MANUFACTURE OF CARBON FIBER NANO-BASED EPOXY COMPOSITE LAMINATES USING A VACUUM-ASSISTED RESIN TRANSFER MOLD

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ABSTRACT

Increasing demand for low cost manufacturing process while producing composite structure with good quality was the driver for initiating this research project. Vacuum-assisted resin transfer molding (VARIM) represents one of the rapidly growing new molding technology and this process operates with low cost tooling, making it possible to inexpensively produce large, complex parts in one process. However, there are some disadvantages of this process, including: (1) low fiber volume fraction, (2) poor wetting of pre-formed fibres, and (3) formation of voids through the thickness and between the pre-formed layers, all of these are directly attributable to the chemical properties of the resin and the processing procedures.

In this study, natural nanotubes of Halloysites were incorporated into the epoxy resin to improve the fracture toughness properties of composite materials, and this composite resin could affect the processing parameters. In order to manufacture good quality epoxy-based nano-composite materials using the VARTM process, different processing techniques and auxiliary devices have been developed. These techniques and devices for improving the process are described and discussed in detail in this paper.

1 INTRODUCTION

Application of advanced composite materials to load carrying structures in different industrial sectors has prompted the search for toughened materials having improved resistance to impact damage and delamination. The toughened materials will have higher design allowable strains as compared with the conventional materials, hence the structural weight could be reduced and resulted in more economical benefits.

Nanoclays have been incorporated in polymer systems because of the improved mechanical properties [1], [2], [3] and [4]. In this study, continuous carbon fiber reinforced epoxy resin with different concentrations of nanoclays will be formulated and evaluated with a set of test methods for characterizing the resin dominated composite properties. One cost-effective processing technique for manufacture of carbon fiber-reinforced composites is vacuum-assisted resin transfer molding (VARTM). In this process, the resin is driven by a vacuum to fill the mold. A wide variety of products are now manufactured using this method, ranging from small armrests for buses to large components for water-treatment plants [5] [6]. In closed-mold VARTM processing, the resin is injected into a closed-cavity containing a fiber preform. The impregnation of the resin is a complex process and is greatly influenced by several factors, such as the orientation of the fibrous preform, mold temperature, resin viscosity, and injection pressure [7], [8], [9] and [10]. The mechanical properties of polymer/nanoclay composites are affected by the degree of dispersion of the clay in the polymer matrix. Therefore, clays should be pre-dispersed in the epoxy resin before they are injected into the mold cavity during the VARTM process.

2 EXPERIMENTAL

2.1 Materials Incorporated into Parts during Fabrication

2.1.1 Unidirectional Carbon Fiber Sheets (Toray T 700), Fig.1

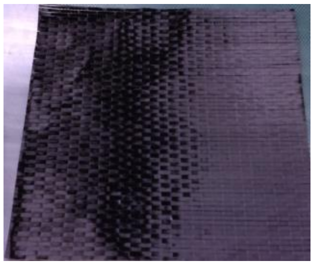


Figure 1. A Unidiretional carbon fiber sheet

Properties	Unit	T700-200	Test method
Areal weight	g/m^2	200	ASTM D3776
Tensile strength	kg/cm-ply	460	ASTM D3039
Tensile modulus	kg/cm-ply	25800	ASTM D3039
Tensile strength for design	MPa	4200	ASTM D3039
Tensile modulus for design	GPa	235	ASTM D3039
Elongation	%	1.8	ASTM D3039

Table 1. Properties of unidirectional carbon fiber sheets (Toray T 700)

2.1.2 Epoxy Resin

Epoxy: Shell Epon 815, Hardener: hardener (diethylene triamine (DETA))

	Specification	Test method
Material	Room Temperature Cured Epoxy Resin	
Work life at 25Deg.C	60-100 min.	ASTM D2471
Viscosity at 25Deg.C	900-1000 cps	ASTM D2471
Tensile strength Completely cured for 7 days at 25 Deg.C	>30 MPa	ASTM D638
Tensile modulus Completely cured for 7 days at 25 Deg.C	>3.5 GPa	ASTM D638

Table 2. Properties of resin for unidirectional carbon fiber sheets

2.1.3 Nano-material

Specification: Halloysite Nanoclay- Product number: 685445-500G, made by Sigma-aldrich company of USA

Diameter × L	30-70 nm × 1-3 μm , nanotube
Color	75-96, Hunter Brightness
Refractive index	n20/D 1.54
CAS number	1332-58-7
Formula	H4Al2O9Si2 · 2 H2O
Molecular Weight	294.19
Pore size	1.26-1.34 mL/g pore volume
Surface area	64 m2/g

Table 3. Properties of Halloysite

Halloysite is a two-layered aluminosilicate with a predominantly hollow nano-tubular structure. The hollow halloysite nanotubes can be used as controlled release carriers and components of coatings and nano-composites Fig. 2.

