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Dispersant optimization using design of experiments for SiC/vinyl ester nanocomposites

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Abstract

The effect of dispersants on particle dispersion and flexural properties of SiC/vinyl ester nanocomposites was studied by factorial and response surface designs. The results show that the coupling agent ‘*gamma*-methacryloxy propyl trimethoxy silane (MPS)’ has no adverse side effect on the flexural properties as illustrated by the good correlation between maximizing the flexural strength and minimizing the agglomerates. However, the dispersant ‘BYK-W 966’ has a slight adverse side effect on the flexural properties although it improves dispersion at higher dosage. With an optimal dosage of MPS and W966, a small amount of SiC in 0.5 wt% results in 8% increase in strength and 14% increase in modulus. The flushing operation using the dispersant ‘1-octanol/decane’ achieves an excellent SiC dispersion but it does not result in improved flexural properties. This confirmed that a better state of nanoparticle dispersion does not necessarily lead to improved flexural properties. A good dispersion coupling with a strong filler/matrix interfacial bonding is the key to obtain enhanced flexural properties.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Polymer nanocomposites are hybrid structures where one phase has at least one dimension in the nanosize range (usually defined as 1–100 nm). Compared to particles with sizes in the micrometre range, nanoparticles have a large surface area and, consequently, a nanocomposite may exhibit special properties arising from phase interactions at interfaces [1]. However, the degree of enhancement of a particular property is highly dependent on the filler/matrix material system used, the filler/matrix interfacial bonding, and the state of dispersion of the filler throughout the matrix [2].

Covalent ceramic materials like silicon carbide (SiC) have been recognized as potential candidates for structural

applications because of their superior mechanical properties (strength, stiffness and hardness), chemical (oxidation and corrosion resistance) and thermal stability at high temperatures. The low viscosity coupled with rapid curing rate at room temperature and relatively low cost of vinyl ester resins have led to their extensive use as matrix materials for reinforced composites. This paper examines the dependence of flexural properties on the SiC/vinyl ester interfacial bonding and the state of SiC dispersion using statistically designed experiments.

2. Experiment

2.1. Materials

The matrix resin used was Derakane momentum 411-350, which is an epoxy vinyl ester resin. The hybrid

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molecular structure of epoxies and polyesters contributes to its excellent mechanical strength, as well as chemical and solvent resistance. The aromatic rings provide good mechanical properties and heat resistance. The ether linkage contributes to good chemical resistance. The ester groups and two C=C double bond linkages are located at the end of the polymer chains, which lead to the high reactivity of the terminal unsaturation of vinyl ester resin. Curing was achieved by addition of 2.0 wt% of Trigonox 239A catalyst. 0.3 wt% of cobalt naphthenate (CoNap) promoter was added to promote the decomposition of the catalyst during room temperature cure.

30 nm SiC powder with composition of SiC more than 95%, oxygen 1–1.5%, and carbon 1–2% was used. The β -SiC, a cubic zinc blende structure or 3C-SiC with a stacking order A, B and C (where A, B and C denote the three distinct layers), is the majority phase as specified by the manufacturer.

A non-ionic methacrylate ester-functional silane, *gamma*-methacryloxy propyl trimethoxy silane (MPS), was chosen as the coupling agent and dispersant. The coupling mechanism depends on a stable link between the organofunctional group (Y, chosen for chemical reactivity with the vinyl ester resin) and hydrolysable groups (X, intermediates in formation of silanol groups for bonding to SiC surfaces) in compounds of the structure X_3SiRY . Best wet-strength retention is obtained with three hydrolysable groups on silicon. Although there are three reactive silanols ($\sim Si-OH$) per molecule, reactive sites on a SiC particle surface are so spaced that not more than one silanol group per MPS molecule can bond to the SiC surface. The remaining silanol groups may condense with adjacent silanols to form a siloxane layer ($Si-O-Si$) or remain partly uncondensed at the surface. The organofunctional group ‘methacrylates’ exhibits the best wet strength with polyester and the functional group $-(CH_2)_3Si(OMe)_3$ of methacrylate additive exhibits the highest flexural strength of polyester glass laminates [3]. The functional group $-(CH_2)_3Si(OMe)_3$ reacts with hydroxylated SiC surfaces through hydrogen bonding and through covalent siloxane ($Si-O-Si$) bonds [4]. In addition, the organofunctional group ‘methacrylates’ could copolymerize with styrene monomers in the vinyl ester during cure [5]. Therefore, MPS may act as a bridge to bond the SiC to the vinyl ester resin with a chain of covalent bonds. This could lead to the strongest interfacial bond.

