EXPERIMENTAL STUDY OF THE DYNAMIC MECHANICAL PROPERTIES OF VAPOR-GROWN CARBON NANOFIBER/VINYL ESTER NANOCOMPOSITES FABRICATED USING COUPLED HIGH-SHEAR MIXING AND ULTRASONICATION

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ABSTRACT

Recent advances in the field of polymer nanocomposites and nanophased hybrid composites have provided new opportunities in the design and fabrication of novel light-weight structural materials for use in automotive parts. Though preliminary studies show promising improvements in the mechanical, thermal, and other properties of traditional composites reinforced with small amounts of nanoreinforcing agents including nanotubes, nanofibers, nanoclays, etc., a more systematic study is needed encompassing formulation, mixing, and processing of nanocomposites. This is specifically true because of issues with the dispersion of nanoreinforcements in the polymer matrix and a lack of knowledge with respect to the factors affecting the ultimate properties of interest. In this study, which builds on our previous studies [1,2], a designed experimental approach has been employed to study the effect of three formulation factors on the viscoelastic properties of vapor-grown carbon nanofiber/vinyl ester nanocomposites. These factors are: nanofiber weight fraction, nanofiber type (pristine/oxidized), and use of a dispersing agent. The mixing procedure used in these studies was a coupled high-shear mixing/ultrasonication technique. Using analysis of variance and regression techniques, a response surface model was developed for the current design and optimal conditions were determined. The nanofiber weight fraction was the major factor with significant effect on the storage and loss moduli, while the other factors had minor effects. The results were further compared to the cases studied previously [1,2] where the mixing method involved only ultrasonication or high-shear mixing.

1. INTRODUCTION

Nanotechnology science and engineering has been the focus of research during the past few years [3]. In the field of materials engineering, the use of nano-scale constituents, which by definition have at least one dimension less than 100 nm [4], in traditional structural materials has brought about promising results with respect to improvements in mechanical [5,6], thermal [7,8], and electrical [9,10] properties. The automotive industry has long strived to improve the fuel economy in vehicles by utilizing methods such as weight reduction. Nanocomposites are candidate materials for this purpose. They are composed of traditional composites where the matrix properties have been enhanced by incorporation of small amounts of nano-scale materials. In this study, vapor-grown carbon nanofibers (VGCNFs) were incorporated into a thermosetting vinyl ester (VE) resin as a candidate structural nanocomposite material for automotive parts. These nanophased resins can further be incorporated in "hybrid" continuous fiber or laminated composites. The selection of the nanoreinforcement/matrix combination was largely based on cost-effectiveness and performance considerations. A design of experiments [11] was conducted taking into account three formulation-related factors in the fabrication of VGCNF/VE nanocomposites, i.e. nanofiber type, nanofiber weight fraction, and the use of dispersing agent. The dynamic mechanical properties of the fabricated nanocomposites (storage and loss moduli) were selected as responses of interest. A response surface model was further developed using nonlinear regression analysis of the data.

2. EXPERIMENTAL

2.1 Materials

Derakane 441-400 (Ashland Co.), an epoxy vinyl ester resin with 33% styrene content, was used as the thermosetting matrix resin. Two vapor-grown carbon nanofiber (VGCNF) grades were used as nanoreinforcing agents: 1) PR-24-XT-LHT (Applied Sciences Inc.), a pristine grade that has been heat-treated at 1500°C with an average diameter of 150 nm, surface area of 35-45 m^2/g, and dispersive surface energy of 155 mJ/m^2; 2) PR-24-XT-LHT-OX (Applied Sciences Inc.), a surface-oxidized grade with other properties similar to PR-24-XT-LHT. Methyl ethyl ketone peroxide (MEKP) (U.S. Composites Inc.) was used as the curing agent. Cobalt naphthenate 6% (North American Composites Co.) was used as the curing promoter. In order to remove air bubbles introduced to the resin/VGCNF blend during mixing and processing, a combination of two air release agents were used: BYK-A 515 and BYK-A 555 (both from BYK Chemie GmbH). BYK-9076 (BYK-Chemie GmbH), an alkylammonium salt of a high molecular weight copolymer, was used as the dispersing agent.

2.2 Formulations

The general nanocomposite formulations are shown in Table 1. Compositions are formulated based on 100 parts of the resin (parts per hundred parts resin or phr).

