COVER SHEET

Title: Response Surface Study of Vapor-Grown Carbon Nanofiber/Vinyl Ester Nanocomposites Fabricated Using High-Shear Mixing

Authors: Sasan Nouranian Hossein Toghiani Thomas E. Lacy Charles U. Pittman, Jr.

ABSTRACT

Nanocomposites are being considered as promising candidates in different automotive structural parts because of their enhanced properties achieved at extremely low reinforcement weight fractions. However, the nano-scale size of these reinforcements poses a serious challenge to the formulation, processing, and fabrication of these nanocomposites. Therefore, a thorough study of the factors affecting the ultimate mechanical properties of these materials is of prime importance. Previously, the viscoelastic properties of a typical low-cost vapor-grown carbon nanofiber (VGCNF)/vinyl ester nanocomposite were studied utilizing a common dispersion technique, namely ultrasonication [1]. Though the ultrasonication method proves beneficial for the achievement of a certain degree of nanoreinforcement dispersion in the resin matrix, its utilization is limited to the production at the laboratory-scale. In this study, high-shear mixing has been used for the dispersion of VGCNF in vinyl ester resin. Three factors were selected for a general full factorial design of experiments approach as in our previous work [1]. The nanocomposite storage and loss moduli were used as the responses in this study and a response surface model was developed for each response. Using these models, the optimal conditions were determined. The high-shear mixing technique yields better enhancement of storage modulus compared to ultrasonication indicating greater nanodispersion was achieved.

INTRODUCTION

Today, two fundamental interrelated issues in the design and manufacture of vehicles and aircraft are weight and fuel consumption. For this reason, developing new

Sasan Nouranian and Hossein Toghiani, The Dave C. Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762, U.S.A.

Thomas E. Lacy, Department of Aerospace Engineering, Mississippi State University, Mississippi State, MS 39762, U.S.A.

Charles U. Pittman, Jr., Department of Chemistry, Mississippi State University, Mississippi State, MS 39762, U.S.A.

light-weight materials with mechanical properties and crash performance similar to or improved in comparison with traditional structural materials is a top research priority in the materials engineering field. Polymer nanocomposites are among the most promising candidates for this purpose. They are reinforced systems where the reinforcement is a fiber, tube, clay, rod, etc. with at least one dimension less than 100 nm [2]. The extremely small size of these reinforcements can impart exceptional property enhancements to the matrix at the molecular scale. Though many useful applications have been proposed for these nanoreinforced systems in the automotive industry [3], the difficulty in achieving a uniform product due to fabrication issues [4] has hindered the wide commercialization of polymer nanocomposites.

Vapor-grown carbon nanofibers (VGCNF) are relatively inexpensive nanoreinforcements with typical diameters of 70-200 nm and lengths of 50-200 microns [5]. These high aspect ratio fibers are increasingly being employed in different thermoplastic and thermoset resin systems where promising mechanical property enhancements [6,7] and interesting behavior at different loading conditions [8] have been observed. In this study, the widely used vinyl ester resin, reinforced with VGCNF, has been studied. This thermoset nanocomposite can be used as a standalone structural material or alternatively as a nanophased matrix in traditional long fiber reinforced composites. These latter materials are known as "hybrid composites", where the nanoreinforced matrix imparts certain interlaminar mechanical property enhancements [9,10].

Many researchers have attempted to process and characterize VGCNF/vinyl ester nanocomposites [11]. However, the response surface study of the aforementioned system, where the effects of different formulations and processing factors on mechanical properties are evaluated, has not been conducted. This is an essential element in establishing a basic knowledge of the interplay between design parameters. We previously conducted a response surface study on the viscoelastic properties of VGCNF/vinyl ester nanocomposites prepared using ultrasonication [1]. Though ultrasonication is useful for laboratory-scale processing of nanocomposites, it is inappropriate for large-scale mixing of nanocomposite ingredients. In this study, we continue our analysis of these systems by employing more readily scalable high-shear mixing. The factors of this study are the same as before: 1) type of nanofiber, 2) use of dispersing agent, and 3) nanofiber weight fraction. In selecting these formulation parameters, attention was given to available dispersion-enhancing techniques: use of a dispersing agent and surface functionalization of nanofibers.