BYK-W 966, registry number: 223251-74-9, consists of salts of alkylamides and esters. The specific chemical identity of proprietary ingredients is a trade secret. The general description is that it is relatively low in molecular weight, has high acid numbers and may be classed as unsaturated polymeric esters. This wetting and dispersing additive improves the dispersion and reduces compound viscosity so that a higher filler loading in the resin is possible. Its function is to encapsulate the filler, resulting in an entropic dispersion which will achieve optimum physical and chemical properties. In addition to its primary performance in helping disperse and wet the filler in the resin, the wetting agent, being unsaturated, reacts chemically with the polyester resin during curing. Hence the hydrophobic wetting agent also acts as an efficient coupling agent that reacts with both filler and resin. When both the silane coupling agent ‘MPS’ and the dispersant ‘W966’ are used together, a synergistic performance (viscosity reduction, flexural strength enhancement) is obtained [6].

Table 1. Fit details for DOE1.

Predictive model for agglomerate size (μm)
Coded levels (−1, 1):
Agglomerate size = $5.725 - 2.825 * MPS - 1.775 * W966 + 1.375 * MPS * W966$

A flushing operation using the long-chain alcohol ‘1-octanol’ and paraffinic hydrocarbon ‘decane’ was employed to disperse the SiC nanoparticles in the vinyl ester resin [7, 8]. R-OH are non-ionic molecules which rely on hydrogen bonding primarily and van der Waals forces secondarily to attach themselves to SiC particle surfaces and serve as dispersant. Chain length is a factor in dispersion and a separation of 20–60 nm is necessary to overcome the van der Waals forces for colloid stability, but the eight carbon rule (oleophilic–hydrophilic balance point) is generally a workable guide for dispersant design.

2.2. Design of experiments

SAS, produced by the SAS Institute, was employed as the statistical software for the design of experiments (DOE). The SiC content used in this study is 0.5 wt% of vinyl ester. The dispersant dosage is expressed as a fraction of the weight of SiC nanoparticles.

The first experiment (DOE1) was designed to study the interaction between MPS and W966. A two-level full-factorial design was chosen to achieve the experimental objective. The low (−1) level was chosen at 0 wt%, and the high (+1) level was chosen at 67 wt% of SiC particle loading as per the theoretically calculated monolayer dispersant coverage [9].

The second experiment (DOE2) was designed to determine the optimum dosage of MPS and W966 to achieve the maximum flexural strength. The state of dispersion was also set as the response in order to examine the correlation between the state of particle dispersion and flexural properties for different dispersants. Response surface methodology (RSM) using the central composite design was employed as the experimental design to achieve the experimental objective. The four factorial points (n_f) were set with −1 and +1 level at 20 and 114 wt% of SiC particle loading, respectively. A uniform-precision design with five centre points (n_c) at 67 wt% (0 level) of SiC was used to estimate the mean square error (MS_E) and the sum of the square of curvature effect ($SS_{curvature}$). Four (2×2) axial points (n_a) with −1.414 level set at 0 wt% and +1.414 level set at 134 wt% of SiC were augmented to the factorial points to make the design rotatable.

3. Results and discussion

Optical microscopy was used to characterize the SiC dispersion. The maximum size of observed SiC agglomerates, denoted by ‘agglomerate size’ in μm , was measured. Table 1 shows the fit details for ‘agglomerate size’. The main effects plot indicates that both MPS and W966 reduce the dispersion variation as shown by the narrower 95% confidence intervals from level −1 to +1, figure 1. Figure 2 shows that both MPS and W966 improve the SiC dispersion significantly as shown by the smaller ‘agglomerate size’ from level −1 to +1.

Figure 1. Main effects plot for 'agglomerate size' showing that both MPS and W966 reduce the dispersion variation.

