

VISCOELASTIC PROPERTIES OF VAPOR-GROWN CARBON NANOFIBER/VINYL ESTER NANOCOMPOSITES

Sasan Nouranian¹, Hossein Toghiani¹, Thomas E. Lacy², Charles U. Pittman, Jr.³

¹Dave C. Swalm School of Chemical Engineering
Mississippi State University, Mississippi State, MS 39762

²Department of Aerospace Engineering
Mississippi State University, Mississippi State, MS 39762

³Department of Chemistry
Mississippi State University, Mississippi State, MS 39762

ABSTRACT

Recently growth has occurred in the use of nanocomposites in automotive and aerospace applications. This is based on emerging data that the use of small amounts of nanoreinforcements compared to large amounts of traditional reinforcements in structural materials, brings about a variety of improvements in mechanical and other properties. Here, a low-cost vapor-grown carbon nanofiber/vinyl ester nanocomposite's viscoelastic properties have been studied. The study has been conducted using a design of experiments approach, taking into consideration three formulation-related factors: type of carbon nanofiber, use of dispersing agent to enhance the dispersion of nanofibers in the matrix, and carbon nanofiber weight fraction. Nanofiber weight fraction has a major effect on the storage modulus (stiffness), while both the use of dispersing agent and nanofiber weight fraction has major effects on the loss modulus (energy dissipation). An optimized response surface model was thereby developed. Property enhancements over the entire temperature range were further studied and an overall effectiveness of dispersing agent at higher pristine nanofiber loadings was observed. The results of this study can be used as a guide in designing structural nanocomposite based on stiffness and energy-dissipation considerations, which are important in automotive or aerospace strength and crash applications.

1. INTRODUCTION

A recent worldwide energy concern has driven the automotive industry towards application of innovative measures for increasing the fuel economy in vehicles. Weight reduction as a means to achieve this goal requires the use of novel light-weight structural materials without compromising their mechanical properties or performance characteristics. The same is true for the aerospace industry. During the last decade, interest has increased in the use of polymeric nanocomposites in conjunction with traditional composites as weight reduction candidates, even though nanocomposite commercialization has been largely limited due to fabrication issues [1]. New automotive applications for nanocomposites are emerging [2], but in recent years, interest

has grown in the use of “hybrid” composites. One class of such materials is traditional short- or continuous-fiber reinforced laminated composites where the matrix is a resin continuous phase containing nanosized fibers, fillers, clays, etc. Only a small amount of nanoreinforcement is added to the matrix of these materials. In doing so, pronounced improvements in certain (especially interlaminar) mechanical properties can occur [3,4].

Vinyl ester resins are among the most common thermoset resins used in the manufacture of commercial composite laminates. These resins impart good mechanical properties at a lower cost compared to epoxies. Currently, various carbon and non-carbon nanoreinforcement materials are available. Vapor-grown carbon nanofibers (VGCNFs) are relatively inexpensive compared to single- and multi-walled carbon nanotubes. They have typical diameters of 70-200 nm and lengths of 50-200 microns [5] which translates into a high aspect ratio. Increased production of these nanofibers will encourage their exploration as property-enhancing nanophases in many applications in near future.

A systematic study of the viscoelastic responses of vapor-grown carbon nanofiber/vinyl ester nanocomposites has not been conducted in a designed experimental study. As an initial step in studying hybrid composites, a thorough understanding of the effect of both formulation and processing parameters on mechanical properties of the nanoreinforced matrix is desirable. In the first part of our study, the effect of VGCNF/vinyl ester nanocomposite formulation parameters on viscoelastic properties is addressed. This report is appropriate for a general audience concerned with the field of nanocomposite formulation and design. In future studies, the effect of processing will also be included in the analysis. Based on a general full factorial experimental design, the effect of three formulation parameters on the storage and loss moduli and tan delta were investigated.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Materials

Derakane 441-400 (Ashland Co.), an epoxy vinyl ester resin, was used as the thermosetting matrix resin. This resin has a low styrene content of 33%, and possesses good mechanical, thermal, and corrosion properties. It also has good infusion characteristics, appropriate for use in vacuum-assisted resin transfer molding (VARTM) processes. VARTM is a common technique for the fabrication of laminated composite structures.

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, surface area of 35-45 m²/g, and 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. These nanofibers were used as-received without any further modifications.

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 promoter. Its presence significantly accelerates peroxide decomposition, speeding the curing reaction. 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). These additives facilitate the removal of air bubbles after mixing and during curing of the resin by altering the surface tension. 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, which is 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 [6-8]. Materials used for this study are summarized in Table 1.

Table 1 – Materials used for the preparation of thermoset nanocomposites

Material	Function	Manufacturer
Derakane 411-400	Epoxy vinyl ester resin	Ashland Co.
Cobalt naphthenate 6%	Promoter (catalyst)	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 and 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.

2.2 Formulations

The general formulation for the nanocomposites used in this investigation is shown in Table 2. 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 2).

Table 2 – General 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 ¹
VGCNF ² (vapor-grown carbon nanofiber)	0.00/0.25/0.50/0.75/1.00
MEKP (hardener)	1.00

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

2.3 Equipment and Data Analysis Software

All materials were prepared using a Stir-Pak laboratory mechanical stirrer (Cole-Parmer Instrument Co.) and 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 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 [9].

2.4 Design of Experiments

The effect of several formulation factors on viscoelastic properties of the nanocomposites, i.e. storage modulus, loss modulus, and tan delta were investigated because of the importance of stiffness and toughness properties of structural automotive parts. Three formulation-related factors were selected as indicated in Table 3. 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.

Table 3 – Factors, their designations and 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

¹parts per hundred resin

Due to the mixed-level nature of the problem, a general full factorial design was made with 20 experimental treatments (runs). These runs are shown in Table 4 (Sec. 3.1.1).

2.5 Specimen Preparation

The following procedure was used for specimen preparation:

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 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 mixture 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 mixture was then mixed for 5 min. by Stir-Pak mechanical stirrer at 1500 rpm followed by one hour sonication at an amplitude of 20% in continuous mode (no pulse). The cup was

mounted on a special vortex mixer that shook the cup for a uniform power input and was cooled by a high-speed fan. For this study, a batch based on 75 g resin was prepared. The ultrasonic processor tip was placed half-way in the mixture, in the middle of the cup.

3) The hardener (MEKP) was then added to the mixture 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 the mixtures' viscosities. Care has to be taken not to remove an excess amount of the styrene, even though a small amount might be removed together with the air bubbles.

5) The resin was gently poured in 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.

2.6 Dynamic Mechanical Analysis (DMA)

Test specimens with the average size of 35×12.5×3.5 mm³ were cut from the molded specimens. Dynamic Mechanical Analysis (DMA) was conducted according to ASTM D 5418 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. Three separate measurements were obtained for each run (Table 4) and average values were calculated and used in the analysis.

3. RESULTS AND DISCUSSION

3.1 Statistical Analysis

3.1.1 Analysis of Variance (ANOVA)

At least three measurements were performed for each experimental treatment. Each cut specimen was tested 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 °C (close to room temperature) were used for the statistical analysis. The experimental treatments and responses are shown in Table 4.

Table 4 – Randomized experimental setup and measured responses

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	No	0.75	2616	55
2	Oxidized	Yes	0.00	2007	162
3	Pristine	Yes	1.00	2652	64
4	Pristine	No	0.50	2660	49.5
5	Oxidized	Yes	0.50	2591	59
6	Pristine	Yes	0.25	2598	76
7	Oxidized	Yes	0.75	2650	68
8	Pristine	Yes	0.50	2515	100
9	Oxidized	No	1.00	2587	52
10	Oxidized	Yes	0.25	2579	72
11	Oxidized	No	0.25	2500	70
12	Oxidized	Yes	1.00	2566	69
13	Oxidized	No	0.00	2186	58
14	Pristine	No	1.00	2449	43
15	Oxidized	No	0.50	2652	59
16	Pristine	No	0.25	2728	65
17	Pristine	Yes	0.75	2481	53
18	Pristine	No	0.75	2407	43
19	Pristine	Yes	0.00	2007	162
20	Pristine	No	0.00	2186	58

¹Values correspond to measured values at 27 °C and are the average of 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 given curing conditions, and do not necessarily match the values mentioned in the resin's brochure. A comparison of storage modulus values for vinyl ester resins at several curing conditions was reported by Li [10].

An analysis of variance (ANOVA) was performed on each of the responses. A square root transformation was made for the loss modulus response. For each case, different fitting models (linear, quadratic, cubic, etc.) were evaluated and the most appropriate ones based on the highest adjusted and predicted r-squared values were selected. This resulted in a response surface reduced cubic model for the storage modulus and a response surface reduced linear model for the loss modulus. The ANOVA results for the final models are shown in Tables 5 and 7.