EXPERIMENTAL

Materials

The thermosetting resin used in this study was Derakane 441-400 (Ashland Co.), an epoxy vinyl ester resin [1]. This resin has low styrene content (33%), and possesses good mechanical, thermal, and corrosion properties. It also has good infusion characteristics, which makes it appropriate for use in vacuum-assisted resin transfer molding (VARTM). VARTM can be used for the fabrication of traditional and hybrid nanophased laminated composite structures under vacuum or under pressure.

Two vapor-grown carbon nanofiber (VGCNF) grades were used: 1) PR-24-XT-LHT (Applied Sciences Inc.), a pristine grade that has been heat-treated at 1500°C. It has an average diameter of 150 nm, a surface area of 35-45 m²/g, and a dispersive surface energy of about 155 mJ/m²; 2) PR-24-XT-LHT-OX (Applied Sciences Inc.), a surface-oxidized grade with other properties similar to PR-24-XT-LHT. Surface oxidation introduces hydroxyl, carbonyl, and carboxylic acid functions onto the VGCNF surfaces. These nanofibers were used as-received without any modifications.

Methyl ethyl ketone peroxide (MEKP) (U.S. Composites Inc.) was used as the curing agent (hardener). Cobalt naphthenate 6% (North American Composites Co.) was used as the catalyst promoter. Its presence significantly accelerates peroxide decomposition (at ambient and at higher temperature), speeding the curing reaction.

A combination of two air release agents were used to remove air bubbles trapped in the resin/VGCNF blend during mixing and processing: BYK-A 515 and BYK-A 555 (both from BYK Chemie GmbH). These surfactant-type additives facilitate the removal of air bubbles after mixing and during curing of the resin. If air bubbles are not removed, voids will be formed in the final cured specimen, which negatively affects the mechanical properties.

BYK-9076 (BYK-Chemie GmbH) was used as the dispersing agent (also known as dispersant). It is an alkylammonium salt of a high molecular weight copolymer. This agent has been successfully employed for the wetting and dispersion enhancement of carbon blacks in polyesters, vinyl esters, and epoxy systems. BYK Chemie recommends BYK-9076 for vapor-grown carbon nanofibers in vinyl esters. Numerous researchers have used this additive to aid dispersion of nanoreinforcements [12-14]. Materials used for this study are summarized in Table I.

Material	Function	Manufacturer			
Derakane 411-400	Epoxy vinyl ester resin	Ashland Co.			
Cobalt	Promoter (catalyst)	North American Composites Co			
naphthenate 6%		North American composites co.			
BYK-A 515	Air release (antifoam) agent	BYK Chemie GmbH			
BYK-A 555	Air release (antifoam) agent	BYK Chemie GmbH			
BYK-9076	Wetting/dispersing agent	BYK Chemie GmbH			
PR-24-XT-LHT	Pristine vapor-grown carbon nanofiber (VGCNF)	Applied Sciences Inc.			
PR-24-XT-LHT-OX	Oxidized vapor-grown carbon nanofiber (VGCNF-OX)	Applied Sciences Inc.			
MEKP	Curing agent (hardener)	U.S. Composites Inc.			

TABLE I. LIST OF MATERIALS AND THEIR SUPPLIERS

Formulations

The nanocomposite formulations used in this investigation are shown in Table II. All ingredients were weighed based on 100 parts resin. The amounts of resin, promoter, air release additives, and hardener were fixed by weight, while VGCNF and dispersing agent amounts were varied based on the formulation (Table II).

Ingredient	Weight (g)				
Derakane 441-400 (vinyl ester resin)	100				
Cobalt naphthenate 6% (promoter)	0.20				
BYK-A 515 (air release agent)	0.20				
BYK-A 555 (air release agent)	0.20				
BYK-9076 (dispersing agent)	1:1 ratio with respect to VGCNF ¹				
VGCNF ² (vapor-grown carbon nanofiber)	0.00/0.25/0.50/0.75/1.00				
MEKP (hardener)	1.00				

TABLE II – NANOCOMPOSITE FORMULATIONS

¹Dispersing agent is varied directly with VGCNF as indicated by the experimental design

²Pristine and oxidized nanofibers were used as indicated by the experimental design

Equipment and Data Analysis Software

Resin/additive/VGCNF blends were prepared using a laboratory high-shear mixer (Model L4RT-A, Silverson Machines Ltd). The resin/VGCNF blends were molded in chrome-plated molds (TMI Co.) and cured in an oven (Fisher Scientific). The final nanocomposite specimens were tested using a TA Instruments Q800 Dynamic Mechanical Analyzer. The design of experiments and subsequent data analysis were performed by Stat-ease DesignExpert® software [15].

