MANUFACTURE OF SIZEABLE MULTISCALE COMPOSITES THROUGH ENHANCEMENT OF RESIN FLOW IN THE RIDFT PROCESS

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ABSTRACT: The introduction of carbon nanotubes (CNTs) to composite laminates has led to a paradigm shift in the application of advanced composites. To harness the advantages of incorporating nanomaterials in the creation of multiscale multifunctional composites, viable techniques for manufacturing sizable components must be developed. This paper reports on an effort using the Resin Infusion between Double Flexible Tooling (RIDFT) process for the manufacture of multiscale composites. An evaluation of several designs of RIDFT flow distribution channels were made to determine the best configuration for viscous flow of up to 10,000cPs. The optimized FDC configuration was used to infuse 1 and 2wt.% CNTs in vinyl ester resin. This work also determined that the addition of 60wt.% of styrene monomer was necessary to allow for CNT dispersion using a 3-roll calendaring mill. Flexural test results showed improvement in mechanical properties as CNT concentration was increased.

KEYWORDS: *Nano-Structures, Mechanical Properties, Electron Microscopy, Resin Flow*

1.0 INTRODUCTION

This as demonstrated recently by Boeing's 787 Dreamliner, where advanced composites make up 50 wt.% of the primary structure, composites have definitely found their way into the commercial aerospace industry. Nonetheless, as composites continue to gain acceptance in safety critical structures there is still the need to improve through thickness properties. This may be achieved by the inclusion of nanomaterials such as carbon nanotubes (CNTs) within the resin rich interlaminar regions of composite structures. The exceptional physical properties of carbon CNTs combined with their high aspect

ratios and low density make their use imperative in a new generation of multiscale, multifunctional high performance advanced composites [1]. CNT inclusions may provide enhanced strength properties as well as electromagnetic interference (EMI) shielding, the ability to tailor infrared (IR) and radar cross section (RCS) signatures [2], and the altering of the thermal behavior, etc. of multiscale composite structures.

A major inhibitor to the adoption of polymer composites has been manufacturing methodologies. They are too slow, too expensive, environmentally unfriendly, not versatile, unable to deliver consistent results, etc. The addition of nanomaterials only amplifies the manufacturing difficulties by radically increasing the viscosity of the resin systems. As such, filtration of the CNTs, and dispersion issues are notable [1-4]. By their nature, the large surface area of CNTs induces strong attractive forces between the CNTs themselves, yielding excessive agglomeration [5], and bundle formation. These agglomerates must be broken down to a minimum, to allow for improved interfacial interaction of the CNTs and the resin matrix [4, 6]. Furthermore, in order to improve the matrix properties, the CNTs must be well dispersed within the resin, prior to resin infusion and is thus critical to the successful manufacture of CNT based multiscale composites.

High-energy sonication has been widely used for the dispersion of CNTs in resins prior to composite fabrication [1, 5-10]. Although ultrasonic processing presents a quick and easy method to incorporate the CNTs into the resin mixture, it results in damage to the CNTs. Recently [1] calendaring which was introduced by Gojny et al [5, 11-13] and advanced by Thostenson et al [7] has gained popularity as a means to disperse CNTs due to its efficiency and scalability, making it suitable for high volume, high rate production. Nonetheless, the increased resin viscosities resulting from CNT inclusions have meant that most reported works utilized an 'open' mold approach to manufacture these composites. In cases where Vacuum assisted Resin Transfer Molding (VaRTM) has been utilized, the resulting components are usually small lab-sized components. This work is an attempt at manufacturing larger multiscale composite components by harnessing the advantages of the RIDFT process.

The RIDFT process decouples the resin flow and geometry forming elements of most infusion processes such as VaRTM. Resin infusion is performed with a mostly 2-D flow front as the reinforcing fabrics are held 'flat' between two flexible diaphragms [14, 15]. RIDFT is a two-stage process: infusion of fibers is the first stage of the process, which

involves completely wetting the fibers with the resin matrix, followed by the second stage of the process – vacuum forming (Figure 1).