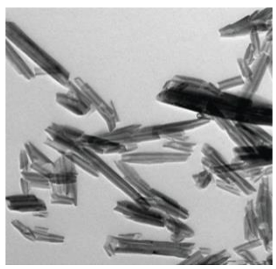


Figure 2. TEM of nanomaterial

2.2 Preparation of Resin Systems for Resin Transfer

2.2.1 Dispersion of nano particle (clay)

Nano particle was added as the percentage of weight to the total weight of the resin. Different percentages of weights i.e. 0%, 2%, 3.5 %, and 5% were used for the tests. The weight of the hardener used was calculated as 3 parts of hardener to 10 parts of epoxy. Nano particle was added to the hardener and mixed gently to avoid any lumps of the powder. After a uniform solution was formed, this solution was stirred uniformly using a magnetic stirrer and a sonicator for around 2 hours. Fig. 3.

(a) (b)

Figure 3. (a) Nanoparticle added to hardener, (b) Stirring the solution

2.2.2 Mixing of Resin Containing Nanoparticle

Resin contained of two parts: Epoxy and Hardener including Nano clay. The amount of epoxy used was calculated as 10 parts of epoxy for 3 parts of hardener including nano clay. Hardener including nano clay after 2 hours of stirring was added to the epoxy. Fig. 3. This mixture was stirred continuously till the clouds of the nano clay disappeared in the mixture. Stirring was followed by degassing of the mixture to remove all air bubbles that were generated in the mixture while stirring. Degassing was done by keeping the mixture in vacuum for 10 minutes. The resin was ready to use after the degassing process. The processing time played a very crucial role in the resin infusion which was approximately 90 minutes. Hence every time the resin was prepared just before infusion process.

(a) (b)

Figure 4. (a) Epoxy resin mixing, (b) Degassing

2.3 Procedures for Preparing The Top Mold before Resin Injection

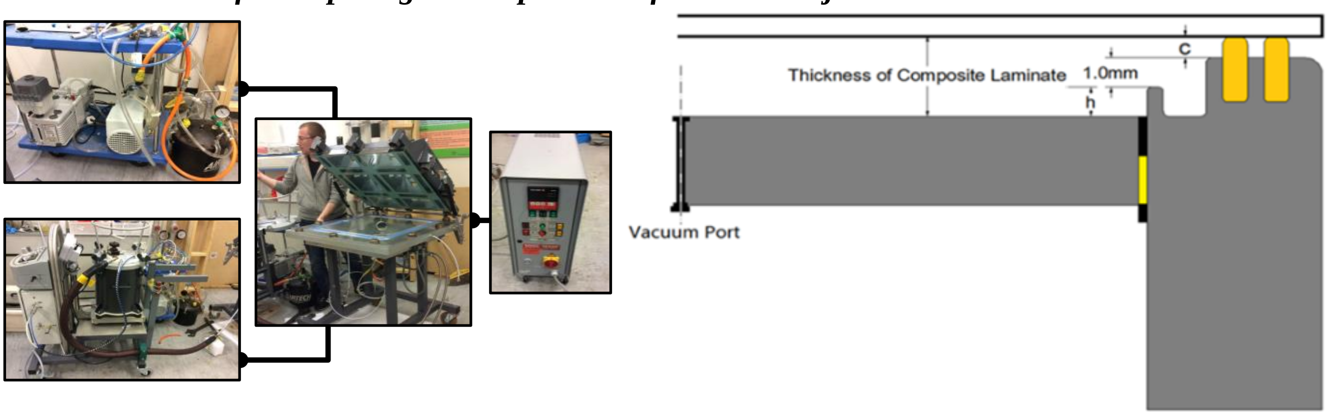


Figure 5. VARTM system and cross section view of a closed mold

To have a high fiber content laminate which would have better mechanical properties, a maximum number of layer of carbon fiber sheets would always be designed for the laminate. With this arrangement that a maximum number of layers and a highly tightened closed mold would be used, the fiber bundles of the carbon fiber sheets would be well compacted and no gaps would be existed between the fibers. The resin incorporated with the nano-particles will be very difficult to flow through the fiber bundles and to impregnate the carbon fiber sheets will be impossible.

In order to overcome the above problem, the following procedures have been developed;

- The gauge height (h) for the bottom plate of the mold would have to adjust first based on the calculation, (h) is calculated based on a fiber volume of 35~40%, (Table 4, 5) so that resin can flow freely into the carbon fiber lay-up (stage 1).