Table 5 – ANOVA (partial sum of squares) results for storage modulus response

Source	Sum of squares	Degree of freedom	Mean square	F value ⁽¹⁾	Prob>F ⁽²⁾
Model	7.932×10 ⁵	7	1.133×10 ⁵	15.05 ⁽³⁾	<0.0001
A: Type of nanofiber	3150.05	1	3150.05	0.42	0.5299
B: Use of dispersant	2203.40	1	2203.40	0.29	0.5984
C: Nanofiber weight fraction	28891.11	1	28891.11	3.84	0.0738
BC	38378.03	1	38378.03	5.10	0.0434 ⁽⁴⁾
C ²	3.024×10 ⁵	1	3.024×10 ⁵	40.16	<0.0001 ⁽⁴⁾
BC ²	0.16	1	0.16	2.135×10 ⁻⁵	0.9964
C ³	1.404×10 ⁵	1	1.404×10 ⁵	18.65	0.0010 ⁽⁴⁾
Residual	90348.92	12	7529.08	-	-
Total sum of squares corrected for the mean	8.836×10 ⁵	19	-	-	-
Other model statistics					
Standard deviation: 86.77 Mean: 2480.85 Coefficient of variance %: 3.50 Predicted residual sum of squares: 2.305×10 ⁵			R-squared: 0.8977 Adjusted r-squared: 0.8381 Predicted r-squared ⁽⁵⁾ : 0.7392 Adequate precision ⁽⁶⁾ : 11.879		

¹Mean square for the term divided by mean square for the residual²Probability 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 noise⁴Model term is significant⁵Predicted r-squared (0.7392) is in reasonable agreement with adjusted r-squared (0.8381).⁶Measures the signal to noise ratio. A value greater than 4 is desirable. Here, we have an adequate signal.

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

$$S = 2627.81 + 12.55 \times a + 16.36 \times b - 161.50 \times c - 61.95 \times bc - 293.93 \times c^2 - 0.21 \times bc^2 + 395 \times c^3 \text{ (MPa)} \quad [1]$$

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 6 together with the corresponding actual factors for reference.

Table 6 – Coded and actual factors

Factor Type	Factor designation	Levels				
		1	2	3	4	5
Actual	A	Pristine	Oxidized	-	-	-
Coded	a	-1.0	1.0	-	-	-
Actual	B	Yes	No	-	-	-
Coded	b	-1.0	1.0	-	-	-
Actual	C	0	0.25	0.50	0.75	1.00
Coded	c	-1.0	-0.5	0.0	0.5	1.0

Table 7 – ANOVA (partial sum of squares) results for loss modulus response⁽¹⁾

Source	Sum of squares	Degree of freedom	Mean square	F value ⁽²⁾	Prob>F ⁽³⁾
Model	32.44	3	10.81	7.72 ⁽⁴⁾	0.0021
A: Type of nanofiber	0.070	1	0.070	0.050	0.8258
B: Use of dispersant	16.30	1	16.30	11.64	0.0036 ⁽⁵⁾
C: Nanofiber weight fraction	16.07	1	16.07	11.48	0.0038 ⁽⁵⁾
Residual	22.40	16	1.40	-	-
Total sum of squares corrected for the mean	54.84	19	-	-	-
Other model statistics					
Standard deviation: 1.18 Mean: 8.31 Coefficient of variance %: 14.23 Predicted residual sum of squares: 36.84			R-squared: 0.5915 Adjusted r-squared: 0.5149 Predicted r-squared ⁽⁶⁾ : 0.3282 Adequate precision ⁽⁷⁾ : 8.427		

¹The square root transform has been applied to the 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 0.21% chance that this F value could occur due to noise.

⁵Model term is significant.

⁶Predicted r-squared (0.3282) is in reasonable agreement with adjusted r-squared (0.5149).

⁷Measures 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:

$$L^{1/2}=8.31+0.059\times a-0.90\times b-1.27\times c \quad [2]$$

Model predictions in terms of actual factors are shown in Figure 1.

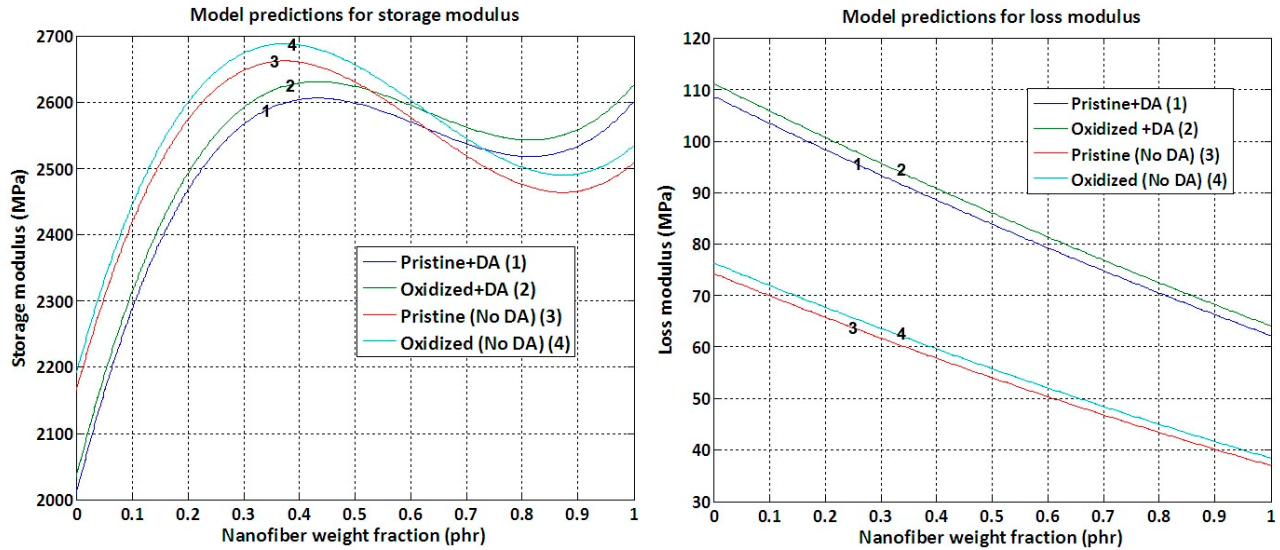


Figure 1 – Model predictions based on actual factors for the storage and loss moduli.

Note: DA=dispersing agent

3.1.2 Numerical Optimization

In order to determine the optimal conditions for the factors under study, a numerical optimization was performed on the statistical models based on some selected goals (maximizing either storage modulus or both storage and loss modulus). Using desirability functions and 140 starting points in the response surface model, the optimal conditions were calculated. The results are shown in Table 8.

Table 8 – Optimal conditions based on set goals

Goal	Factors	Storage modulus	Sqrt(Loss modulus)	Desirability ⁽¹⁾	Optimal conditions ⁽²⁾		
Maximize storage modulus	All in ⁽³⁾ range	(Maximize) Importance: 5 of 5	(In range) Importance: 3 of 5	0.945	A	B	C
					Oxidized	No	0.37
Maximize both storage and loss modulus	All in range	(Maximize) Importance: 5 of 5	(Maximize) Importance: 3 of 5	0.696	A	B	C
					Oxidized	Yes	0.36

¹This value ranges from 0 to 1.

²The conditions correspond to factor levels as described in Table 3.

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

The viscoelastic responses analyzed so far were restricted to room temperature. A general viscoelastic behavior is better studied by comparing the responses over the entire temperature range (27-160°C). Next, the trends in property changes are shown and compared in a qualitative manner.

3.2 Qualitative Study of the Viscoelastic Behavior over the Entire Temperature Range

3.2.1 Storage Modulus

Prob>F values of Table 5 indicate that the nanofiber weight fraction (factor C) and associated terms (BC, C², and C³) have significant effects on the storage modulus at room temperature (<0.05). The contribution of each factor to the storage and loss moduli can be visualized by separately comparing each factor.

3.2.1.1 Effect of Nanofiber Weight Fraction

The nanofiber weight fraction has a pronounced contribution to the storage modulus. This effect is shown in Figure 2 for both pristine and oxidized nanofibers in the presence and absence of dispersing agent.

As can be seen by comparing the storage modulus graphs (Figure 2), the nanofiber weight fraction has a more profound effect in the case of pristine nanofiber. An increase of 25% in storage modulus of the nanocomposite is noticed for the addition of 0.25 phr pristine nanofiber at room temperature. However, at higher nanofiber loading levels, the enhancement of the storage modulus at this temperature drops to around 12%. With the addition of dispersing agent, the trend is somewhat changed and we witness an increase of around 21% at the highest loading level of the nanofiber (1.00 phr). For oxidized nanofiber, the increase in storage modulus of the nanocomposite at room temperature remains almost constant at 20% at moderate to high loading levels (0.50-1.00 phr) of nanofiber. The situation is nearly the same for the cases, with or without dispersing agent.

For all cases, the storage modulus remains almost constant up to ~50°C and starts to drop after that. The effects of nanoreinforcement and other components of nanocomposite formulation on storage modulus decrease as the temperature increases, and are totally lost at temperatures above 100-110°C.

These results suggest that nanocomposites containing pristine nanofibers are more sensitive to nanofiber weight fraction and the use of dispersing agent compared to nanocomposites containing oxidized nanofibers. The nanocomposites containing pristine nanofibers behave more like those containing oxidized nanofibers when a dispersing agent is present in their formulation. However, this behavior is only observed at high nanofiber weight fractions. A similar contributing mechanism might act in the case of nanofiber surface oxidation (better interfacial adhesion between nanofibers and the matrix) and the dispersion-enhancement of the dispersing agent (surfactant-like behavior at the interface).