Table 1 – Nanocomposite formulations

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
VGCNF (vapor-grown carbon nanofiber)	0.00/0.25/0.50/0.75/1.00
MEKP (hardener)	1.00

2.3 Equipment and Data Analysis Software

The materials were prepared using a laboratory high-shear mixer (Model L4RT-A, Silverson Machines Ltd) and an ultrasonic processor Model GEX750-5C (Geneq Inc.) combined with an analog 120V vortex mixer (Fisher Scientific). The resin/VGCNF blends were molded in chrome-plated molds (TMI Co.) and oven cured (Fisher Scientific). The nanocomposite test specimens were analyzed by a TA Instruments Q800 Dynamic Mechanical Analyzer. The design of experiments, data analysis, and regression studies were performed by Stat-ease DesignExpert® software [12].

2.4 Design of Experiments

The experimental design consisted of a general mixed-level full factorial design with three factors (two categorical and one numerical). Dispersion enhancement measures including the use of dispersing agent and nanofiber surface functionalization were included in the design. Factors and their levels are shown in Table 2.

Table 2 – Factors and their respective levels

Factor designation	Factor	Levels				
		1	2	3	4	5
A	Type of VGCNF	Pristine	Oxidized	-	-	-
B	Use of dispersing agent	Yes	No	-	-	-
C	Amount of VGCNF (phr[1])	0	0.25	0.50	0.75	1.00

[1]parts per hundred resin

2.5 Specimen Preparation

The constituents were added to a 240 ml cup in the order of resin, promoter, air release agents, dispersing agent, and VGCNF. The batch size was about 75 g. The blend was then mixed in the high-shear mixer for 10 min at 3000 rpm and 5 min at 4000 rpm (total mixing time 15 min) followed by one hour sonication at an amplitude of 20% in continuous mode. The cup was mounted on a special vortex mixer that shook the cup for a uniform ultrasonic power input and was cooled by a high-speed fan. The hardener (MEKP) was added to the mixture and hand mixed for 5 min at ambient temperature. The blend was then degassed for 5-15 min at a pressure of 8-10 kPa until all the air bubbles were removed. Next, the resin was gently poured in the mold and cured in a pre-heated oven (5 h at 60 °C and 2 h at 120 °C).

2.6 Dynamic Mechanical Analysis (DMA)

Test specimens (35×12.5×3.5 mm) were cut from the molded specimens. Dynamic Mechanical Analysis (DMA) was conducted in single cantilever mode on a dual cantilever clamp, with amplitude of 15 µm, at a fixed frequency of 10 Hz, a heating rate of 5˚C/min, and a temperature range of 27 ˚C to 160 ˚C (ASTM D 5418). Three separate measurements were obtained for each treatment and average values were used in the analysis.

3. RESULTS AND DISCUSSION

3.1 Analysis of Variance (ANOVA)

Two viscoelastic responses, i.e. storage modulus (a measure of material stiffness) and loss modulus (a measure of energy-dissipation in the material) were used in this study. Though these responses were obtained for a temperature range encompassing all material transitions (27-160

˚C), the values at 27 ˚C were used for the analysis. The treatments and responses are shown in Table 3.

Table 3 – Randomized treatments and measured responses

Run	Type of VGCNF	Use of Dispersing Agent	Nanofiber Weight Fraction (phr)	Storage Modulus (MPa)	Loss Modulus (MPa)
1	Oxidized	No	0.75	2691	43
2	Oxidized	Yes	0.00	2186	58
3	Pristine	Yes	1.00	2609	44
4	Pristine	No	0.50	2603	43
5	Oxidized	Yes	0.50	2517	44
6	Pristine	Yes	0.25	2661	45
7	Oxidized	Yes	0.75	2599	47
8	Pristine	Yes	0.50	2768	48
9	Oxidized	No	1.00	2559	43
10	Oxidized	Yes	0.25	2532	42
11	Oxidized	No	0.25	2575	41
12	Oxidized	Yes	1.00	2728	45
13	Oxidized	No	0.00	2186	58
14	Pristine	No	1.00	2686	43
15	Oxidized	No	0.50	2706	45
16	Pristine	No	0.25	2563	45
17	Pristine	Yes	0.75	2573	42
18	Pristine	No	0.75	2566	45
19	Pristine	Yes	0.00	2186	58
20	Pristine	No	0.00	2186	58

The average variations in measured storage and loss moduli were 1-4% and 3-8%, respectively. A reduced quadratic model was selected for the storage modulus based on the statistical analysis. Using a similar analysis, a reduced cubic model was selected for the loss modulus. An analysis of variance (ANOVA) was further performed on these responses. The ANOVA results for the response models are shown in Tables 4 and 5.