- The top plate of the mold will be lowered down so that it would just touch the rubber seal of the mold (Table 6) and then the vacuum is applied to the mold.
- The resin incorporated with nano-particle is then gradually transferred into the mold.
- Once the resin is fully wet the carbon fiber sheets, the top mold is tightened again till it reaches the calculated gauge height.

With the above procedures, the resin incorporated with nano-particles can flow easily into the layup and impregnate the carbon fiber sheets. The excessive resin can then be squeezed out during the second stage of tightening the upper mold, hence a laminate with a designated fiber volume content can be produced.
It is interested to notice that if the flow rate is too high, then air could be trapped in the lay-up. If the flow rate is too low, the lay-up couldn't be totally impregnated. It is very important to balance these two parameters so an optimum process can be established. Lots of experiments have been carried out to investigate the relationship between the injection pressure and the flow rate of resin with and without nanoparticles, the data is presented in (Table 7, 8).

Thickness of laminate (mm)	Volume fraction (%)	Thickness of a ply (mm)	Resin flow time (min)
2.3	50	0.23	33
2.5	46	0.25	15
3.0	38	0.3	6
3.2	35	0.32	2

Table 4. Fiber volume fraction and resin flow rate in stage 1 (2% nano-particle)

Fiber volume fraction (%)	Resin flow rate (cm/min)	Distribution of nanoparticles	Quality of laminate
50	<1	No nano-particle	Good
46	1.8	Very little	Good
38	4	Even	Good
35	12.5	Even	Poor

Table 5. Laminate quality related to fiber volume fraction and resin flow rate

Height	< 0.3 mm	0.5 mm	1.0 mm	1.2 mm
Injection pressure	> 3 bar	2.5 bar	1.5 bar	1 bar

Table 6. Rubber seal height related to pressure (c)

Pressure (bar)	Fiber volume fraction (%)	Resin flow rate (cm/min)
1.0		≈0.5
1.5	50	≈0.7
2.0		≈1.0

Table 7. Injection pressure and resin flow rate (no nano-particle)

Injection pressure (bar)	1.0	1.5	2.0
Resin flow rate (cm/min)	4	7	15

Table 8. Injection pressure and resin flow rate (2% of nanoparticles)

Based on the experimental data and an empirical approach, an equation has been developed to estimate the fiber volume content of a laminate and the flow time for the resin to totally impregnate the carbon fiber sheets. The equation is:

$$t = h + 1.0 + c \tag{1}$$

From Fig.5 the thickness (t) can be estimated according to the following equation:

t = h + 1.0 + c

t: thickness of laminate

h： the gauge length between the bottom mold and the inside rim of the resin flow channel

c： the gauge length between the top mold and the outside rim of the resin flow channel, the gap is round 0.2～0.4 mm such that the mold can be sealed and air-tightened, a shim is used for controlling the gauge and the tolerance is ± 0.05 mm. Fig.5

Example:

If the fiber content of the laminate is designed to be 50% and its thickness is 2.2 mm, and the nano-particle content in the resin is 2%, then the cured thickness of each layer is 0.22 mm and the areal weight is 200g/m^2, so a total number of 10 layers is required.

First of all, the h of the mold has to be determined.

t = h + 1.0 + c

First, the fiber volume (in stage 1) before applying the total pressure is assumed to be 38%, from Table 4,

t = 10 x 0.3mm= 3 mm,

From Table 6, 1 bar injection pressure is used

c = 1.2 mm

3 mm = h+1.0 mm+ 1.2mm

h = 0.8 mm

Once the bottom plate of the mold has been adjusted according to the calculated gauge height (h), the top plate could be closed up till it would touch the rubber seal. Through the top glass mold, the lay-up inside the mold can be observed whether the position is secured according to the design. Also, it is important to ensure there is no air leak in the mold. Once the mold is closed, vacuum would be applied to the mold and the resin would be injected with a bar pressure to the mold through the PVC hoses.

2.4 Curing of Composite Laminate inside The Mold

The viscosity of resin during the infusion is very critical. Based on the study of the rheology of this resin system, the viscosity of the resin shall be less than 1000 cps for at least 6 minutes so that the resin can flow and impregnate the whole lay-up. Fig.6.