Figure 2. Interaction plot for 'agglomerate size' showing that both MPS and W966 improve the SiC dispersion, and MPS * W966 interaction appears significant.

Also, the MPS * W966 interaction effect appears significant as indicated by the non-parallelism of the – and + lines. A box plot displays the minimum, the maximum, the lower and upper quartiles (the 25th percentile and the 75th percentiles, respectively), and the median (the 50th percentile) of the measured parameters. Box plot for 'agglomerate size' shows that both MPS and W966 improve dispersion and reduce dispersion variation significantly, as illustrated by the decrease in 'agglomerate size' and variability of 'agglomerate size' from level –1 to +1, figure 3. A Lenth plot for 'agglomerate size' shows that both MPS and W966 improve dispersion significantly, figure 4. The positive MPS * W966 interaction effect estimate is attributed to the poor SiC dispersion without MPS and W966 (–1, –1). The desirability function was set to minimize 'agglomerate size'; 0 is least desirable and 1 is most desirable. Figure 5 shows that high level of MPS and W966 gives the highest desirability (0.88) of minimizing the 'agglomerate size'. Improved dispersion occurs when both MPS and W966 are at high level, figure 6. The DOE1 results confirmed that the interaction between MPS and W966 is significant, and a synergistic performance is obtained when both MPS and W966 are used together.

DOE2 was carried out with 'agglomerate size' and STRENGTH as the responses, where STRENGTH in MPa denotes the flexural strength of nanocomposites. 3-point bending tests were performed per ASTM D790 'standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials' using procedure A. Table 2 shows the fit details for 'agglomerate size' and STRENGTH. Box plots of MPS show that the dosage level 67 (centre point) gives the best dispersion and also the maximum flexural strength, figures 7 and 8. Figure 9

Figure 3. Box plot for 'agglomerate size' showing that both MPS and W966 improve dispersion and reduce dispersion variation.

Figure 4. Lenth plot for 'agglomerate size' showing that both MPS and W966 improve dispersion.

Figure 5. Prediction profile plot showing that high level of MPS and W966 gives the highest desirability of minimizing the 'agglomerate size'.

shows that increasing the W966 dosage to 134 gives the best dispersion. However, the maximum flexural strength occurs at the dosage level 67 and increasing W966 dosage to 134

Figure 6. Contour and surface plots showing that improved dispersion occurs when both MPS and W966 are at high level.

Figure 7. Box plot of MPS showing that the minimum agglomerate size occurs at dosage level 67.

(the best dispersion dosage) decreases the flexural strength, figure 10. Dosage of MPS and W966 at approximately 67 and 101, respectively achieves the best dispersion, figure 11. However, dosage of both MPS and W966 at approximately 67 gives the highest flexural strength, figure 12. A simultaneous optimization of multiple responses was run using the numerical optimizer. The prediction profile plot shows that dosage of both MPS and W966 at approximately 67 achieves the optimal setting, which provides the highest flexural strength and a moderate dispersion, figure 13. A further increase of W966 dosage beyond 67 provides the best dispersion but results in a tremendous decrease in flexural strength. Figures 14 and 15 show the contour and surface plots and an overlay contour plot, respectively. A close optimal region between minimizing ‘agglomerate size’ and maximizing STRENGTH was observed, which indicates that a positive correlation exists

Figure 8. Box plot of MPS showing that the maximum strength occurs at dosage level 67.

Figure 9. Box plot of W966 showing that the minimum agglomerate size occurs at dosage level 134.

Figure 10. Box plot of W966 showing that the maximum strength occurs at dosage level 67.

between the state of particle dispersion and the flexural strength of nanocomposites. The slight difference in optimal region is attributed to W966, which indicates an optimal dosage level at 67 for maximizing STRENGTH but at 134 for minimizing ‘agglomerate size’.

A confirmation run for the optimum setting (both MPS and W966 at the dosage level of 67 wt% of SiC) shows that a small amount of SiC in 0.5 wt% results in 8% increase in strength and 14% increase in modulus, figure 16 and table 3.