Table 4 – ANOVA results for reduced quadratic model for the storage modulus

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	5.509×10^5	4	1.377×10^5	14.76	$< 0.0001^1$
A-Type of Nanofiber	744.20	1	744.20	0.080	0.7815
B-Use of Dispersing Agent	72.20	1	72.20	7.737×10^{-3}	0.9311
C-Nanofiber Weight Fraction	3.561×10^5	1	3.561×10^5	38.16	$< 0.0001^1$
C²	1.940×10^5	1	1.940×10^5	20.79	0.0004^1
Residual	1.400×10^5	15	9332.24		
Total (Corrected)	6.909×10^5	19			

Other model statistics	
Standard deviation: 96.60	R-squared: 0.7974
Mean: 2534.00	Adjusted R-squared: 0.7433
Coefficient of variance %: 3.81	Predicted R-squared[2]: 0.6549
Predicted residual sum of squares: 2.384×10^5	Adequate precision[3]: 9.847

[1]Model term is significant

[2]Predicted R-squared (0.6549) is in reasonable agreement with adjusted R-squared (0.7433).

[3]Measures signal to noise ratio. A value greater than 4 is desirable.

Table 5 – ANOVA results for reduced cubic model for the loss modulus

Source	Sum of squares	Degree of freedom	Mean square	F-value	p-value
Model	606.57	5	121.31	25.74	$< 0.0001^1$
A-Type of Nanofiber	1.25	1	1.25	0.27	0.6146
B-Use of Dispersing Agent	4.05	1	4.05	0.86	0.3696
C-Nanofiber Weight Fraction	15.23	1	15.23	3.23	0.0938
C²	193.14	1	193.14	40.98	$< 0.0001^1$
C³	105.63	1	105.63	22.41	0.0003^1
Residual	65.98	14	4.71		
Total (Corrected)	672.55	19			

| Other model statistics	
Standard deviation: 2.17	R-squared: 0.9019
Mean: 46.85	Adjusted R-squared: 0.8669
Coefficient of variance %: 4.63	Predicted R-squared[2]: 0.8147
Predicted residual sum of squares: 124.60	Adequate precision[3]: 13.417

[1]Model term is significant

[2]Predicted R-squared (0.8147) is in reasonable agreement with adjusted R-squared (0.8669).

[3]Measures signal to noise ratio. A value greater than 4 is desirable.