Design of Experiments

The effect of several formulation factors on viscoelastic properties of the nanocomposites, i.e. storage modulus, and loss modulus were investigated because, stiffness and toughness are important for structural automotive parts. Three formulation-related factors were selected as indicated in Table III. Factors A (type of VGCNF) and B (use of dispersing agent) were treated as categorical variables with discrete values, while factor C (VGCNF weight fraction) was treated as a continuous numerical variable.

Factor designation	Factor	Levels					
		1	2	3	4	5	
А	Type of VGCNF	Pristine	Oxidized	-	-	-	
В	Use of dispersing agent	Yes	No	-	-	-	
С	Amount of VGCNF (phr ¹)	0	0.25	0.50	0.75	1.00	

TABLE III. FACTORS OF STUDY AND THEIR LEVELS

¹parts per hundred resin

Due to the mixed-level nature of the problem, a general full factorial design was conducted with 20 treatments (runs). These treatments are shown in Table IV.

Specimen Preparation

The following procedure was used for specimen preparation [1]:

1) Ingredients were added and weighed in a 240 ml cup in the order of resin, promoter, air release agents, dispersing agent (if used in the treatment), and then VGCNF. Before the addition of nanofibers, the mixture was mixed by hand to make sure that the promoter, air release agents and the dispersing agent were uniformly mixed with the resin. A hazy appearance resulted due to the presence of air release agents in the system. The dispersing agent was added to the resin prior to the addition of nanofibers.

2) The cup containing the mixture was then put in an ice bath and its contents were mixed using the high-shear mixer for 10 min. at 3000 rpm followed by 5 min. at 4000 rpm. Each batch was prepared based on 75 g resin was. Cooling the mixture was necessary because the temperature rose during mixing, which could lead to premature curing and viscosity issues at later stages of the process.

3) The hardener (MEKP) was then added and mixed by hand with a metal bar for 5 min at ambient temperature.

4) The mixture was degassed for 5-15 min at ambient temperature using a vacuum pump at pressures of -85 to -95 kPa until all the air bubbles were removed. The degassing time was different for each formulation because of the differences in their viscosities. Care has to be taken not to remove styrene, even though a small amount might be removed together with the air bubbles.

5) The resin was gently poured into the molds and cured in a pre-heated oven (5 h at 60 °C and 2 h at 120 °C). This cure schedule yielded adequate curing.

Dynamic Mechanical Analysis (DMA)

Test specimens $(35 \times 12.5 \times 3.5 \text{ mm}^3)$ were cut from the cured molded composites. Dynamic Mechanical Analysis (DMA) was conducted according to ASTM D 5418 in single cantilever mode on a dual cantilever clamp, with amplitude of 15 μ m, at a fixed frequency of 10 Hz, a heating rate of 5 °C/min, and a temperature range of 27 °C to 160 °C. Three separate measurements were obtained for each run (Table IV) and average values were calculated and used in the analysis.

RESULTS AND DISCUSSION

Statistical Analysis

Analysis of Variance (ANOVA)

At least three measurements were performed for each experimental treatment. Each cut specimen was tested only once and averages were calculated. Two viscoelastic responses were used in the analysis: storage modulus (a measure of material stiffness) and loss modulus (a measure of material energy-dissipating capability). The values obtained at 27 $^{\circ}$ C (close to room temperature) were used for the statistical analysis. The experimental treatments and responses are shown in Table IV.