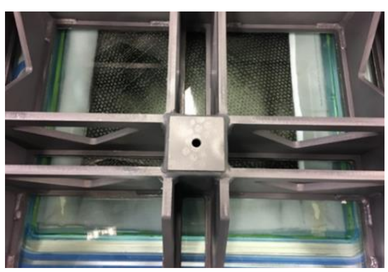


Figure 6. Resin flow inside the mold

2.5 Non-destructive Inspection of Composite Laminates

Ultrasonic technique is one of the most widely used methods which can give information on the size and location of defects. In addition, automated ultrasonic C-scan systems can provide safe, accurate and reliable inspections at high speed. Due to these advantages, the ultrasonic C-scan has been established as the primary inspection method for composite materials.

During the infusion process, some amount of air may be trapped between the plies or fiber bundles. During the curing process, this air fills spaces between plies and fibers and forms interlaminar voids or porosity. In order to ensure the good quality of the laminate, flaws of this type should be detected by ultrasonic C-scan.

The ultrasonic equipment used was Tec Scan 7 axis immersion Scanner Model: TCIS-1100 (automated immersion system), in association with TecView UT software package and Work station which includes data acquisition and analysis and contour following module. The software used is a data acquisition, control and imaging software, running under Microsoft Windows XP. It has a graphical user interface and is packed with features including real time A/B/C-scan imaging, powerful post processing modes like zoom pan cursors and waveform capture and display on sample location.

A panel (T was manufactured with several built in defects such as voids, porosity and delamination, Fig. 7. This panel was examined with C Scan using the through transmission technique, and the scan result, has been used as a reference or bench mark to determine the quality of the panels made in this project. The panel has been sectioned as shown white line in the Fig. 8. Porosity and delamination exist in area A (orange, yellow, green color) Fig 9., no defects in Area B (blue color), and porosity and delamination exist in Area A and C (orange, yellow and green color). Fig.9.

Figure 7. Panel T was trimmed along the white line for visual inspection of defects

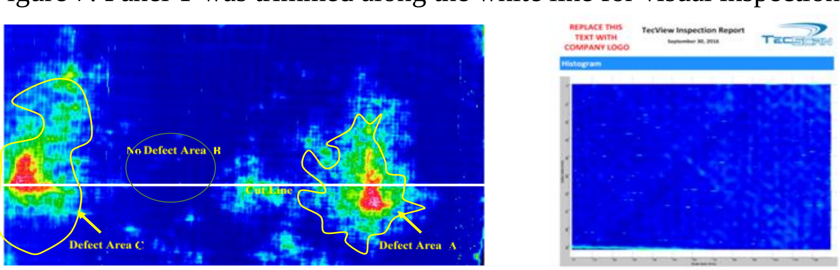


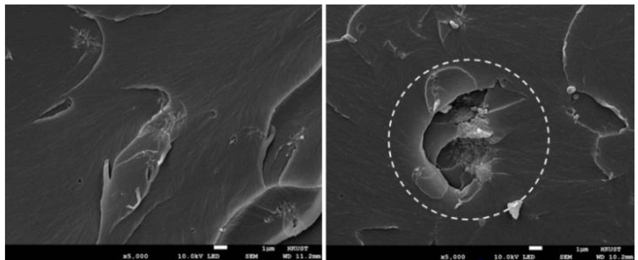
Figure 8. Ultrasonic C scan result of panel T and typical C- scan result of a defect free panel

(a) (b) (c)

Figure 9. (a) Area: porosity and delaminations, (b) Area: no defects exist, (c) Area: porosity and delamination

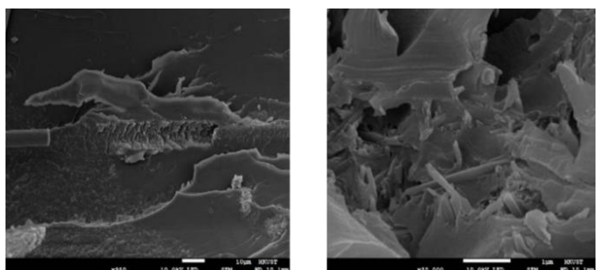
2.6 SEM Examination of Cross Section of Composite Laminate

To examine the existence of halloysite nanotubes within the composite laminate. SEM were conducted and are presented in the following Figures of 10 and 11.



(a) (b)

Figure 10. (a) (Magnification of 5,000) The fracture surface of composite materials,
(b) (Magnification of 5,000) The dot circle represented the fracture site of nanoparticles



(a) (b)

Figure 11. (a) (Magnification of x550) The fracture of carbon fiber,
(b) (Magnification of 20,000) The halloysite nanotubes embedded in the resin

2.7 Mechanical Properties of Carbon Fiber Reinforced Nano-Epoxy Composite Laminate

In order to evaluate the effects on the mechanical properties of carbon fiber reinforced nano-epoxy composite laminate manufactured by VARTM, a material characterization test matrix focused on the resin dominated properties has been established and is presented in Table 9.