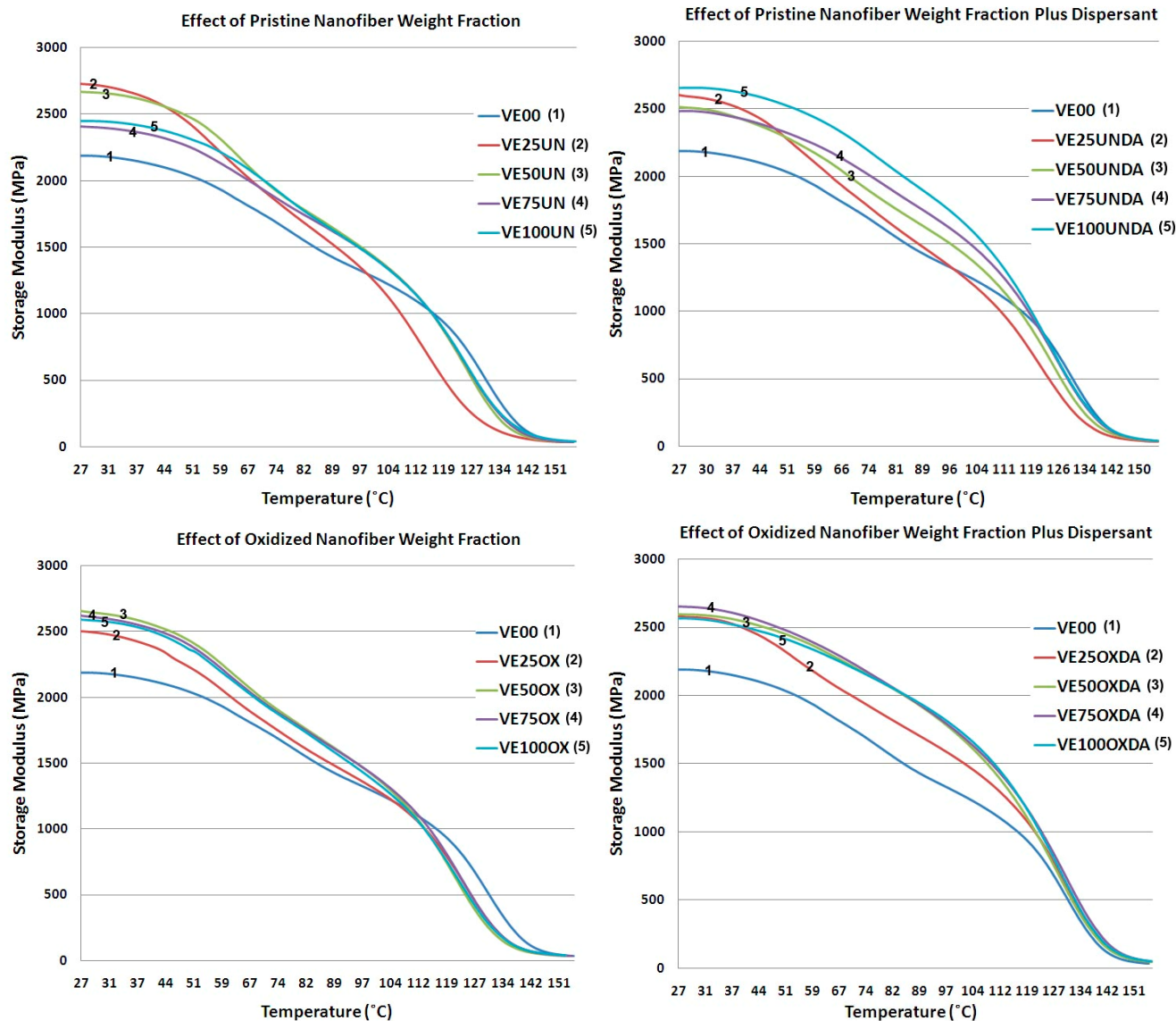


Figure 2- Effect of pristine and oxidized nanofiber weight fraction on the storage modulus, both in the presence and absence of dispersing agent. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fraction $\times$ 100, UN=unoxidized (pristine), OX=oxidized, and DA=dispersing agent

3.2.1.2 Effect of Nanofiber Type

The total effect of nanofiber type on the storage modulus is minor (compare mean square values of the factors in Table 5). However, an interesting trend is observed when comparing the storage modulus curves of pristine and oxidized nanofibers for the cases with and without dispersing agent at different nanofiber weight fractions. These are shown in Figures 3 and 4.

In the absence of dispersing agent, pristine nanofibers give a higher increase in the storage modulus compared to the oxidized nanofiber at lower nanofiber weight fractions (0.25 phr) (Figure 3). The storage modulus increase is almost the same at intermediate weight fractions

(0.50 phr), and it reverses at higher weight fractions (0.75 and 1.00 phr). The situation is somewhat different when the dispersing agent is present (Figure 4). The oxidized nanofiber exhibits a larger modulus increase at low to moderate nanofiber weight fractions, while at high weight fraction (1.00 phr) this situation reverses in favor of pristine nanofiber.

This phenomenon was discussed in the previous section. It again seems that at high nanofiber weight fractions, increasing clustering and agglomeration of nanofibers start to make their negative impact on mechanical properties. However, the use of dispersing agent alleviates some of the problems associated with bad dispersion of nanofibers. The combined effect of surface oxidation and dispersing agent is not favorable at high nanofiber weight fractions (SEM/TEM verification is pending).

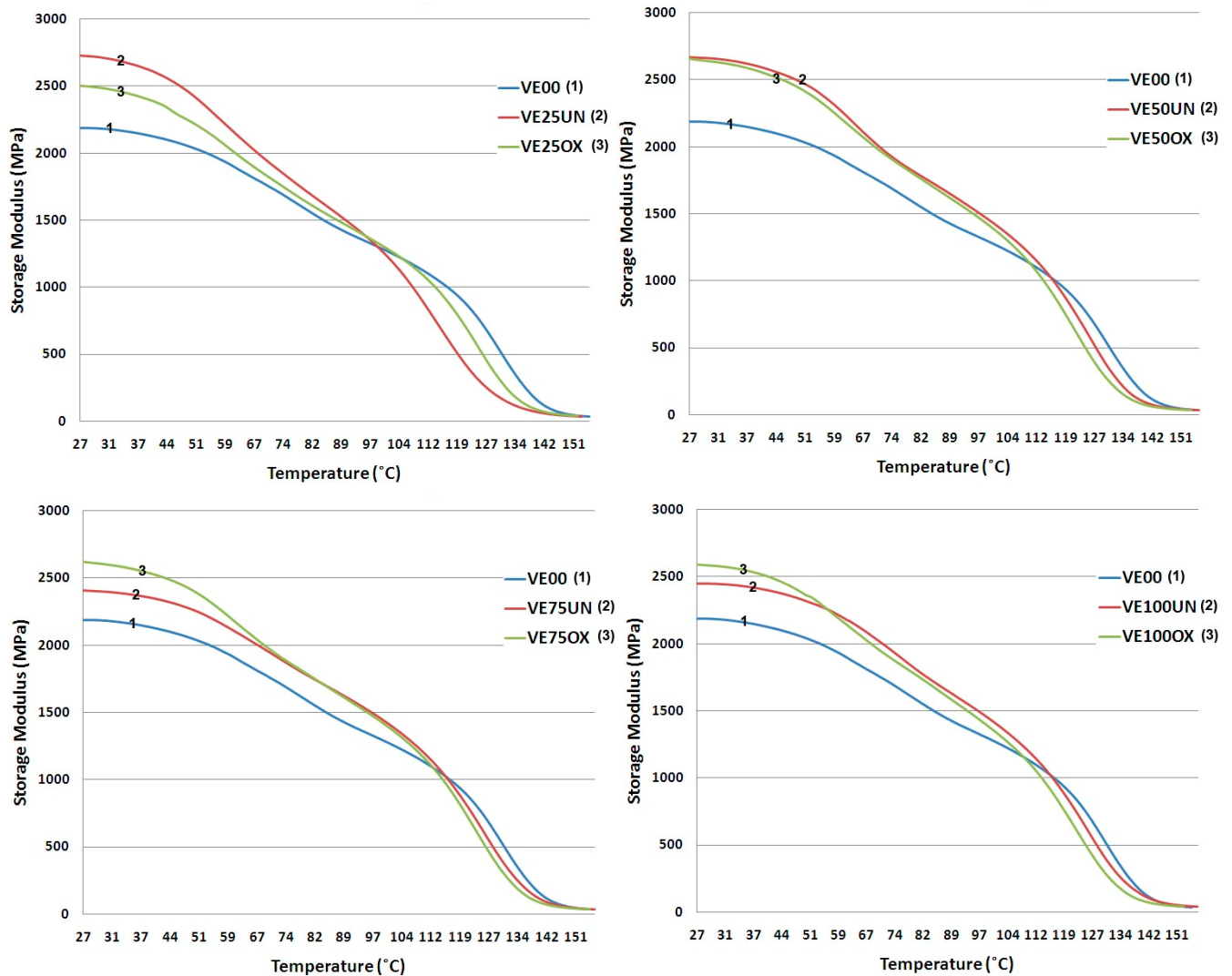


Figure 3 - Effect of nanofiber type on the storage modulus at different nanofiber weight fractions. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), OX=oxidized