Run	Type of nanofiber	Use of dispersing agent	Nanofiber weight fraction (phr)	(Response 1) ¹ Measured Storage Modulus (MPa)	(Response 2) ¹ Measured Loss Modulus (MPa)
1	Oxidized	Yes	0.25	2578	48
2	Oxidized	Yes	1.00	2643	49
3	Oxidized	No	1.00	2673	45
4	Pristine	Yes	0.25	2551	51
5	Pristine	Yes	0.00	2007	162
6	Pristine	No	0.50	2527	43
7	Oxidized	No	0.50	2632	44
8	Oxidized	Yes	0.00	2007	162
9	Pristine	Yes	0.50	2746	49
10	Oxidized	Yes	0.50	2648	59
11	Oxidized	No	0.00	2186	58
12	Pristine	No	0.75	2488	50
13	Oxidized	No	0.25	2582	45
14	Pristine	No	0.25	2674	48
15	Pristine	No	1.00	2691	50
16	Pristine	Yes	1.00	2676	51
17	Pristine	Yes	0.75	2713	50
18	Oxidized	Yes	0.75	2682	47
19	Pristine	No	0.00	2186	58
20	Oxidized	No	0.75	2604	46

TABLE IV. TREATMENTS AND MEASURED RESPONSES

¹Values correrspond to values measured at 27 °C (the average of at least three separate measurements)

The average variations in measured storage and loss moduli were 1-4% and 3-8%, respectively. These values correspond to the values obtained at the curing conditions applied in this study and could change at a different cure protocol. A comparison of storage modulus values for vinyl ester resins at several curing conditions was reported by Li [16].

Storage Modulus

An analysis of variance (ANOVA) was performed on the storage modulus data. Different regression models (linear, quadratic, cubic, etc.) were evaluated and the most appropriate one based on the highest adjusted and predicted r-squared values was selected. This resulted in a cubic model with all terms used in the polynomial equation. The ANOVA results for the final model are shown in Table V.

			- 010			
Source	Sum of squares	Degree of freedo	es om	Mean square	F value ⁽¹⁾	$Prob > F^{(2)}$
Model	9.953×10^{5}	11		90482.15	24.68	< 0.0001 ⁽³⁾
A: Type of nanofiber	110.14	1		110.14	0.030	0.8667
B: Use of dispersant	22489.02	1		22489.02	6.13	0.0383 ⁽⁴⁾
C: Nanofiber weight fraction	4218.00	1		4218.00	1.15	0.3147
AB	3025.80	1		3025.80	0.83	0.3902
AC	57.60	1		57.60	0.016	0.9033
BC	27878.40	1		27878.40	7.60	0.0248 ⁽⁴⁾
C ²	2.633×10^{5}	1		2.633×10^{5}	71.82	< 0.0001 ⁽⁴⁾
ABC	2190.40	1		2190.40	0.60	0.4618
AC ²	330.29	1		330.29	0.090	0.7717
BC ²	37648.29	1		37648.29	10.27	0.0125 ⁽⁴⁾
C ³	1.095×10^{5}	1		1.095×10^{5}	29.87	0.0006 ⁽⁴⁾
Residual	29330.52	8		3666.31		
Total sum of						
squares corrected	1.025×10^{6}	19				
for the mean						
	Ot	ther mod	lel sta	atistics		
Standard deviation: 60.55				R-squared: 0.9714		
Mean: 2524.70				Adjusted r-squared: 0.9320		
Coefficient of variance %: 2.40				Predicted r-squared ⁽⁵⁾ : 0.7540		
Predicted residual sum of squares:				Adequate precision ⁽⁶⁾ : 15.618		
2.52	21 × 10 ⁵					

TABLE V. ANOVA TABLE FOR STORAGE MODULUS

¹Mean square for the term divided by mean square for the residual

²Probability value associated with F value for the term (<0.05 indicates significant effect, >0.10 indicates insignificant effect)

³Selected model is significant. There is only 0.01% chance that this F value could occur due to noise ⁴Model term is significant

⁵Predicted r-squared (0.7540) is in reasonable agreement with adjusted r-squared (0.9320).

⁶Measures the signal to noise ratio. A value greater than 4 is desirable. Here, we have an adequate signal.

Figure 1 shows normal and variation plots for storage modulus data. All the studentized residuals lie on a straight line, which indicates that the normality assumption for ANOVA is valid. Furthermore, the random scatter of residuals is an indication that the constant variance assumption is also valid.