Figure 1: The RIDFT process

In the first stage, dry fiber reinforced sheets are placed between two silicone sheet membranes. The sheets are then vacuum sealed. Resin is pulled between the sheets by vacuum until the fibers are completely wet. At the end of the infusion process, the fiber-resin assembly is vacuum formed over a male or female mold, yielding in the final part geometry. Figure 2 illustrates the process steps.

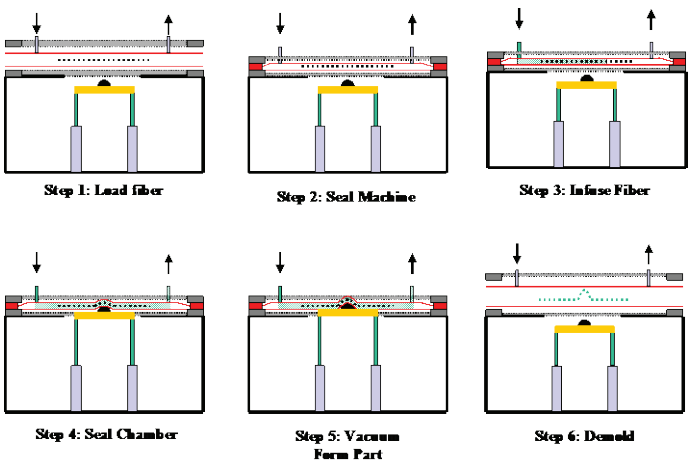
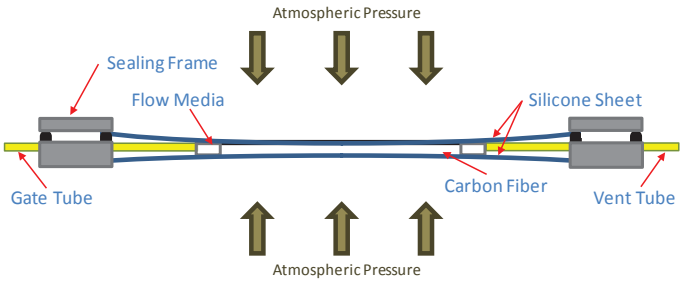
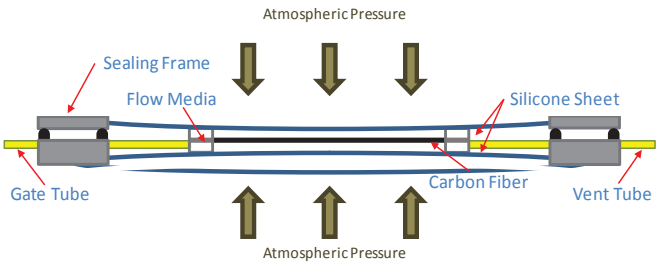


Figure 2: The RIDFT process steps [14]

Resin infusion is performed 'flat' (Figure 1) in the RIDFT process making it an ideal candidate for infusing large structures doped with CNTs since permeability issues are of less concern [16]. A benefit of using the RIDFT process for the manufacture of multiscale composites is the ability to create unobstructed paths that allow resin to flow from one end of the infusion to the other, reducing the effects of CNT filtration as resin flows through the fiber reinforcements. These flow paths are enabled through the use of temporary flow distribution channels (FDCs) (Figure 3) which direct resin flow through temporary 'pipes' over the top surface of the reinforcement assembly in addition to in-plane flow through the fiber preform.



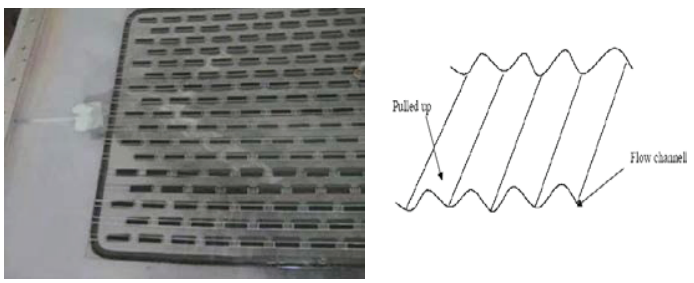
(a) Without flow distribution channels



(b) Raised path with flow distribution channels

Figure 3: Creating flow paths by utilizing temporary flow distribution channels [16]

This way, filtration is mostly reduced to the through thickness (laminate) direction, rather than lengthwise. In use, the FDC is simply placed over the top silicon sheet of the RIDFT equipment (see Figure 4(a)). Vacuum is then applied to the FDC to selectively create temporary flow paths as seen in Figure 4(b). Once resin infusion is accomplished, the FDC is released from the silicon sheet by removing the vacuum. The sheet straightens out on its own, and allows for good surface finish during the forming step.