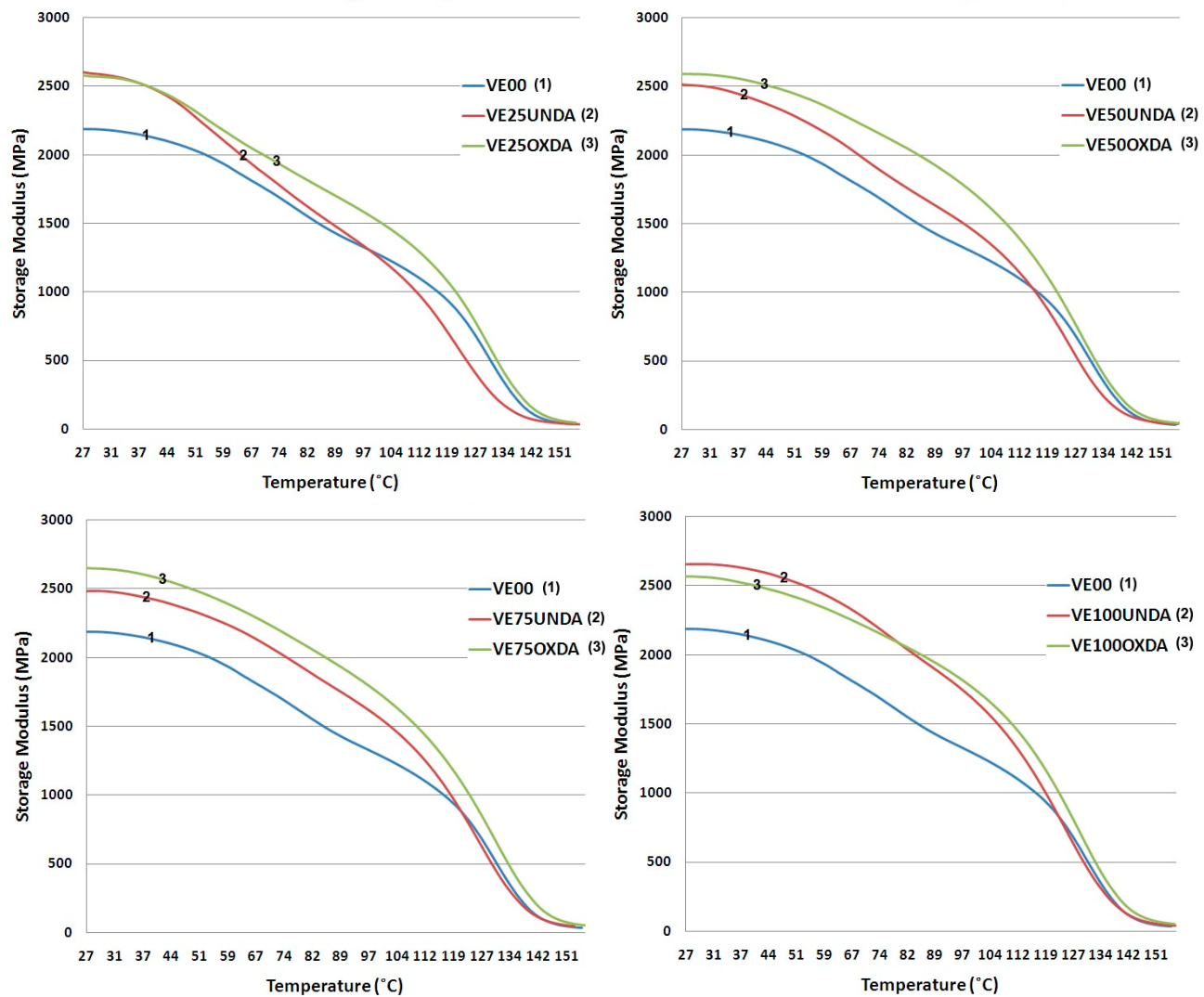


Figure 4 - Effect of nanofiber type on the storage modulus at different nanofiber weight fractions. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), OX=oxidized, and DA=dispersing agent

3.2.1.3 Effect of Dispersing Agent

Again, the total effect of the dispersing agent on the storage modulus is minor (compare mean square values of the factors in Table 5). However, we notice that the effect of the dispersing agent on improving the storage modulus of pristine nanofibers becomes noticeable at higher weight fractions (0.75 and 1.00 phr), while it is a reverse situation at low to intermediate weight fractions (Figure 5). A 1:1 ratio of the dispersing agent and nanofiber were used in preparing these specimens. Higher concentrations of dispersing agent improves the dispersion of nanofibers and hence the storage modulus.

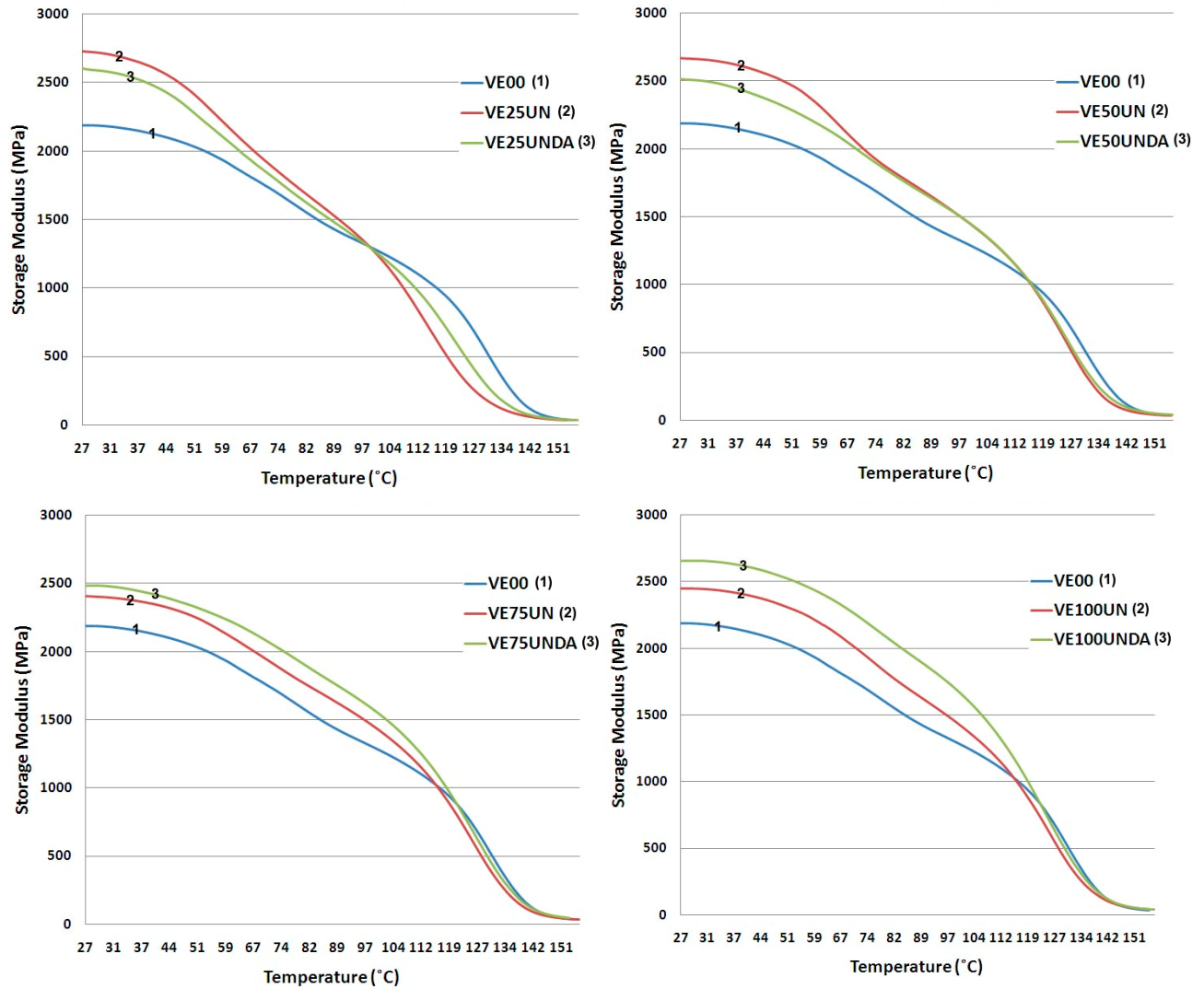


Figure 5 - Effect of dispersing agent on the storage modulus at different nanofiber weight fractions. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, numbers=weight fractions $\times$ 100, UN=unoxidized (pristine), and DA=dispersant

The effect of dispersing agent on improving the storage modulus of specimens with oxidized nanofibers is negligible (Figure 6).