TEST TYPE	Type	Ply Count	Fiber orientation	Dimension (mm)	Properties	Test replicates
Short Beam Shear ASTM D2344	Inter-laminar Shear	10	[0°/90°/0°/90°/0°]s	12.7 by 110	Strength	5
Flexural Strength ASTM D2344	Shear	10	[0°/90°/0°/90°/0°]s	4.6 by 13.8	Strength	5
90° Tension ASTM D3039	Transverse	10	90°	19.1 by 228.6 tabbed	Strength	5
Laminate Compression ASTM D3410-75	laminate	16	[45°/0°/-45°/90°]2s	19.0 by 114.3	Strength	5
Impact BBS 7250	Damage	24	[45°/0°/-45°/90°]3s	152 by 102	Strength	6

Table 9. Test Matrix- mechanical properties of carbon fiber reinforced nano-epoxy composite laminates

It is believed that an addition of small amount of nanoclays into the fiber reinforced epoxy composite system can improve the mechanical properties through the reinforcement of clay particles in the matrix rich region in order to bring the improvement in interfacial and impact properties.

Based on the preliminary experiments, the nanoclay will agglomerate in the resin and form clusters with relatively large sizes, which will have a distinct influence on the molecular mobility of the resin. It is very important that the nanoparticles would be dispersed evenly in the resin so that the resin containing nanoparticle can flow and penetrate in between the preform layers or fiber bundles. For this reason, the mechanical stirring followed by ultrasonic dispersion was used to produce the epoxy/clay hybrids when preparing the VARTM composites. In order to have relatively fiber contents of the composite laminate as well as to facilitate the flow of the resin, a procedure for preparing the mold has been developed and proved to be functionally satisfactory. In the SEM observations, the nanoclay particles were dispersed within the resins between the lamina, and some large particles collected at the edges of the preform layers and less nanoparticles in the fiber bundles.

TEST TYPE	Nanoparticles content by weight			
	0%	2%	3%	5%
Short Beam Shear (MPa)	54.9 ± 1	59.4 ± 3 (+8%)	59.8 ± 2 (+9%)	60.3 ± 2 (+10%)
Flexural Strength (MPa)	676.4 ± 25	773.1 ± 38 (+14%)	771.3 ± 36 (+14%)	768.7 ± 14 (+14%)
90° Tension (MPa)	34.1 ± 2	40.3 ± 3 (+18%)	41.4 ± 4 (+22%)	40.47 ± 0 (+19%)
Laminate Compression (MPa)	226.4 ± 3	247.3 ± 6 (+9%)	245.4 ± 6 (+8%)	244.7 ± 9 (+8%)
Impact (Damaged area) (mm^2)	863.0 ± 9	701.3 ± 13 (-19%)	771.0 ± 8 (-11%)	817.3 ± 7 (-5%)

Table 10. Summary of test results

Overall, the matrix-dominated mechanical properties of the composite laminates have been enhanced by the introduction of nanoclay particles into the resin, Table 10. The improved properties of composite laminate with 3% and 5% of the nanoparticle appeared to marginal as compared with 2%. However, the impact resistant property of composite laminate with 2 % nanoclay performed the best. The total absorbed energy required to break the composites (or delamination) in between the lamina was depended on both the matrix and the interface properties between the matric /carbon fiber. The nanoclay/ carbon fiber/ epoxy ternary cohesive microstructure appeared to provide a system for better impact resistant property.

3 CONCLUSIONS AND RECOMMENDATIONS

1. For resin to flow in a high fiber content preform in the mold, a special procedure has been developed using two stages of applying clamping pressure of the top mold. With these processing procedures, laminates with 50% of fiber content have been manufactured.
2. Techniques and procedures for dispersion of natural nanotubes of Halloysites in the resin have been developed.

3. Test results showed the laminates with 2% of nanotubes of Halloysites can enhanced the matrix dominated properties such as flexural strength, short shear strength, compression strength and 90^0degree transverse strength by 10 to 15 %.
4. Impact damage area of laminate with 2% of nanotubes of Halloysites subjected to 1.5 J and 2.0 J impact energy can be reduced by 20 % and 18%, respectively.
5. It appeared that laminates with 2% of nanotubes of Halloysites performed the best in the mechanical properties.
6. Further investigation should be carried out to understand the mechanism of the enhancement of nanoparticle to the composite laminate.
7. Flow model, scale effect and permeability of different stacking sequences should be further study.

4 ACKNOWLEDGEMENT

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