(a) (b)

Figure 4: (a) FDC on top silicon sheet during resin infusion; (b) Schematic follow channel [15]

This work set out to use the RIDFT process to manufacture multiscale composite components consisting of IM7 carbon fibers and vinyl ester resin containing 2 wt.% CNTs, and measuring 45.72 cm × 60.96 cm (18 in × 24 in). As such, this paper also reports on efforts to optimize viscous fluid flow in the RIDFT process by assessing different configurations of the FDCs.

2.0 EXPERIMENTAL

2.1 Improving Viscous Fluid Flow

Eight flow distribution channel (FDC) configurations were investigated in this work. The FDCs were made with straight and chevron designed geometries. The panels were assessed for optimal viscous resin flow using neat vinyl ester resin, in addition to silicone fluids with viscosities ranging from 5000 – 10,000 cPs. The viscous silicone fluids were intended to simulate the viscosities of CNT-doped resins at different doping concentrations. The CNTs used here were the NC3101; thin functionalized MWCNTs. Vinyl ester resin with a viscosity of 60 cPs was used, and the laminates were reinforced with IM7-12K satin weave carbon fiber. The CNTs were dispersed in the resin using a calendaring mill.

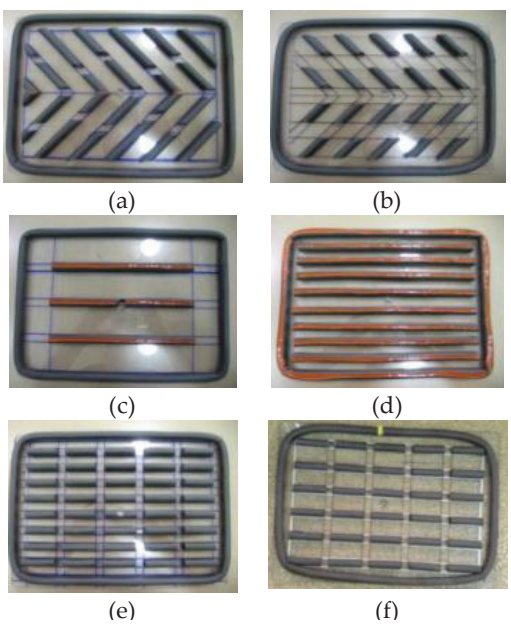
3.0 DISCUSSION OF RESULTS

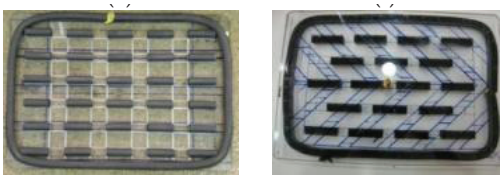
Figure 5(a) shows the first chevron shaped FDC. It was designed with 2.5 cm (1 inch) spacing between each chevron to allow the resin to flow into large areas and through the 1.3 cm (0.5 inch) gaps along the legs of the chevron. This FDC did not successfully complete the saturation process using the neat vinyl ester resin (60 cPs), due to the alternating gaps down the middle of the flow channel. Instead of rapidly forcing the resin outward and through the gaps within the legs and continuing the infusion process, the resin stalled at the beginning of the flow channel for an extended period, before it began to flow through the panel. To eliminate this problem with the first panel, the design was changed to have a clear 2.5 cm (1 inch) path through the middle of the flow channel, and along the legs, but still keeping the main chevron shape.

