with the size of a fully developed plastic zone in front of the crack tip. Thickness of the toughened interlayer was found to be between 200 and 500μm, that should be sufficient to allow a plastic zone to be fully developed in front of the crack tip. A piece of aluminum film, 15 μm thick and 57 mm long, was inserted in the toughened interlayer of each laminate to simulate a starting defect. At the end of the lay up procedure, a caul plate was placed on top of the laminate to insure uniform thickness. After that, the vacuum bagging technique was applied so that the laminate cured under atmospheric pressure and room temperature. After an initial room temperature cure in the vacuum bag, each laminate was post-cured at 90°C for 4 hours.

Test specimens were cut from the laminates using a water-cooled diamond saw and dried in a vacuum oven for 12 hours, prior to the testing.

Prior to testing some of the specimens were polished for monitoring crack propagation and development of damage zone in front of the crack tip, using an optical microscope. The polishing was carefully conducted using five different grades of sand paper (from 220 to 1200 grids) and 6μm diamond paste. In some cases, 1μm diamond paste was used to obtain mirror like surface.

TESTING PROCEDURES

All specimens were pre-cracked following the method concluded in the previous work [5], to generate a fatigue pre-crack of 2 - 5 mm in front of the insert film. Both, pre-cracking and testing were performed on an Instron 4505 Universal Testing Machine.

Neat resin Mode I SENB test

In addition to composite testing, the fracture toughness of the toughened resin was measured, following the ASTM D5405-91a, using single-edge-notched bend (SENB) specimens. Cross-head speed was 10 mm/min.

Mode I DCB test

The DCB specimen geometry used in this study has nominal length of 120 mm, width of 20 mm and thickness of 5 mm. Loading was applied over the aluminum end tabs. Cross-head speed was 2 mm/min. The crack propagation was followed using marks on the side of the specimen. A load-displacement plot provided data for each crack length. The data reduction and calculation of G_{Ic} were done using the experimental compliance method (Berry's method) [6]. The critical strain energy release rate is given by the expression:

$$G_{Ic} = \frac{nP\delta}{2Ba} \tag{1}$$

where *P* is the applied force, δ displacement, *B* average width of the specimen, *a* measured crack length and *n* a slope factor calculated from the logarithmic plot of *C* versus *a*, under the assumption that the compliance is expressed as:

$$C = Ka^n \quad \text{where n} \leq 3 \tag{2}$$

The correction factors for the large displacements were used when displacement - crack length ratio was larger than 0.4.

Mode II ENF test

Geometry of the ENF specimens was the same as those for DCB test. The specimen was placed in 3-point bend fixture with half-span length L set to 50mm. The ratio of the original crack length to half-span length, a_o/L, was 0.5. Testing speed was 1 mm/min and a load-displacement curve was obtained for the calculation of the mode II critical strain energy release rate, G_{IIc}, based on the Direct Beam Theory [6]. The G_{IIc} is expressed as:

$$G_{IIc} = \frac{9a^2P\delta}{2B(2L^3 + 3a^3)} \tag{3}$$

where L, a, and B are half-span length, starter crack length and width of the ENF specimen while P and δ are force and displacement recorded during the testing.

Micrographs of the fracture surfaces were taken using a Cambridge S360 scanning electron microscope. The specimens were coated with a thin layer of gold before the SEM examination.

RESULTS AND DISCUSSION

Neat resin Mode I SENB test

The results of the testing are given in following table.

Table 1: Fracture toughness of the resin with different ABS particle concentrations

ABS %	G_{Ic} [J/m^2]	Std. Deviation %
0	307	5
3.5	638	20
7	642	16
15	1076	16

It is clear that more than 100% fracture toughness increase was obtained for the addition of only 3.5% of ABS. Same increase of fracture toughness was obtained with 7% of ABS, while the fracture toughness was tripled in specimens with 15% of ABS.

Particle distribution of modified resins was examined using an optical microscope. Surfaces of polished specimens with different percentages of ABS particles are shown on the Figure 1. Distribution of the particles was uniform in all cases with noticeable irregular particle shape. Size of the particles was between 10 and 200μm.