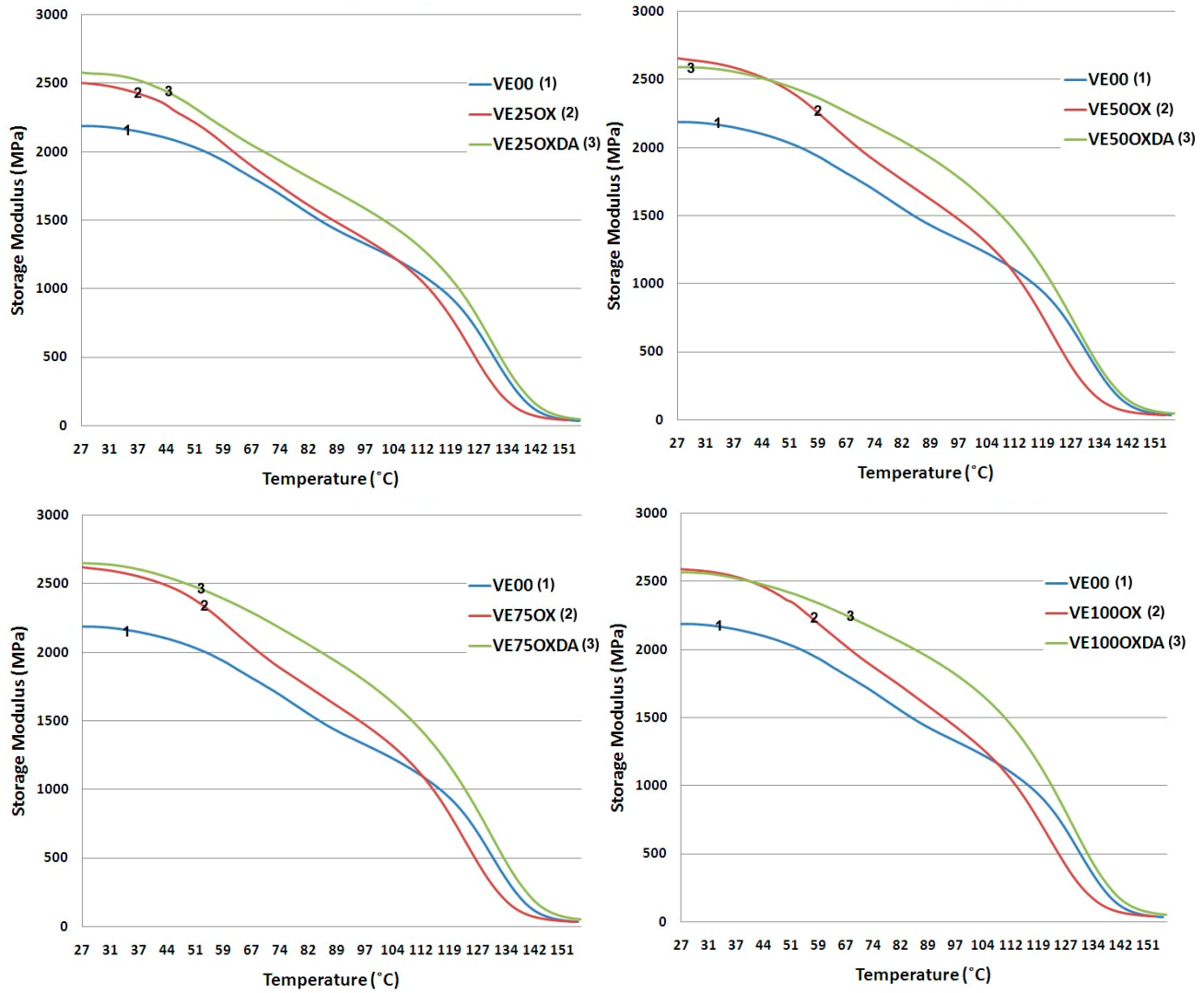


Figure 6 - Effect of dispersing agent on the storage modulus at different nanofiber weight fractions. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, OX=oxidized, and DA=dispersing agent

3.2.2 Loss Modulus

Prob>F values of Table 7 show that the dispersing agent (factor B) and nanofiber weight fraction (factor C) have significant effects on the loss modulus (<0.05). As before, the contribution of each factor to the storage and loss modulus can be visualized by separately comparing each factor.

3.2.2.1 Effect of Nanofiber Weight Fraction

Nanofiber weight fraction has a moderate effect on the loss modulus. The effect can be better visualized by looking at the curves in Figure 7.

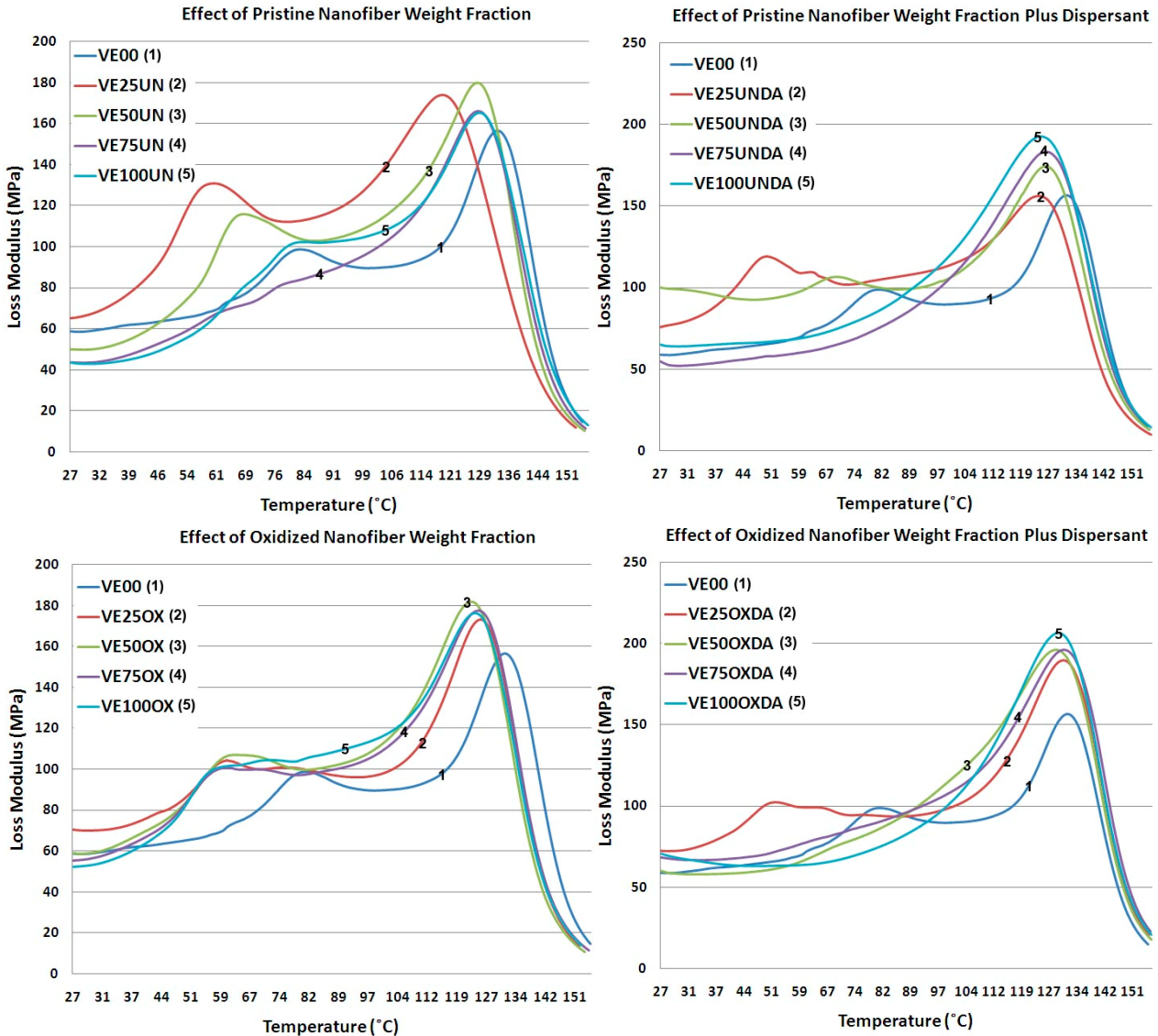


Figure 7 - Effect of pristine and oxidized nanofiber weight fraction on the loss modulus in the presence and absence of dispersing agent. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), OX=oxidized, and DA=dispersing agent

The loss modulus can be examined by considering the values at 27°C (the temperature of ANOVA study) and comparing these with the neat resin. The loss modulus increases with the addition of nanofibers at low nanofiber weight fractions (0.25 and 0.50 phr), but decreases at high weight fractions. The increase is more profound (30-70%) when dispersing agent is present at low pristine nanofiber weight fractions, while the effect is not much noticeable with oxidized nanofibers under same conditions. The loss modulus of all nanofiber-loaded specimens exceeds the neat resin values above temperatures that vary between 35-95°C depending on the formulation. This can be used as a guide for tailor-making certain nanocomposite energy dissipation characteristics depending on the temperature range of interest.

This seems to be a general characteristic for these nanocomposites. The loss modulus peak temperature (glass transition temperature (T_g)) is increased by the addition of nanofibers. This temperature is one of the definitions of glass-transition temperature in the dynamic mechanical analysis. The T_g is shifted to lower temperatures, from around 130°C to 120-125°C in the case of pristine nanofibers with and without dispersing agent, and oxidized nanofibers without dispersing agent. This is a 5-10°C decrease in T_g . This decrease does not occur for the oxidized nanofibers with dispersing agent.

The vinyl ester has a characteristic “hump” or secondary peak in the loss modulus curve at the temperature range of 60-90°C. There is an energy-dissipation mechanism associated with the material in this temperature range. This secondary peak is generally shifted to lower temperature ranges by the addition of nanofibers. However, an interesting phenomenon is noticed when dispersing agent is used at intermediate to high nanofiber loadings for both pristine and oxidized nanofiber cases. The “hump” disappears at these loading levels. The dispersing agent totally exterminates the above-mentioned energy-dissipation mechanism in this temperature range.

3.2.2.2 Effect of Nanofiber Type

Nanofiber type has a negligible total effect on the loss modulus at room temperature. However, at low nanofiber weight fractions and in the absence of dispersing agent, the pristine nanofiber gives higher loss moduli over a major portion of temperature range compared to the oxidized nanofiber (Figure 8). There is an overlapping of curves at intermediate nanofiber loading levels (0.50 phr), and situation reverses at higher loading levels.