This (FDC 2) is shown in Figure 5(b). The design gives three straight channels of travel throughout the length of the panel. The problem with this particular design is that the path through the middle of the channel is uninterrupted. The resin flowed straight through the center, never venturing off to fill in the remaining areas of the panel. After 160

seconds of flow, dry areas were noticeable. Figure 5(c) shows the first straight flow channel tested for the designs effectiveness during the infusion process. The design of FDC 3 incorporated four 3.8 cm (1.5 inch) channels with uninterrupted paths for travel. The main setback with the design is that such large gaps did not allow the creation of clear paths 'pipes'. The FDC was unable to completely lift the top silicone sheet. This created additional hindrance on the resin during the infusion. Figure 5(d) shows the fourth FDC configuration with several parallel pathways that are 1.3 cm (0.5 inch) wide. The reduced pathways result in more but smaller channels that act to pass viscous resins at a faster rate. The FDC worked as planned but, as with the other panels, the center filled in first and the outer panels slowly traveled along until they reached the vacuum end of the composite. Fill time was 62 seconds. To assist with the travel of the resin, 1.3 cm (0.5 inch) gaps were introduced to form horizontal paths in the fifth FDC design as shown in Figure 5(e).

The horizontal paths enabled resin flow into other channels. This reduced the rate at which the center became completely filled and increased the rate in which the outer areas became filled with resin. This particular design showed the most effectiveness in terms of time to completely infuse; the process was completed in approximately 24 seconds.





(g) (h)

Figure 5: Flow distribution channel designs

Table 1 gives a summary of the assessment of FDCs 1 – 5 based on neat vinyl ester flow (60 cPs). In order to simulate the increase in resin viscosity with addition of CNTs, silicone fluids at 2,000, 8,000 and 10,000 cPs were employed instead of CNTs to reduce cost. Infusion of the silicone at all resin viscosities were investigated using the FDCs. However, FDCs 1, 2, and 3 (Figures 5 (a)-(c)) were not investigated at the higher viscosities, since they were found ineffective at the lower viscosity of 60 cPs (Table 1).

Table 1: Assessment of FDC design based on low viscosity (60 cPs) resin

FDC #	Geometry	Spacing (cm)	Gap (cm)	Flow Completion	Time (s)
1	Chevron	2.5	1.3	No	-
2	Chevron	2.5	2.5	No – with dry spot	160
3	Straight	3.8	-	No	-
4	Straight	1.3	-	Yes	62
5	Straight	1.3	1.3	Yes	24

As seen in Table 2, FDC 5 was successfully used to infuse silicone fluids at 2,000 cPs, completely wetting out the fibers in 3mins:30s, but was unable to successfully infuse the higher viscosity fluids at 8,000 and 10,000 cPs. The inability to infuse the higher viscosity fluids was attributed to the spacing distance of 1.3 cm. Thus, FDC 6 (Figure 5(f)) was created by widening the spacing sizes to 2.5 cm (1 inch), and keeping the breaks at 1.3 cm (0.5 inch). The resulting flow looked good but yielded a dry spot at the center of the FDC 6.

Table 2: Assessment of FDC design based on medium to high viscosity fluids

FDC #	Geometry	Spacing (cm)	Gap (cm)	Flow Time at Fluid Viscosity		
				2000 cPs	8,000 cPs	10,000 cPs
5	Straight	1.3	1.3	3mins:30s	N/A	N/A
6	Straight	2.5	1.3	4mins:30s (dry spots)	8mins:20s (dry spots)	N/A
7	Straight	2.5	2.5	4mins:20s (dry spots)	8mins:15s (dry spots)	N/A
8	Straight but staggered	2.5	1.3	4mins:00s	8mins:00s	9mins:47s

FDC 7 (Figure 5(g)) was made with wider gaps, i.e., 2.5 cm (1 inch) spacing and 2.5 cm (1 inch) breaks. FDC 7 resulted in similar dry spots seen with FDC 6. The final design tested (FDC 8) combined the two previously mentioned aspects. This particular design incorporated the same 2.5 cm (1 inch) channels as in FDC 7, but with 1.3 cm (0.5 inch) breaks as with FDC 6. However, the breaks were staggered as seen in Figure 5(h). The staggering of the breaks between the walls eliminated the dry spots during the infusion process. The 10,000 cPs fluid was successfully infused using this FDC configuration. This configuration was used in infusing the CNT-doped resins.