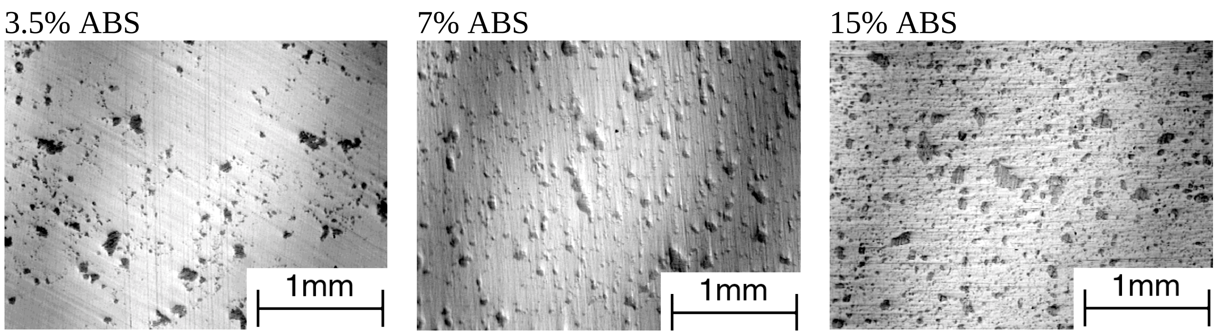


Fig. 1: Modified resins - particle distribution

Mode I DCB test

As mentioned before, all specimens had fatigue pre-crack to ensure that the starting crack tip was in the middle interlayer region. This requirement is important because the interlayer toughening can be effective in mode I only if crack grows through the interlayer. Otherwise, possible interfacial (adhesive) fracture instead of interlayer (cohesive) fracture can lead to low fracture toughness enhancement or no enhancement at all.

The results of the mode I testing are shown in Figure 2.

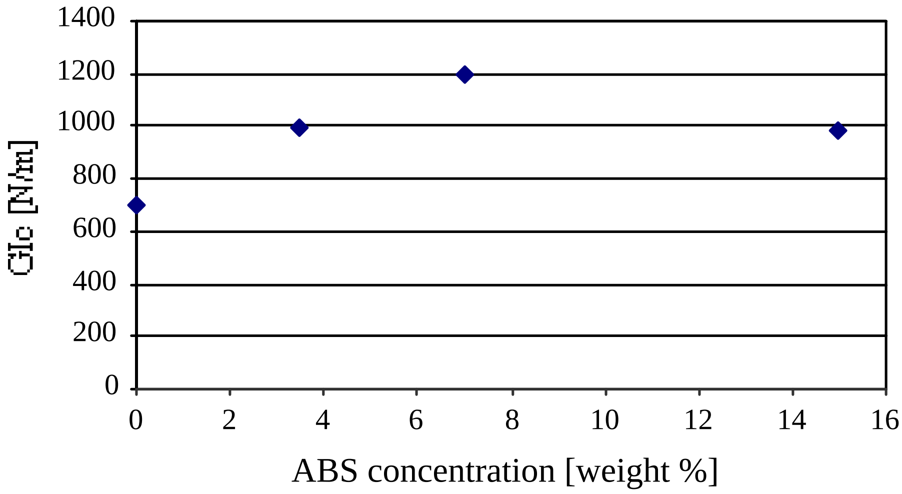


Fig. 2: Mode I strain release energy rate versus weight percentage of ABS particles

The Figure 2 shows that resin modification with ABS particles brings a significant increase in the fracture toughness. From 700J/m^2 for the base material, G_{Ic} value was increased to 1000 J/m^2 with 3.5% ABS addition, to 1200 J/m^2 with 7% ABS addition while 15% ABS addition caused a slight decrease in fracture toughness to about 1000 J/m^2, but still higher than the fracture toughness of the base material. Delamination fracture for the base material was based on the extensive fiber bridging, that was completely absent in the ABS-modified specimens. This was a supporting evidence for cohesive fracture through the interlayer. Evidence for this can be found on Figures 3(a) and 3(b).