3.2 Response Curves and Model Predictions

The response curves based on the response surface models for the storage and loss moduli are shown in Figure 1.
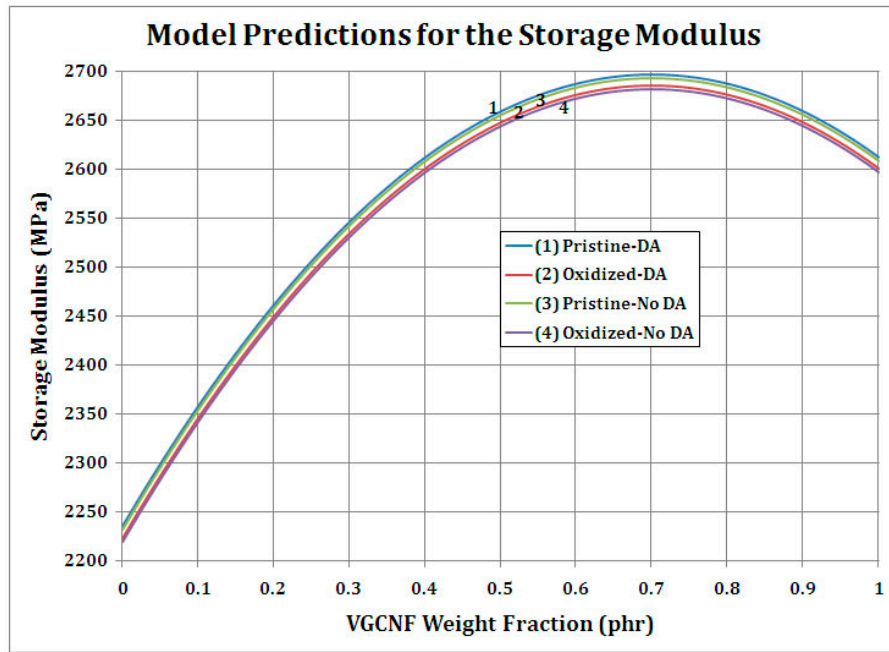
a)
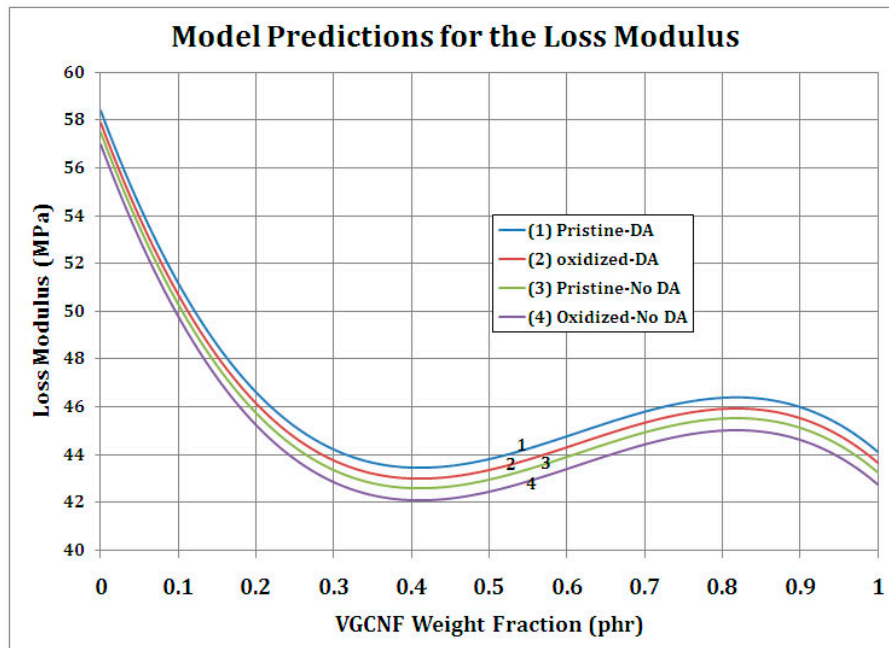
b)

Figure 1 – Response curves based on the model predictions for a) storage modulus and b) loss modulus. Note: DA=dispersing agent

The effect of dispersing agent and nanofiber type are not significant on either storage or loss modulus. This is evidenced by their high p-values in Tables 4 and 5 and the graphs in Figure 1. However, a small increase in the storage and loss moduli is observed when pristine nanofibers and dispersing agent are used. The higher storage modulus in these cases can be attributed to better dispersion of nanofibers in the presence of dispersing agent. Moreover, it is anticipated that the dispersing agent acts better on pristine nanofibers. The loss modulus (measure of toughness) is typically reduced when the storage modulus (measure of stiffness) is increased by increase in the addition of VGCNF to the system. Interestingly, the dispersing agent, acting a "plasticizer" in the nanocomposite, yields higher loss modulus and improves the toughness of the material. This is especially useful for improving crash performance of automotive parts. In light of this dual effect of increase in both storage and loss modulus, more versatile automotive part designs can be made.

VGCNF weight fraction has significant effect on both responses. The maximum storage modulus is achieved at around 0.7 phr of VGCNF. Previously, the optimal weight fraction was observed to be 0.37 phr for the ultrasonication and 0.45 for the high-shear mixing [1,2]. This indicates a shift in peak of the storage modulus towards higher nanofiber weight fractions as the intensity of the mixing increases. Figure 2 compares the storage modulus response curves for all three mixing methods.
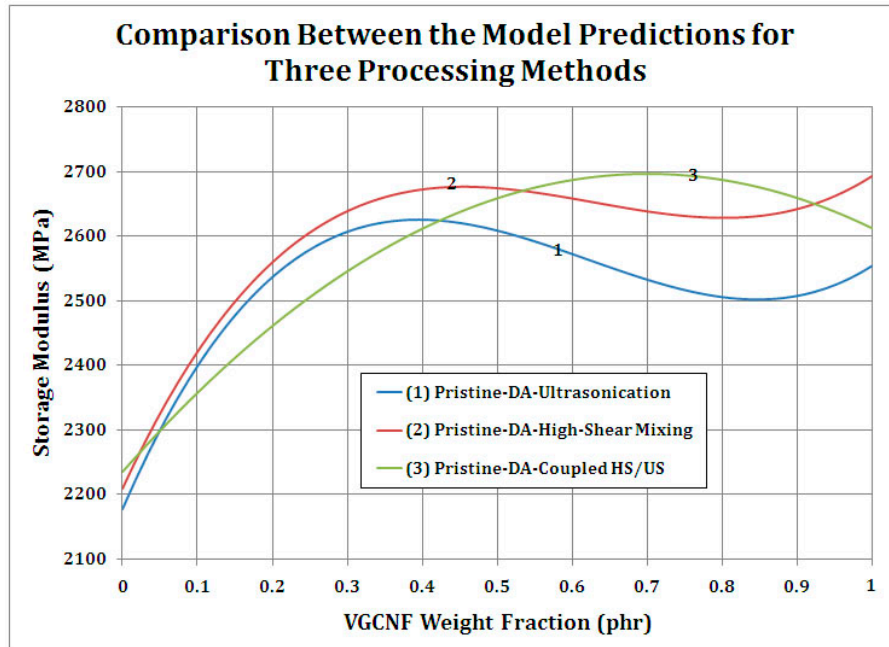