In the presence of dispersing agent, pristine nanofiber generally performs better at lower nanofiber loading levels and temperatures below 100°C (Figure 9). However, at higher nanofiber weight fractions, the behavior becomes almost identical for both pristine and oxidized nanofiber cases. The dispersing agent and nanofiber surface oxidation effects compete with each other at higher nanofiber loadings and sometimes mask each other's individual effects. The total result will be a balance between these two, something that was previously noticed with storage modulus (Sections 3.2.1.1 and 3.2.1.2).

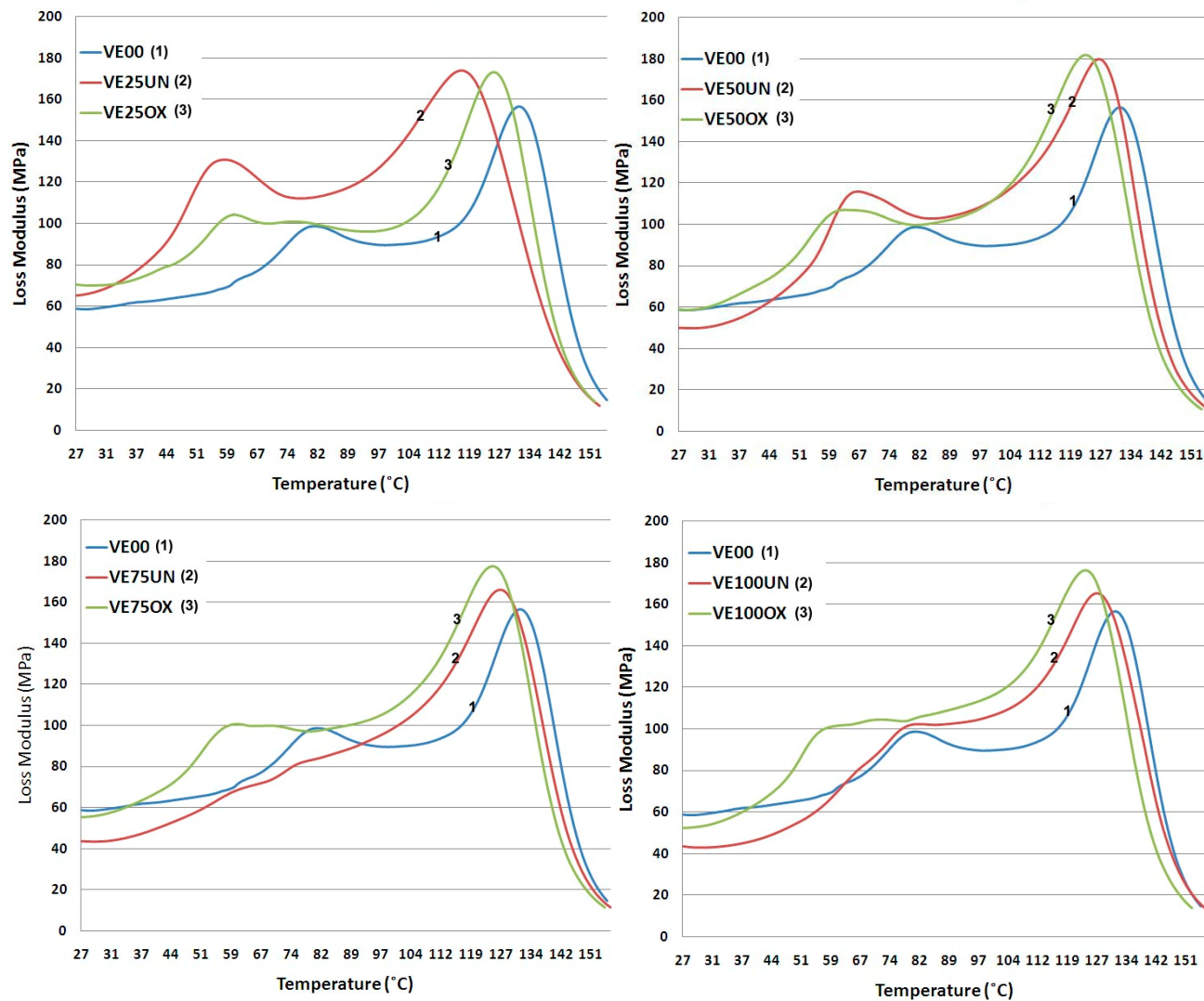


Figure 8 - Effect of nanofiber type on the loss modulus in the absence of dispersing agent. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), and OX=oxidized

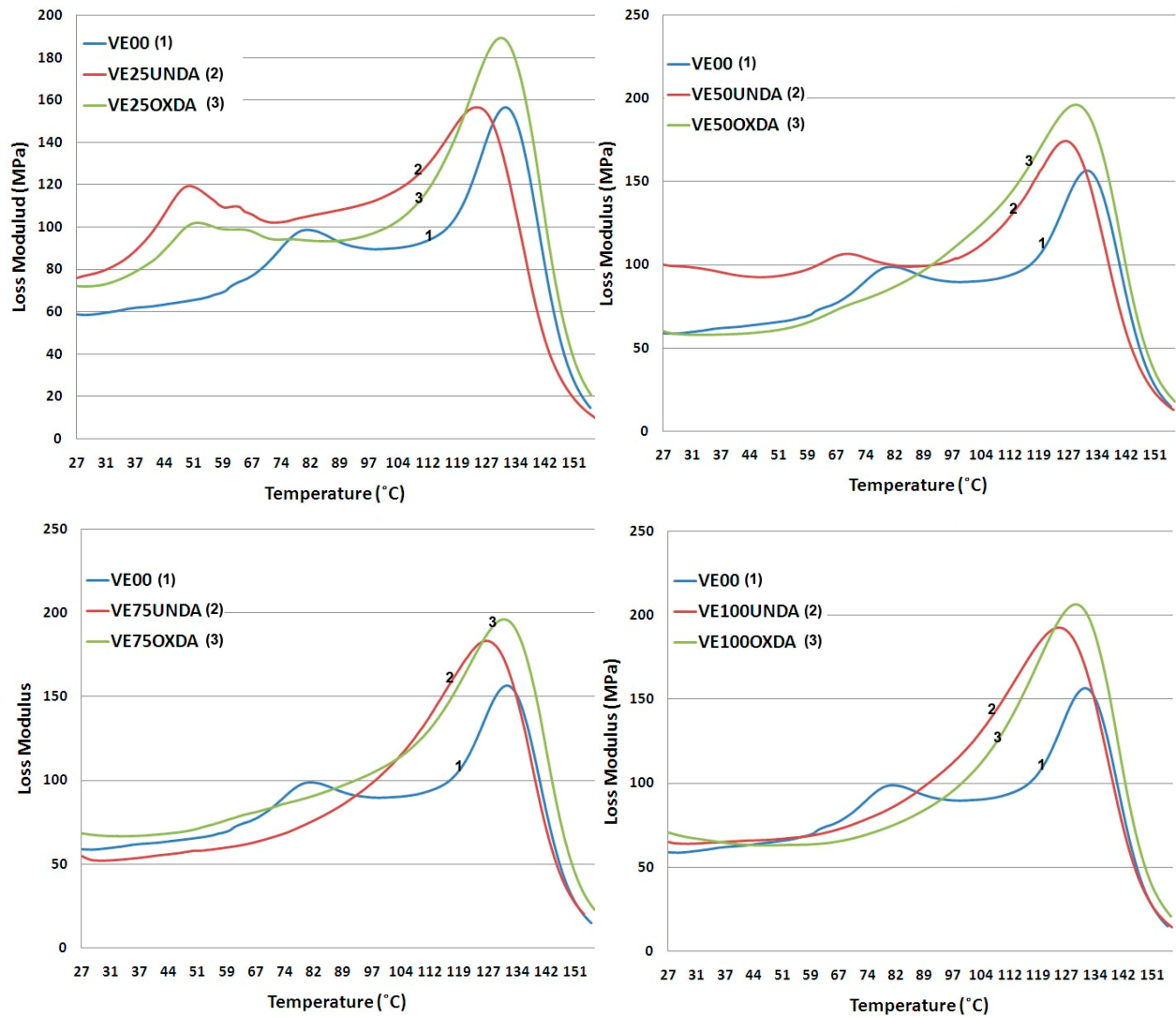


Figure 9 - Effect of nanofiber type on the loss modulus in the presence of dispersing agent. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), OX=oxidized, and DA=dispersant

3.2.2.3 Effect of Dispersing Agent

The dispersing agent has a major effect on the loss modulus around room temperature. This major effect can be seen for the pristine nanofiber below 50-60°C (Figure 10). Above this temperature, the loss modulus is initially higher for the specimens without dispersing agent, but the reverse is experienced at higher nanofiber and dispersing agent weight fractions. Again, an overlapping of curves is noticed at intermediate weight fractions (0.50 phr). In addition, the characteristic “hump” disappears (Section 3.2.2.1).