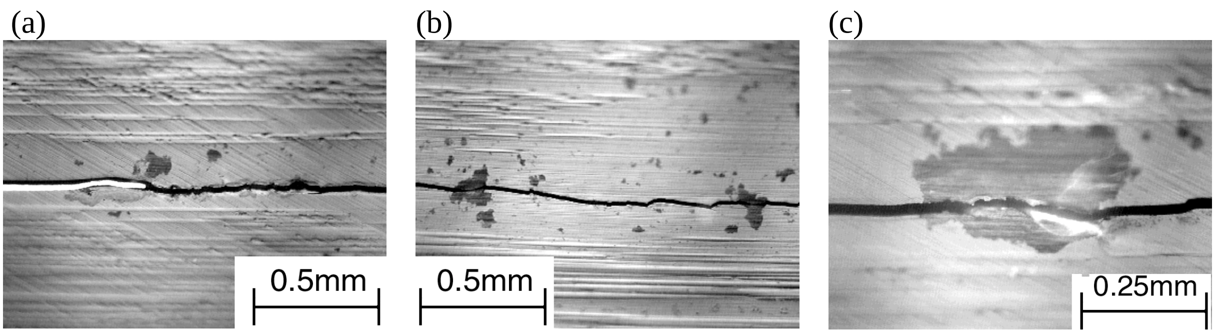


Fig. 3: 3.5% ABS layer - side view images of crack propagation in Mode I

The images in Figure 3 were taken from specimens 3.5% ABS layer but the same behavior was observed for all percentages of ABS concentration. However, the force-displacement curve was highly influenced by particle concentration. Specimens with 3.5% ABS addition exhibited extremely unstable crack growth, similar to fracture behavior of the base material under mode II loading. After initiation, crack would rapidly grow to ~50 mm of length in one big jump. This kind of behavior failed to give more than one value of G_{Ic}, calculated using beam theory, with initial crack length at the onset of unstable crack growth. Specimens with 7% ABS addition exhibited more stable fracture behavior. After an initial unstable jump, propagation of the crack was stable for ~10 mm and than become unstable again. The G_{Ic} value for the specimens interlayer-modified with 7% ABS, in Figure 2, was obtained during the 10 mm of stable crack growth. Fracture behavior of the specimens with 15% ABS layer was completely stable. This large difference in the fracture behavior indicates that the physical presence of the particles in the interlayer may not be the only explanation for that. We believe that the interlayer was not simply original vinyl-ester with particulate inclusions made of ABS, but a mixture of ABS-modified vinyl-ester and ABS particles. This conclusion is further explored using Raman spectroscopy.

Basic toughening mechanisms for the interlayer-modified composites under mode I loading can be influenced by both: chemical modification of the resin and the physical presence of the particles acting as strong stress concentrators. An optimum concentration of ABS will produce highest G_{Ic} values and that concentration should be close to 7%, as suggested in Figure 2. Figures 3(b) and 3(c), show that large particles played a more significant role of stress concentrators than small particles, and the crack was easily attracted by them. The crack appears to grow through the large particles causing plastic deformation and microcracking inside the particles (Figure 3(c) - white zones). Changes in the resin properties due to the mixing with ABS particles have contributed to the improvement of interlayer resin fracture toughness (and overall mode I composite fracture toughness) in all three cases of toughening. Evidence for this statement will be found on scanning electron micrographs.

Mode II ENF test

Mode II fracture toughness improvement with addition of ABS was also significant. Layer with only 3.5% addition of ABS brought over 85% of enhancement in G_{IIc} in comparison with the base material without the toughened interlayer. Further addition of ABS in the interlayer (7% and 15%) did not bring any further improvement in composite's G_{IIc}. These results are presented in Figure 4 (G_{IIc} represents G_{IIc}^{max}).

Figure 5 shows mode II crack propagation through a 3.5% ABS layer. The crack seen in Figure 5(a) represents the transition from the fatigue pre-crack to the mode II crack zone. The crack follows the interlayer-fiber interface with extensive deformation of the toughened resin and microcracking around particles (Figures 5(b) and 5(c)). The ABS particles again acted as stress concentrators but this time in a different manner. They initiated microcracking of the surrounding resin with very little deformation of themselves. Figure 6 shows mode II crack propagation through a 7% ABS layer. Fracture behavior was similar but not completely the same with aforementioned behavior of 3.5% ABS layer.