Figure 2 – Comparison between three processing methods for the preparation of VGCNF/VE nanocomposites: 1) ultrasonication, 2) high-shear mixing, and 3) coupled high-shear mixing/ultrasonication for a selected configuration (pristine+dispersing agent)

Figure 3 shows tan delta curves for different nanocomposite systems. As evidenced in this figure, the glass transition temperature (T_g) of VGCNF/VE nanocomposites doesn't differ much from that of the neat resin. The only observation is the decrease in the peak of the curve.
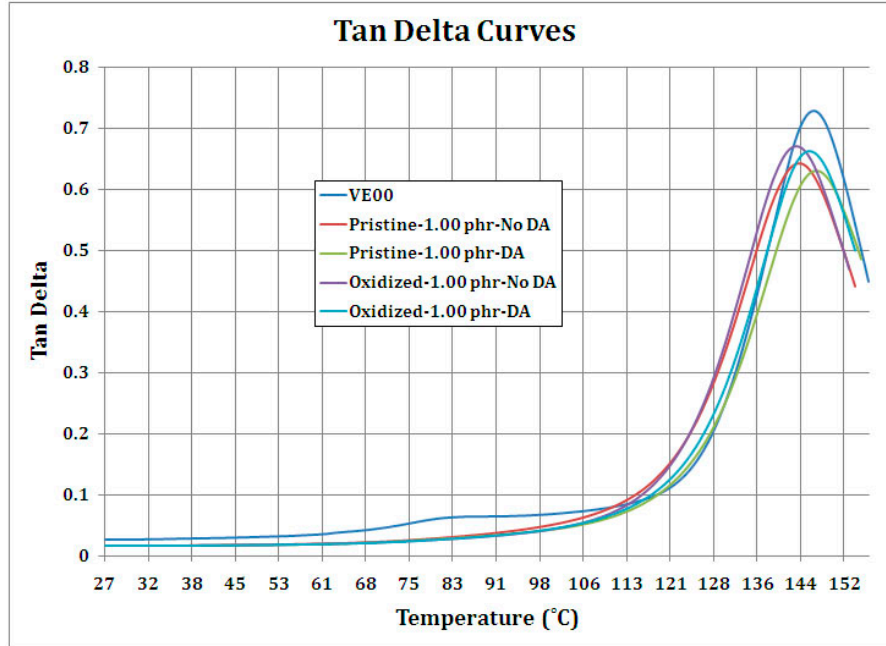
4. CONCLUSIONS

A designed experimental study was conducted on VGCNF/VE nanocomposites considering the individual effect of three factors on the dynamic mechanical properties (storage and loss moduli) of these materials. These factors were type of VGCNF, use of dispersing agent, and VGCNF weight fraction. The results show that in overall, an increase of up to 23% in storage modulus can be achieved by incorporating very small amounts (<1 phr) of a nanoreinforcing agent (VGCNF) into the vinyl ester matrix. In general, the use of dispersing agent leads to both higher stiffness and higher toughness of the nanocomposite by improving the dispersion of nanofibers in the matrix and acting as a "plasticizer" at the same time. The surface oxidation of nanofibers doesn't have a significant effect on the DMA responses. The optimal VGCNF weight fraction in this study was ~0.7 phr.

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