Figure 1. Normal plot of residuals and residual variation plot for checking the normality and constant variance assumptions (Storage modulus)

The response surface model for storage modulus, S, may be expressed in terms of "coded" values of the experimental factors:

$$S=2661.84+3.66\times a-52.26\times b-61.71\times c+12.30\times ab+2.40\times ac-52.80\times bc-274.29\times c2+14.80\times abc-9.71\times ac2+103.71\times bc2+348.83\times c3 (MPa)$$
(1)

Here, coded (non-dimensional) values of the experimental factors are used. For example, use of pristine and oxidized VGCNF would correspond to a= -1.0 and a= +1.0 respectively. Hence, categorical factors are specified using coded values ± 1.0 . The same is true for numerical factor C (VGCNF weight fraction) which varies between -1.0 and +1.0. Coded factors are shown in Table VI together with the corresponding actual factors for reference.

Factor	Factor	Levels						
Туре	designation	1	2	3	4	5		
Actual	А	Pristine	Oxidized	-	-	-		
Coded	А	-1.0	1.0	-	-	-		
Actual	В	Yes	No	-	-	-		
Coded	В	-1.0	1.0	-	-	-		
Actual	С	0	0.25	0.50	0.75	1.00		
Coded	С	-1.0	-0.5	0.0	0.5	1.0		

TABLE VI. CODED AND ACTUAL FACTORS

Loss Modulus

Analysis of variance (ANOVA) for loss modulus data are shown in Table VII. Again, different regression models (linear, quadratic, cubic, etc.) were evaluated and a reduced cubic model was selected based on the highest yielded adjusted and predicted r-squared values. The reduced model did not include all the terms in the polynomial.

Source	Sum of squares	Degree of freedom	Mean square	F value ⁽²⁾	$Prob > F^{(3)}$	
Model	21561.91	9	2395.77	15.01	0.0001 ⁽⁴⁾	
A: Type of nanofiber	4.05	1	4.05	0.025	0.8766	
B: Use of dispersant	16.47	1	16.47	0.10	0.7546	
C: Nanofiber weight fraction	123.09	1	123.09	0.77	0.4004	
AB	8.45	1	8.45	0.053	0.8226	
AC	5.62	1	5.62	0.035	0.8548	
BC	4223.03	1	4223.03	26.46	0.0004 ⁽⁵⁾	
C ²	4375.45	1	4375.45	27.42	0.0004 ⁽⁵⁾	
BC ²	2538.02	1	2538.02	15.90	0.0026	
C ³	1525.23	1	1525.23	9.56	0.0114 ⁽⁵⁾	
Residual	1595.84	10	159.58	-	-	
Total sum of squares corrected for the mean	23157.75	19	-	-	-	
		Other mode	el statistics			
Standa	ard deviation: 1 Mean: 60.75	2.63	R-squared: 0.9311 Adjusted r-squared: 0.8691			
Coefficient	of variance %	: 20.79 ⁽⁶⁾	Predicted r-squared ⁽⁷⁾ : 0.7551			
Predicted residu	ual sum of squa	ares: 5671.40	Adequate precision ⁽⁸⁾ : 13.501			

TABLE VII. ANOVA TABLE FOR LOSS MODULUS⁽¹⁾

¹Reduced cubic model

²Mean square for the term divided by mean square for the residual

³Probability value associated with F value for the term (<0.05 indicates significant effect, >0.10 indicates insignificant effect)

⁴Selected model is significant. There is only 0.01% chance that this F value could occur due to noise. ⁵Model term is significant.

⁶Coefficient of variation is rather large. This could be due to the high value of 162 MPa for neat resin with dispersing agent. This value could be a potential outlier.

⁷Predicted r-squared (0.7551) is in reasonable agreement with adjusted r-squared (0.8691).

⁸Measures the signal to noise ratio. A value greater than 4 is desirable. Here, we have an adequate signal.

Similarly, the response surface model for the loss modulus, L, may be expressed as:

$$L=43.07-0.45\times a+1.41\times b+10.54\times c-0.65\times ab-0.75\times ac+20.55\times bc+35.36\times c^2-26.93\times bc^2-41.17\times c^3$$
(2)

Normal and variation plots for loss modulus data are shown in Figure 2. Again, all the studentized residuals lie on a straight line, which indicates that the normality assumption for ANOVA is valid. The random scatter of residuals is also an indication that the constant variance assumption is valid.