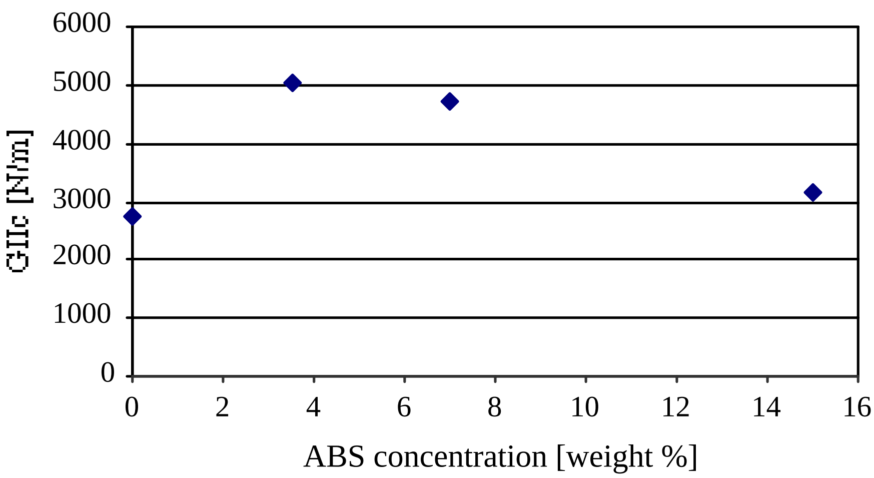


Fig. 4: Mode II strain release energy rate versus weight percentage of ABS particles

Fracture was again interfacial, but in this case the crack was deflected from one interface to another, 6(c), or even propagated through the interlayer, 6(e). Figure 6(f) shows a series of sigmoidal-shaped microcracks in front of the crack tip. That kind of damage was not observed in the 3.5% ABS layer.

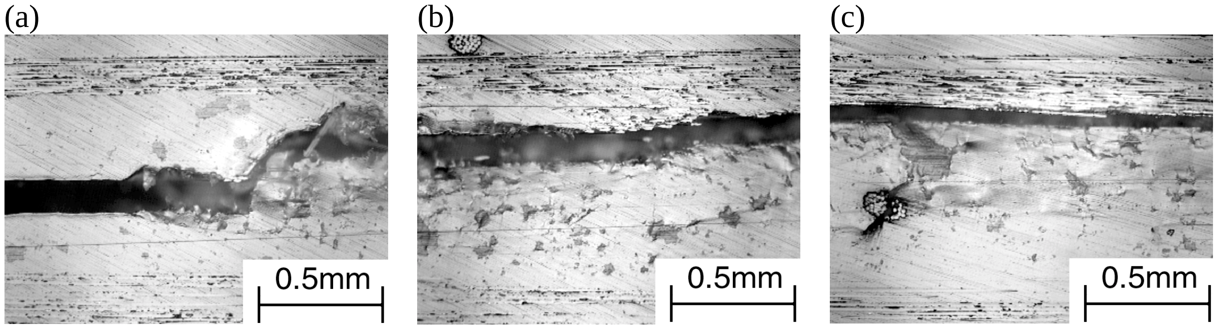


Fig. 5: 3.5% ABS layer - optical micrographs of Mode II crack propagation

It can be concluded that in the case of 7 % ABS layer, the modified resin was weak enough to enable cohesive failure. The cohesive failure may be the consequence of coalescence of microcracks around particles and sigmoidal-shaped microcracks in front of the crack tip.

The above mentioned differences in fracture behavior between specimens toughened with 3.5% and 7% ABS layer could explain the differences in the fracture toughness (Figure 4) of these composites. The 3.5% ABS layer gave optimum response for all toughening mechanisms, obtaining the highest value of G_{IIc}. However, it should be noted that the 15% ABS layer, which did not produce any fracture toughness improvement, exhibited similar fracture behavior to the 7% ABS layer. Further study is being conducted to understand the difference in the toughness improvement.