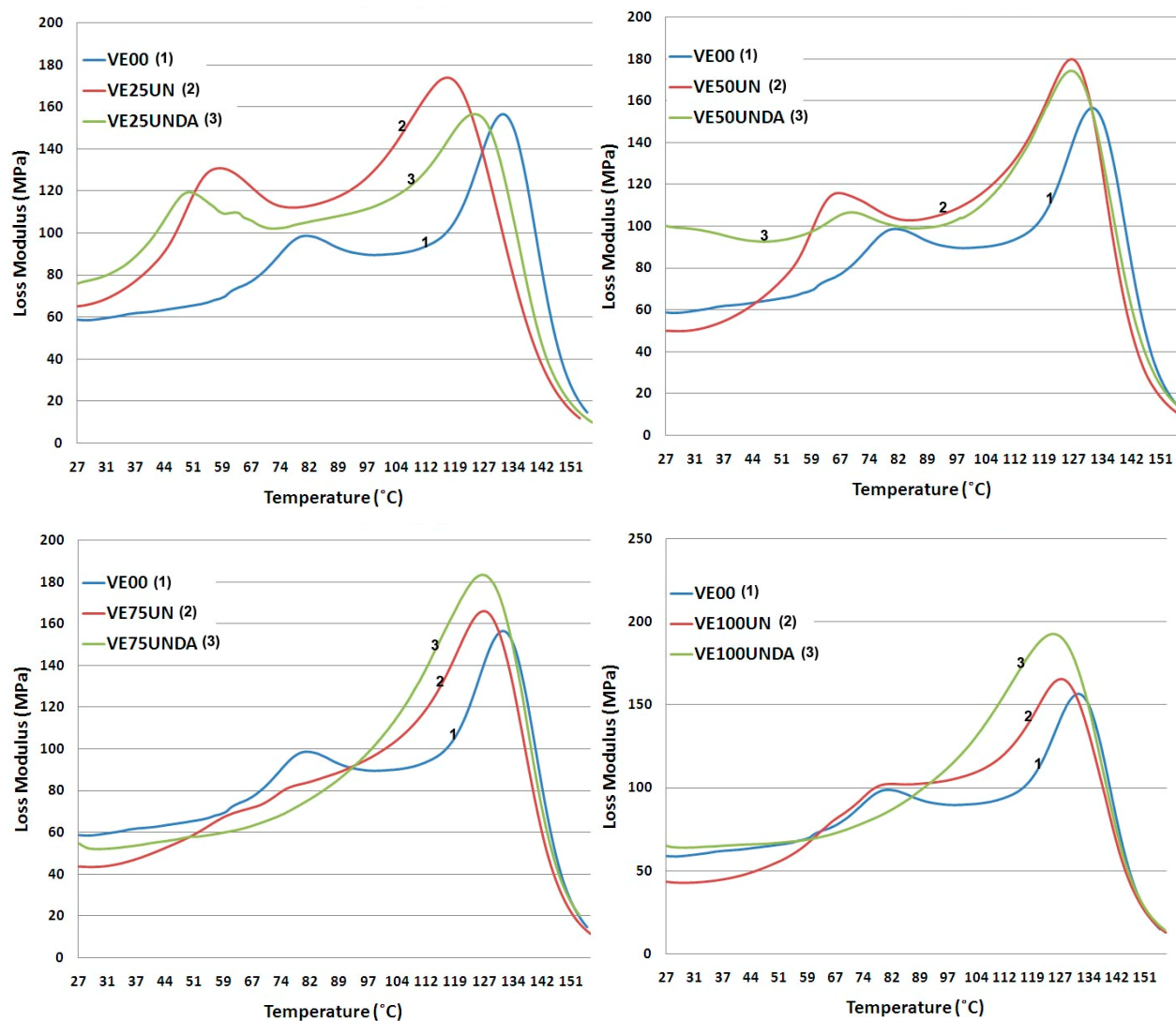


Figure 10 - Effect of dispersing agent on the loss modulus. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), and DA=dispersing agent

The effect of dispersing agent on the loss modulus of oxidized nanofiber-containing nanocomposites is not as profound as the case of pristine nanofibers. Figure 11 shows the loss modulus behavior for the oxidized nanofiber with and without dispersing agent. An increase in the loss modulus occurs in the presence of dispersing agent at higher nanofiber weight fractions and below 50°C. However, the “hump” disappears faster in this case compared to the pristine nanofiber. Therefore, specimens without dispersing agent yield higher loss moduli in the 50-100°C temperature range.

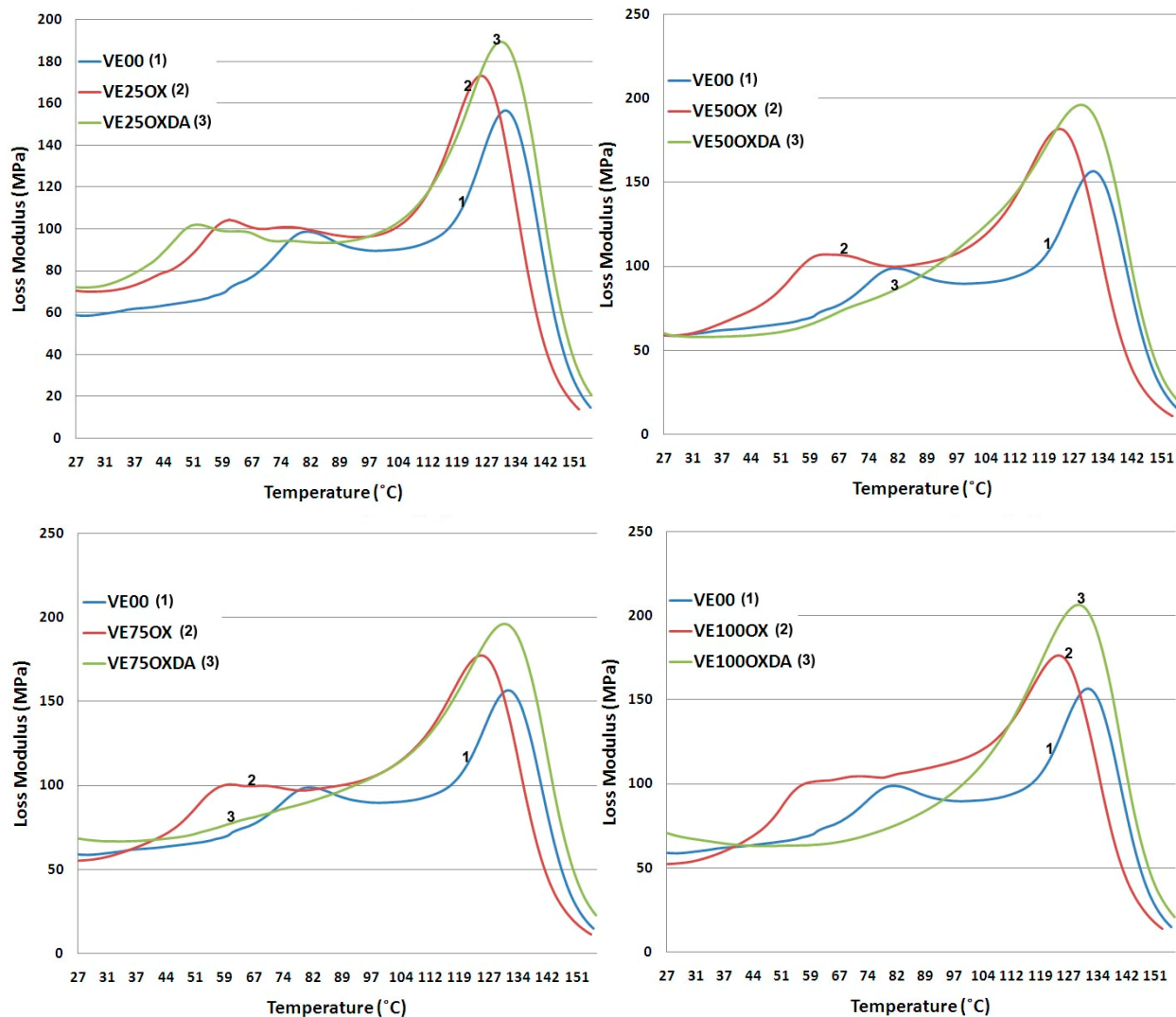


Figure 11 - Effect of dispersing agent on the loss modulus. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions×100, OX=oxidized, and DA=dispersing agent

3.2.3 Tan Delta

Tan delta is the ratio of the loss modulus to the storage modulus, and is a measure of damping. Higher value of tan delta means higher damping. The tan delta peak temperature is another definition for glass transition temperature. Figure 12 shows the effect of nanofiber weight fraction on the tan delta peak (glass transition) temperature. The addition of nanofibers decreases the tan delta peak temperature compared to the neat resin for all cases. Furthermore, in the absence of dispersing agent, the T_g is shifted to lower temperatures for both pristine and oxidized nanofibers. However, the use of dispersing agent seems to minimize the T_g shift. This is more pronounced for the oxidized nanofiber formulations, where T_g does not shift at any nanofiber weight fraction.