Figure 2. Normal plot of residuals and residual variation plot for checking the normality and constant variance assumptions (Loss modulus)

Response Surface Model Predictions

The model predictions in terms of actual factors for the storage and loss moduli are shown in Figures 3 and 4.



Figure 3. Model predictions for the storage modulus. Note: DA=dispersing agent



Figure 4. Model predictions for the loss modulus. Note: DA=dispersing agent

The pristine nanofiber in the presence of dispersing agent (curve 1 in Figure 3) yields the highest storage modulus for nanofiber weight fractions above ~0.25 phr. The effect of dispersing agent is obvious when curves 1 and 3 and when curves 2 and 4 are compared. Use of dispersing agent at moderate to high nanofiber weight fractions yields much improved storage moduli values for both pristine and oxidized nanofibers.

The highest loss modulus is observed for pristine nanofiber without dispersing agent in the range ~ 0.45 to ~ 0.90 phr. Use of dispersing agent yields lower loss moduli in the same range. These effects are discussed in the next section where we consider main effects and interactions between factors for both storage and loss moduli.

Main Effects and Interactions

Storage Modulus

The interaction effects between different factors are summarized in Figures 5-7. These effects can also be elucidated by comparing the curves in the model prediction graph for storage modulus (Figure 3).

Interaction between the Type of Nanofiber (A) and the Use of Dispersing Agent (B)

The use of dispersing agent improves the storage modulus at moderate to high pristine nanofiber weight fractions, while the trend reverses for oxidized nanofibers. At higher loading levels of oxidized nanofibers, the use of dispersing agent actually deteriorates the storage modulus slightly (Figure 5).



Figure 5. Interaction between the type of nanofiber (A) and the use of dispersing agent (B) at two carbon nanofiber weight fractions: 0.5 phr (left) and 1.00 phr (right)

Interaction between the Type of Nanofiber (A) and the Nanofiber Weight Fraction (C)

Figure 6 shows the effect of nanofiber type on the storage modulus in the presence and absence of dispersing agent. In the absence of dispersing agent, the oxidized nanofibers yield higher storage moduli than the pristine nanofibers at weight fractions above ~0.25 phr. When dispersing agent is present, the pristine nanofibers yield higher storage moduli at weight fractions above ~0.45 phr. Furthermore, there is an overall increase in the storage modulus for the pristine nanofibers in the presence of dispersing agent compared to the case where the dispersing agent is absent. This suggests that the dispersing agent acts better on pristine nanofibers at higher nanofiber weight fractions where nanodispersion becomes more difficult, and its effect is comparable to the surface oxidation of nanofibers. The same results had been obtained in the case where ultrasonication was used for mixing the nanofibers into the resin [1].



Figure 6. Interaction between the type of nanofiber (A) and the nanofiber weight fraction (C) in the absence (left) and presence (right) of dispersing agent

Interaction between the Use of Dispersant (B) and the Nanofiber Weight Fraction (C)

The dispersing agent acts better at higher nanofiber weight fractions in the case of pristine nanofibers (Figure 7 –left). In contrast, the oxidized nanofibers yield better storage modulus values in the absence of dispersing agent at higher nanofiber weight fractions (Figure 7 – right). The use of dispersing agent in the range ~0.25 to ~0.90 phr, results in higher storage moduli for both pristine and oxidized nanofibers (Figure 3).



Figure 7. Interaction between the use of dispersing agent (B) and the nanofiber weight fraction (C) for pristine (left) and oxidized (right) nanofibers

Loss Modulus

Figures 8-10 show interaction effects between different factors for the loss modulus. These graphs should be studied in conjunction with Figure 4.

Interaction between the Type of Nanofiber (A) and the Use of Dispersing Agent (B)

The use of dispersing agent yields higher loss moduli values at higher nanofiber weight fraction (Figure 8 -right). This is true for both types of nanofibers.



Figure 8. Interaction between the type of nanofiber (A) and the use of dispersing agent (B) at two weight fractions of carbon nanofibers: 0.5 phr (left) and 1.00 phr (right)

Interaction between the Type of Nanofiber (A) and the Nanofiber Weight Fraction (C)

The loss modulus decreases with increasing nanofiber weight fraction for both pristine and oxidized nanofibers (Figure 9). The nanofiber surface oxidation doesn't seem to have a significant effect on the loss modulus.