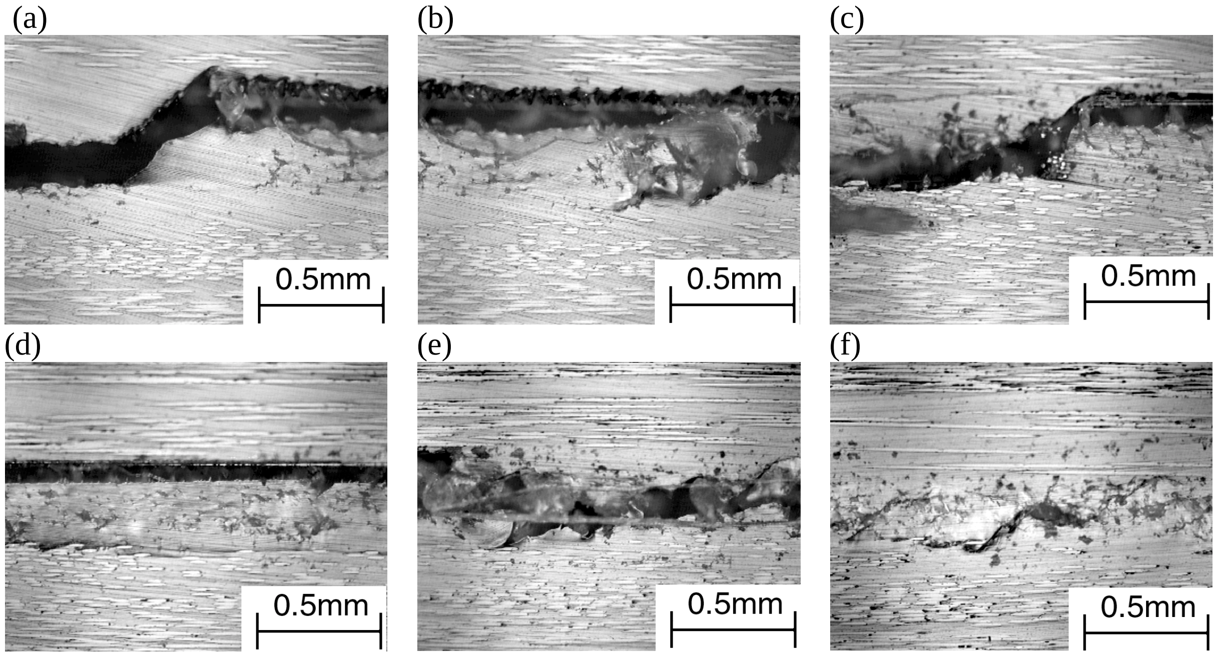


Fig. 6: 7% ABS layer - optical micrographs of Mode II crack propagation

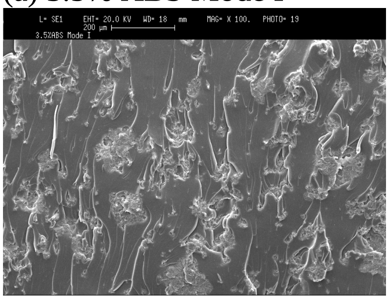
Scanning Electron Microscopy

Figures 7(a)-7(f) illustrate fracture surfaces of the specimens after mode I and mode II interlaminar fracture tests.

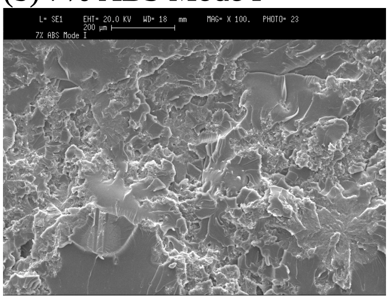
Figure 7(a) shows the brittle-like fracture of the DCB specimen interlayered with 3.5% ABS. The particles and crack propagation through them are visible. Also, resin plastic deformation (Figure 7(a) - white river marks) is quite obvious. Figures 7(b) and 7(c) illustrate a stable crack propagation through DCB specimens modified with 7% and 15% ABS respectively. The resin deformation level is even higher and particles are no longer visible. Using information from the optical and SEM micrographs, together with results of fracture toughness testing for Mode I, a following conclusion can be made. The plastic deformation of the modified resin was the main toughening mechanism. The second important influence was fracture energy absorption by the particles. Larger particles initiated high stress concentration forcing the crack propagation through them. Broken by the propagating crack, they suffered large plastic deformation and microcracking, absorbing significant amount of the fracture energy.

Mode II fracture surface for specimen modified with 3.5% ABS interlayer (Figure 7(d)) exhibited usual hackle-mark damage. The crack was fully interfacial but most of the observed damage was formed in the toughened interlayer. That supports the conclusion made from optical micrographs that major failure for the 3.5 % ABS layer occurred along the interlayer/fibre interface. Increasing the percentage of the ABS brought significant difference in fracture surface of the specimens. With 7% ABS layer failure was only partly interfacial (Figure 7(e) - region completely covered with modified resin) and hackles were hardly noticeable.