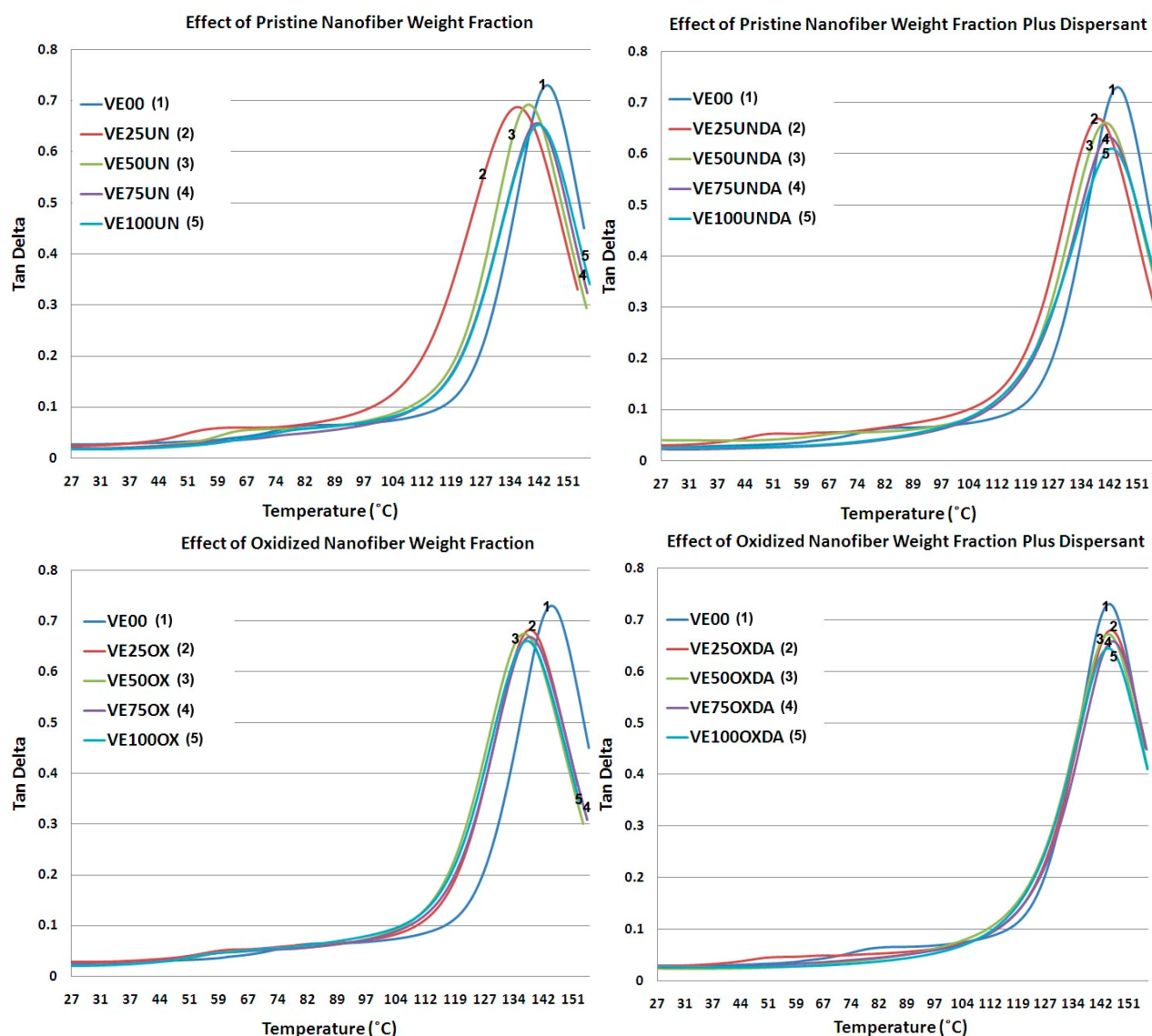


Figure 12 - Effect of nanofiber weight fraction on tan delta. The following abbreviations are used in the upper right corner of each graph: VE=vinyl ester, number=weight fractions $\times$ 100, UN=unoxidized (pristine), OX=oxidized, and DA=dispersing agent

4. SUMMARY AND CONCLUSIONS

Our study shows that up to a 25% increase in the storage modulus at room temperature is achieved by the addition of very small amounts of VGCNF (0.25-1.00 phr). This is an interesting observation that makes nanocomposites particularly attractive. The observed increase is far greater than the rule of mixtures would predict, especially based on the volume fraction of VGCNF. Therefore, the use of this nanoreinforcement in conventional vinyl ester resins provides

enhancements in both stiffness and energy dissipation capabilities that could prove beneficial in structural automotive and aerospace applications. The potential for greater property enhancements for the formulations used here is very likely if mixing/dispersion of nanofibers into the resin can be improved. Removing the nanofiber aggregates and achieving improved dispersion should lead to more profound property enhancements.

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 for room temperature behavior of these nanocomposites, fabricated according to the procedures outlined in this work. The observations made for the viscoelastic behavior of these materials for the studied temperature range can also serve as a useful guide in formulating nanocomposites for different applications. These observations are summarized below:

Storage modulus:

- 1) All nanocomposite specimens yield higher storage modulus than the neat resin.
- 2) Nanocomposites containing pristine nanofibers are more sensitive to nanofiber weight fraction and perform better at lower weight fractions. But, when the dispersing agent is present, they perform better at higher nanofiber weight fractions, because VGCNF dispersion is enhanced. The effect of nanofiber weight fraction in the presence or absence of dispersing agent is not pronounced for nanocomposites containing oxidized nanofibers.
- 3) At lower nanofiber weight fractions, nanocomposites containing pristine nanofibers perform better than nanocomposites containing oxidized nanofibers and the reverse is true at higher weight fractions. If dispersing agent is present, the reverse of the above-mentioned observation is observed.
- 4) Dispersing agent acts better at higher loading levels of pristine nanofibers, while the effect is minimal in the case of oxidized nanofibers at all weight fraction levels. At low nanofiber loadings, pristine nanofibers have less clustering. Thus, at higher loadings, the dispersing agent can have a larger effect on aiding dispersion.

Loss modulus:

- 1) The loss modulus increases for both pristine and oxidized nanofiber containing nanocomposites at low nanofiber weight fractions at room temperature. But, the reverse is observed at higher weight fractions. Comparison is made with the neat resin.
- 2) The dispersing agent acts better with the pristine nanofibers at lower nanofiber weight fractions. But, the effect is minimal with oxidized nanofibers.
- 3) The peak of loss modulus increases for all nanocomposite formulations.
- 4) The glass transition temperature is reduced for all formulations except oxidized nanofibers in the presence of dispersing agent.
- 5) The characteristic secondary peak in the loss modulus is vanished when dispersing agent is used in moderate to high levels.
- 6) Pristine nanofibers give higher loss modulus at lower nanofiber weight fractions, but the reverse is observed at higher weight fractions.

Tan delta:

- 1) The same observations are made as the case of loss modulus curves. The T_g of all formulations are shifted to lower temperatures except oxidized nanofibers in the presence

of dispersing agent.

The results show that manipulation of the dispersing agent in the case of pristine nanofibers might lead to behaviors similar to those of oxidized nanofibers at higher nanofiber weight fractions.

5. FUTURE WORK

The preparation of thermoset nanocomposites, which includes mixing of nanoreinforcements into the matrix and the curing of the resin, has a major role in the ultimate mechanical properties of the nanocomposite. Furthermore, the degree of nanofiber dispersion and the presence of nanofiber clusters (aggregates) in the nanocomposite play an enormous role in its mechanical behavior. Employing different mixing strategies could therefore serve as one possible solution to overcome this issue. We intend to use high-shear mixers and study the effects of extended mixing on breaking apart nanofiber aggregates and the resulting mechanical property enhancements.

In addition, observations of temperature effects on viscoelastic properties of the nanocomposites reveal some interesting phenomena that can be included in the experimental design and subsequent statistical analysis. Therefore, a joint study of formulation and processing factors will be conducted in near future to address these issues and develop a model that would incorporate these factors.

6. ACKNOWLEDGMENT

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.

7. REFERENCES

1. "Auto Applications Drive Commercialization of Nanocomposites". *Plastics, Additives and Compounding* 4 (2002): 30-33.
2. Presting, H., and König, U. "Future Nanotechnology Developments for Automotive Applications." *Materials Science and Engineering C* 23 (2003): 737-741.
3. Sadeghian, R., Gangireddy, S., Minaei, B., and Hsiao, K.-T. "Manufacturing Carbon Nanofibers Toughened Polyester-glass Fiber Composites Using Vacuum Assisted Resin Transfer Molding." *Composites: Part A* 37 (2006):1787-1795.

4. Arai, M., Noro, Y., Sugimoto, K., and Endo, M. "Mode I and Mode II Interlaminar Fracture Toughness of CFRP Laminates Toughened by Carbon Nanofiber Interlayer." *Composites Science and Technology* 68 (2008): 516-525.
5. Applied Sciences, Inc. (Pyrograf III products).
http://pyrografproducts.com/Merchant5/merchant.mvc?Screen=cp_nanofiber.
6. Zhang, W., Joshi, A., Wang, Z., Kane, R.S., and Koratkar, N. "Creep Mitigation in Composites Using Carbon Nanotube Additives." *Nanotechnology* 18 (2007):185703-185708.
7. Xia, H., and Song, M. "Preparation and Characterization of Polyurethane-Carbon Nanotube Composites" *Soft Matter* 1 (2005):386-394.
8. Liao, Y.-H, Marietta-Tondin, O., Liang, Z., Zhang, C., and Wang, B. "Investigation of Dispersion Process of SWNTs/SC-15 Epoxy Resin Nanocomposites" *Materials Science and Engineering A* 385 (2004):175-181.
9. Stat-ease DesignExpert® software. <http://www.statease.com/software.html>.
10. Li, H. "Synthesis, Characterization, and Properties of Vinyl Ester Matrix Resins", *Ph. D. Dissertation in Chemistry* (1998):89.