Figure 9. Interaction between the type of nanofiber (A) and the nanofiber weight fraction (C) in the absence (left) and presence (right) of dispersing agent

Interaction between the Dispersant Use (B) and the Nanofiber Weight Fraction (C)

The loss modulus drops for both pristine and oxidized nanofibers (Figure 10) with increasing nanofiber weight fraction. The decrease is more profound when the dispersing agent is present.



Figure 10. Interaction between the use of dispersing agent (B) and the nanofiber weight fraction (C) for pristine (left) and oxidized (right) nanofibers

Numerical Optimization

The optimal levels for the factors under study were determined based on a numerical optimization that was performed on the statistical models. This was done by maximizing either storage modulus or both storage and loss modulus with different levels of importance. Using desirability functions and 140 starting points in the response surface model, the optimal levels were determined. The results are shown in Table VIII.

Goal	Factors	Storage modulus	Sqrt(Loss modulus)	Desirability ⁽¹⁾	Optim	al Leve	ls ⁽²⁾
Maximize	All in ⁽³⁾	(Maximize)	(In range)		А	В	С
storage modulus	range	5 of 5 Weight: 1	3 of 5 Weight: 1	0.963	Pristine	Yes	0.45
Maximize both	All in	(Maximize)	(Maximize)		А	В	С
storage and loss modulus	range	5 of 5 Weight: 1	3 of 5 Weight: 0.1	0.882	Pristine	Yes	1.00

TABLE VIII. OPTIMAL FACTOR LEVELS

¹This value ranges from 0 to 1.

²The conditions correspond to factor levels as described in Table III. A=type of VGCNF, B=use of dispersing agent or not, and C=amount of VGCNF (phr)

³This means that all factors are within their min to max range.

Comparison of Ultrasonication and High-Shear Mixing

A comparison is made between the storage moduli values from ultrasonication and from high-shear mixing in Figure 11. The ultrasonication data are taken from our previous work [1]. It can be seen that high-shear mixing yields a higher storage modulus for each comparable configuration when compared to ultrasonication mixing. This suggests that high-shear mixing results in better nanofiber dispersion in the resin. This still must be verified by Scanning Electron Microscope (SEM) imaging. Highshear mixing appears to be more effective in breaking nanofiber agglomerates. Since it is more scalable to industrial scale mixing, easier to use and allows shorter processing times, it may be widely employed in the large-scale processing of nanocomposites in the near future.

High-shear mixing of one-dimensional nanofibers has the potential to break fibers, thereby lowering their average aspect ratio. Therefore, while increasing mechanical properties by improving nanodispersion and decreasing the presence of nested nanofiber aggregates, a counter-effect on mechanical properties could occur if the aspect ratio drops significantly. The effect of shear levels and shearing time on VGCNF aspect ratios at this time is unknown. It will also likely be a function of VGCNF loading levels. Furthermore, how the mechanical properties will respond to aspect ratio changes is unknown. These are topics of interest in our laboratory, which are under study.



Figure 3. Model predictions for the storage modulus. Note: DA=dispersing agent, HS=high-shear mixing, SO=ultrasonication

CONCLUSIONS

The models developed for the storage and loss modulus in this study can be used to predict the viscoelastic properties of VGCNF/vinyl ester nanocomposites. However, these models are valid only for room temperature behavior of these nanocomposites, fabricated according to the procedures outlined in this work. High-shear mixing as a method of incorporating nanofibers in the resin has proved to yield better viscoelastic properties, especially higher storage moduli, compared to ultrasonication discussed elsewhere [1]. High-shear mixing requires less processing time and can be scaled up to the industrial scale.

FUTURE WORK

As the next step in our work, we will consider a coupled high-shear mixing and ultrasonication approach to investigate further whether more aggressive mixing of the nanofibers in the resin will result in improved mechanical properties. We speculate that more aggressive mixing might decrease the nanofiber aspect ratio, thereby decreasing mechanical properties. Measuring nanofiber aspect ratio is difficult (aspect ratio ranges are not established for the starting VGCNFs). Such measurements in a liquid resin (after mixing) or in the cured nanocomposite will be extremely challenging. However, experiments measuring composite properties at constant composition, where the only variable is shear magnitude or shear time, will be paired with SEM/TEM to look at the degree of dispersion.