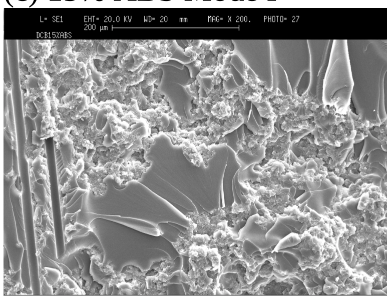
(a) 3.5% ABS Mode I



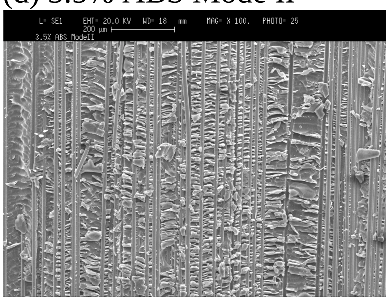
(b) 7% ABS Mode I



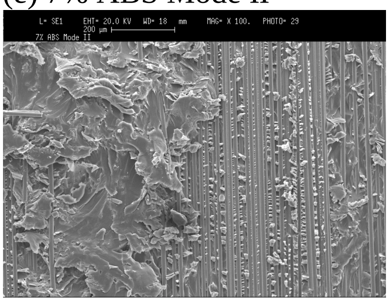
(c) 15% ABS Mode I



(d) 3.5% ABS Mode II



(e) 7% ABS Mode II



(f) 15% ABS Mode II

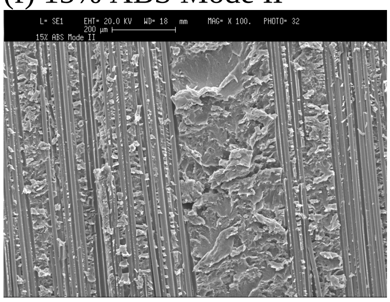


Fig. 7: SEM images of fracture surfaces - Mode I and Mode II
(scale bar represents 200μm)

The modification with 15% ABS addition followed the same trend, hackles almost disappeared and large regions covered with toughened resin were present (Figure 7(f)). These observations are supported in [7] and [4] where authors stated that the tougher is the matrix, the larger will be the hackle spacing and when the matrix is extremely tough the hackle patern disappears. In our case, the extensive hackle formation together with the modified resin deformation absorbed the largest amount of fracture energy (3.5% ABS layer). Based on Figures 7(d) - 7(f), it can be concluded that addition of ABS particles caused significant changes in the resin deformation behavior. Why, obviously tougher interlayers, failed to give higher Mode II fracture toughness values will be further studied

CONCLUSION

The following conclusions can be made from this study:

1. The ABS can be a very promising toughening agent for vinylester/glass fibre composite. Also, this study showed that interlayer toughening of the vinyl-ester/glass fibre composite system is possible and highly effective
2. Varying the particle concentration in the system under study has a significant influence on interlaminar fracture toughness of the material
3. Optimum particle concentrations of ABS were found to be 7% and 3.5% for mode I and mode II respectively. Both modes showed more than 85% increase of the fracture toughness
4. Major toughening mechanisms for mode I were: plastic deformation of the toughened resin followed with plastic deformation and microcracking of the ABS particles. Crack propagation under mode I loading was unstable for 3.5% ABS layer and unstable/stable and completely stable for 7.5% and 15%, respectively. The crack propagated only through the interlayer and did not contact the interlayer-fiber interface. Larger particles were points of high stress concentration. Cracks were often attracted by the particles and grew through them
5. Major toughening mechanisms for mode II interlaminar fracture were: deformation of the modified resin and extensive microcracking of the resin due to the presence of the particles. Cracks propagated along the interface or, sometimes, being reflected from one interface to another. For larger amounts of the ABS particles (7% & 15%) even interlayer crack propagation was observed together with formation of sigmoidal-shaped microcracks in front of the crack tip. Combination of the modified matrix deformation together with microcracking around particles, followed by interfacial cracking, produced the highest G_{IIc} values for the specimens interlayer-modified with 3.5% ABS
6. A future work will be conducted to investigate the influence of particle concentration on impact resistance of the composite, together with the effect of pre-crack conditions on fracture toughness and impact resistance of the composite

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