3.1 CNT-Resin Infusion: Styrene Loss

Measured amounts of CNTs (C-Nano Flo Tube 9000) were mixed with vinyl ester resin and then processed to achieve particulate dispersion, using an Exakt 80E 3-roll calendaring mill. Multiple steps were carried out to disperse the MWCNTs in the resin system. The mixing process and collection of materials is determined by the arrangement of the machine and the rollers [2, 16]. The machine has three rolls (Figure 6). The first roller is the feeder roller. The CNT/vinyl-ester resin mixture is loaded between the first and second roller of the mill. The second roller rotates in the opposite direction.

The first and third rollers rotate in the same direction. The material is collected once it passes over the third roller, which is the apron roller. Thostenson et al. [6] reported on completing ten passes through the calendaring machine with Epon 862 doped with CNTs to get good dispersion. The large gap size started at 50μm and reduced to 30 μm, 20 μm, 10 μm and 5 μm. They passed through each gap distance "at least three times or until segregation of agglomerates in the feed area

was no longer observed." Elsewhere, Thostenson et al. [2] reported that most commercially sold vinyl-ester resin contains 40-60% styrene. During the calendaring operation, much of the styrene is lost through evaporation. As such, it was preferred [2] to add 40wt.% styrene by mechanical stirring into the CNT-resin mix, to resolve the loss.

The gap settings and pass schedule were adjusted in this work due to difficulties presented by the evaporating styrene. Hence, a seven-pass schedule was implemented. In the first two passes, the gaps 1 and 2 (δg) (see Figure 6) were set at distances of 30 and 20 micrometers. The gap sizes in the following two passes were stepped down to 20 and 10 micrometers respectively. During the fifth and six passes of the doped resin, the gap distances were at 10 and 5 micrometers respectively. The final pass through the calendaring machine had each gap distance set at 5 micrometers. The angular velocity for each of the seven passes was set to 90 rpm. Upon completion of the calendaring process, additional styrene was mixed into the resin using a mechanical stirrer at 1500 rpm for ten minutes. The stirring duration was discussed by Thortenson in previous work [2]. After the calendaring process, and addition of 40 wt. % of styrene, the viscosity of the vinyl ester resin doped with 1 wt.% CNT had values ranging from 3800 – 3900 cPs.

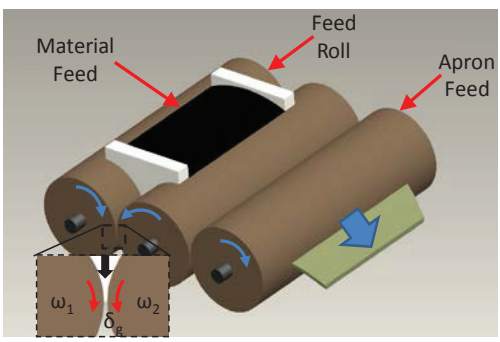


Figure 6: Schematic drawing of 3-roll mill; ω1, ω2 are speeds of rollers 1 and 2; δg is the roller gap [16]

This work found that after 7 passes of neat vinyl ester resin on the calendaring equipment, 60 wt.% of styrene was lost. As such, the effects of adding 40 wt % and 60 wt. % styrene on the resulting flexural properties were investigated. Three sets of composite panels, each with six layers of fibers, were made using the RIDFT process. The first panel set comprised of vinyl-ester resin and carbon fibers. The remaining two panel sets were made with 1 wt.% functionalized CNTs, and had styrene monomer added at 40 and 60 wt.% at the end of the calendaring process. The samples were tested to ASTM Standard D790. The

evaporation of styrene in the vinyl ester resin made it more difficult to run the calendaring process. Moreover, it resulted in a rather thick sludge. The addition of styrene monomer at the end of the calendaring process made the resulting CNT-resin mix more flowable. The panels with the additional 60 wt% of styrene infused with ease. The panels infused with the 40 wt% addition of styrene also infused successfully, but required more time to complete the infusion. Flexural tests were performed on laminates made with the addition of 40 and 60 wt. % styrene and the results are shown in Figure 7.