ACKNOWLEDGMENTS

This work was graciously sponsored by the Department of Energy under contract DE-FC26-06NT42755. Special thanks are afforded to the program monitor, Joseph Carpenter. We also wish to acknowledge Center for Advanced Vehicular Systems (CAVS) at Mississippi State University for their support.

REFERENCES

- Nouranian, S., H. Toghiani, T. E. Lacy, and C. U. Pittman, Jr. 2009 "Viscoelsatic Properties of Vapor-grown Carbon Nanofiber/Vinyl Ester Nanocomposites," presented at SAMPE'09 International Symposium and Exhibition, Changing Times – New Opportunities, Are You Prepared? Baltimore, MD, May 18-21, 2009.
- 2. Schadler L. S., L. C. Brinson, and W. G. Sawyer. 2007 "Polymer Nanocomposites: a Small Part of the Story," JOM, March 2007 issue:53-60.
- Presting, H., and U. König. 2003 "Future Nanotechnology Developments for Automotive Applications," Mat. Sci. Eng. C, 23: 737-741.
- 2002 "Auto Applications Drive Commercialization of Nanocomposites," Plastics, Additives and Compounding, 4: 30-33.
- 5. Applied Scienses, Inc. (Pyrograf III products). http://pyrografproducts.com/Merchant5/merchant.mvc?Screen=cp_nanofiber.
- Zhou, Y., F. Parvin, S. Jeelani, and P. K. Mallick. 2008 "Improvement in Mechanical Properties of Carbon Fabric-Epoxy Composite Using Carbon Nanofibers," *J. Mater. Process. Tech.*, 198(1-3):445-453.
- Gao, Y., P. He, J. Lian, L. Wang, D. Qian, J. Zhao, W. Wang, M. J. Schulz, J. Zhang, X. Zhou, D. Shi. 2006 "Improving the Mechanical Properties of Polycarbonate Nanocomposites with Plasma-Modified Carbon Nanofibers," *J. Macromol. Sci. B*, 45 B(4):671-679.
- Hutchins, J.W., J. Sisti, T. E. Lacy, S. Nouranian, H. Toghiani, and C. U. Pittman, Jr. 2009 "High Strain Rate Behavior of Carbon Nanofiber Reinforced Vinyl Ester," presented at the 50th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Palm Springs, CA, May 4-7, 2009.
- Sadeghian, R., S. Gangireddy, B. Minaei, and K. –T. Hsiao. 2006 "Manufacturing Carbon Nanofibers Toughened Polyester-glass Fiber Composites Using Vacuum Aassisted Resin Transfer Molding," *Composites A*, 37:1787-1795.
- Arai, M., Y. Noro, K. Sugimoto, and M. Endo. 2008 "Mode I and Mode II Interlaminar Fracture Toughness of CFRP Laminates Toughened by Carbon Nanofiber Interlayer," *Compos. Sci. Technol.*, 68: 516-525.
- McMorrow, B., R. Chartoff, and D. Klosterman. 2003 "Processing and Characterization of a Carbon Nanofiber/Vinyl Ester Resin Composite," Presented at SAMPE'03 International Symposium and Exhibition, Advancing Materials in the Global Economy - Applications, Emerging Markets and Evolving Technologies, Long Beach, CA, May 11-15, 2003.
- Liao, Y.-H, O. Marietta-Tondin, Z. Liang, C. Zhang, and B. Wang. 2004 "Investigation of Dispersion Process of SWNTs/SC-15 Epoxy Resin Nanocomposites," *Mater. Sci. Eng. A*, 385:175-181.
- Xia, H., and M. Song. 2005 "Preparation and Characterization of Polyurethane-Carbon Nanotube Composites," *Soft Matter*, 1:386-394.
- 14. Zhang, W., A. Joshi, Z. Wang, R. S. Kane, and N. Koratkar. 2007 "Creep Mitigation in Composites Using Carbon Nanotube Additives," *Nanotechnology*, 18:185703-185708.

- 15. Stat-ease DesignExpert® software. http://www.statease.com/software.html.
- 16. Li, H. 1998 "Synthesis, Characterization, and Properties of Vinyl Ester Matrix Resins," *Ph. D. Dissertation in Chemistry*, Virginia Polytechnic Institute and State University:89.