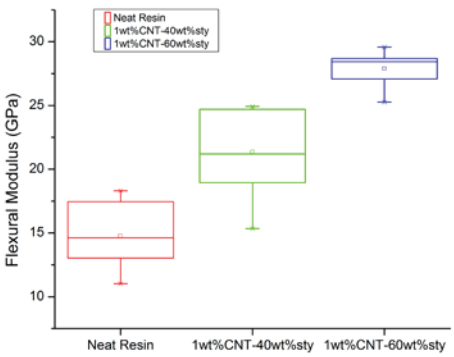


Figure 7: Variation of flexural modulus with CNT content and increasing addition of styrene monomer

From the results, it can be seen that the addition of CNTs improved the flexural properties of the laminates. The chart shows that the mean flexural modulus of the neat resin sample averaged at 14.76 GPa. The MWCNT samples with 40 wt% of styrene included showed the average flexural modulus of the samples to be 21.36 GPa. The MWCNT samples with 60 wt% of styrene average flexural modulus were 27.89 GPa. The graph shows that the 60 wt% styrene sample increased the flexural modulus of the neat sample by 89%. Furthermore, the 60 wt% sample yielded a flexural modulus 77% higher than the 40 wt% sample on the average. The improved behavior of the samples with more added styrene monomer may have been because of improved wetting resulting from the lower viscosity of the CNT-resin mix.

3.2 Multiscale Component Manufacture

In order to demonstrate the efficacy of the RIDFT process for the manufacture of multiscale composites, C-channels (Figure 8) measuring 45.72 cm × 60.96 cm (18 in × 24 in) were made using FDC 8 and as the flow distribution channel. The components were manufactured using four layers of IM7 12k satin weave carbon fiber and Armorstar Ivex-C400

vinyl ester resin. 1 and 2 wt% of MWCNTs were introduced to the resin system and dispersed using the calendaring process previously described. Laminates using neat vinyl ester resin were produced as the baseline.

Figure 8: C shaped RIDFTed multiscale laminates infused with 1 and 2 wt% CNT doped vinyl-ester resin

The initial experiments were attempted with Flo tube 7000 CNTs with an average length of 50μm. However, at 2 wt.% concentration, excessive resin absorption by the CNTs was observed, making it rather dry to the touch (Figure 9a), and can be seen 'hanging' unto the apron feed of the 3-roll mill. As such, shorter CNTs (CNano Technology Flo tube 9000) with an average length of 10μm were implemented. A comparison of the two materials being calendared is shown in Figure 9.

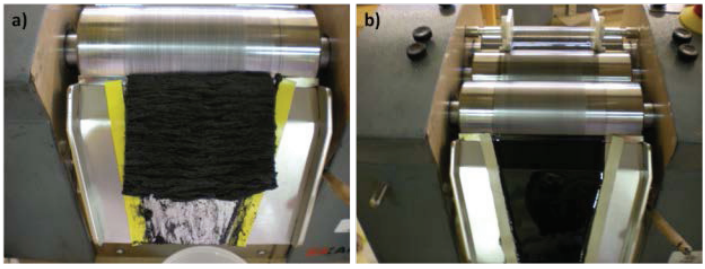


Figure 9: MWCNT Calendaring Comparison (a) Resin and Flo Tube 7000 Mixture (b) Resin and Flo Tube 9000 Mixture

After processing on the 3-roll mill, the dispersed CNT-resin was infused using the RIDFT equipment. Flexural tests were conducted and results may be seen in Table 3. From Table 3, the flexural strength of the multiscale composite with 1 wt.% CNTs is 16% higher than that of the neat resin composite. The 2 wt.% CNT composite resulted in a flexural strength increase of 55%. Figure 10 shows the variation of flexural modulus with CNT content.

Table 3: Flexural properties of multiscale composites

Laminate	Flexural Strength (MPa)	Standard Deviation (MPa)
Neat resin	214.00	42.41
1wt. % CNT resin	248.21	41.81
2 wt. % CNT resin	331.76	41.88

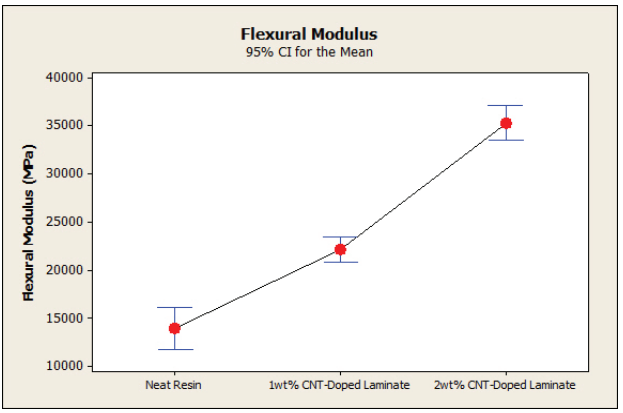


Figure 10: Variation of flexural modulus with CNT content

It may be seen that flexural modulus increases significantly with addition of a small amount of CNT, i.e., 1 and 2 wt.%. Samples were cut out from the cured laminates on the 'inlet' and 'vacuum' ends as seen in the schema in Figure 11, and examined using scanning electron microscopy (SEM). Figure 12 (a) shows an SEM image taken of a 1 wt.% CNT multiscale composite laminate from the infusion end. For the sake of comparison, Figure 12 (b) shows the same laminate at the vacuum end. It can be seen that the CNTs are visible at the vacuum end, having been carried within the resin flowing through the fiber preform and between the fiber layers.

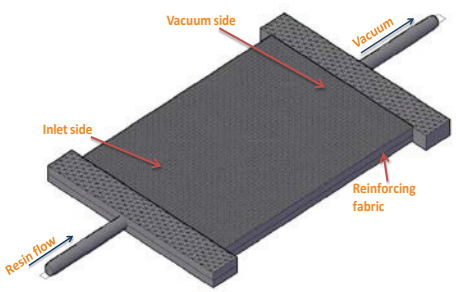
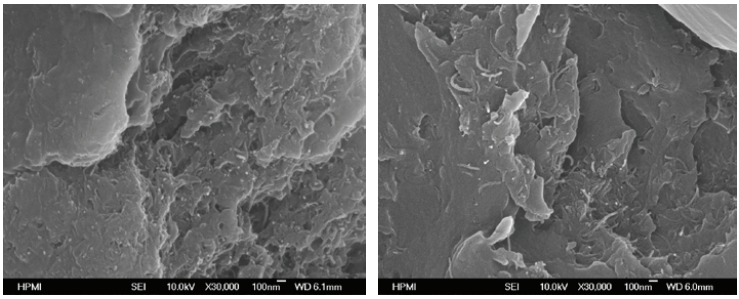


Figure 11: Schema of RIDFT flow set up



(a) (b)

Figure 12: (a) SEM showing a fracture surface of a multiscale laminate viewed from the infusion side; (b) SEM showing a fracture surface of a multiscale laminate with CNTs visible between the fiber layers, viewed from the vacuum side

4.0 CONCLUSION

Eight configurations of the temporary flow distribution channels were assessed for use with the RIDFT process. FDC 8 was selected for its ability to allow viscous fluid flow at the shortest time. It was used to manufacture composite components made from 1 and 2 wt. % CNTs dispersed in vinyl ester resin. A 3-roll mill was used to disperse CNTs in vinyl ester resin. However, the process resulted in a loss of styrene which made the CNT-resin mix extremely thick.

Two concentrations of styrene monomer (40 and 60 wt.%) were added to the processed CNT-resin mix to replenish the styrene lost during the calendaring process. It was determined that the addition of 60 wt.% styrene resulted in improved flexural properties when compared with the addition of 40 wt.%. As such, multiscale laminates were made using 1 and 2 wt. % CNTs, with the addition of 60 wt. % styrene monomer. The results from this work demonstrated that the flexural properties of the RIDFTed multiscale laminates increased with the addition of CNTs. SEM imaging confirmed the successful infusion of the CNTs in the manufactured laminates, thus demonstrating the viability of the RIDFT process for manufacturing multiscale composites with the aid of flow distribution channels.

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