A flushing operation using the long-chain alcohol ‘1-octanol’ and paraffinic hydrocarbon ‘decane’ was employed

Figure 11. Prediction profile plot and contour optimizer showing that dosage of MPS and W966 at 67 and 101, respectively achieves the best dispersion.

Figure 12. Prediction profile plot and contour optimizer showing that dosage of both MPS and W966 at approximately 67 gives the highest strength.

to disperse the SiC nanoparticles in the vinyl ester resin. R-OH relies on hydrogen bonding primarily, about 8 kcal mol^{-1} ,

Figure 13. Prediction profile plot—simultaneous optimization of ‘agglomerate size’ and STRENGTH showing that dosage of both MPS and W966 at 67 achieves the optimal setting.

Figure 14. Contour and surface plots showing a close optimal region between minimizing ‘agglomerate size’ and maximizing STRENGTH.

Table 2. Fit details for DOE2.

Predictive model for agglomerate size (μm)

Coded levels (−1, 1):

$$\begin{aligned} \text{Agglomerate size} = & 2.483802 - 1.804809 * \text{MPS} \\ & - 2.003486 * \text{W966} + 2.707022 * \text{MPS} * \text{MPS} \\ & + 2.299 * \text{MPS} * \text{W966} + 1.313172 * \text{W966} * \text{W966} \end{aligned}$$

Predictive model for STRENGTH (MPa)

Coded levels (−1, 1):

$$\begin{aligned} \text{STRENGTH} = & 135.1018 - 0.987131 * \text{MPS} - 7.385292 * \text{W966} \\ & - 12.5752 * \text{MPS} * \text{MPS} + 1.574595 * \text{MPS} * \text{W966} \\ & - 14.74509 * \text{W966} * \text{W966} \end{aligned}$$

and van der Waals forces secondarily to attach themselves to SiC particle surfaces and serve as dispersant.

SiC : $-\text{Si}-\text{OH}$: $\text{OH}-\text{C}_8\text{H}_{17}$: $\text{C}_{10}\text{H}_{22}$: vinyl ester resin.

As resolution of optical microscopy limited by the wavelength of visible light is around $0.5 \mu\text{m}$ at a magnification of $2k\times$, optical photographs at $500\times$ for the 1 vol% SiC samples confirmed that foams/micro-voids were observed instead of

Figure 15. An overlay contour plot.

Figure 16. Stress versus strain curve—confirmation run of DOE2.

Table 3. Flexural properties—confirmation run of DOE2.

SiC (wt%)	Mixing condition	Ultimate flexural stress, $\sigma_{\max}$ (MPa)		Flexural modulus E (GPa)	
		Mean	SD	Mean	SD
0	Neat resin	126	0.8	2.8	0.07
0.5	With MPS and W966	136	6.4	3.2	0.06

SiC agglomerates and an excellent dispersion was achieved, figure 17. Despite the excellent dispersion, a very low strength (39.9 MPa) and a decrease in modulus (2.6 GPa) were exhibited in the nanocomposites specimen, figure 18. The high microvoid content is presumed to be responsible for the poor flexural properties.

4. Conclusions

The dependence of flexural properties on the SiC/vinyl ester interfacial bonding and the state of SiC dispersion was studied using statistical design of experiments. For the coupling agent 'MPS', a good correlation was observed for the optimal dosage to achieve the maximum flexural strength and the best dispersion. However, for the dispersant 'W966', the optimal

Figure 17. Optical photographs of 1-octanol/decane dispersed SiC/vinyl ester at 100 $\times$ and 500 $\times$, respectively.

Figure 18. Stress versus strain curve—1-octanol/decane dispersed SiC/vinyl ester nanocomposites.

dosage which gives the best dispersion does not achieve the maximum flexural properties. It demonstrates that a strong coupling/interfacial bonding between the nanoparticles and matrix is of vital important for achieving enhanced flexural properties. The flushing operation using long-chain alcohol, which achieves an excellent SiC dispersion but results in very poor flexural properties, further illustrates that an excellent dispersion is not the only criterion for enhanced flexural properties. The 67 wt% optimal dosage determined by the statistical design of experiments is in agreement with the theoretically calculated monolayer dispersant coverage [9]. Also, the observed synergistic performance of MPS and W966 and the optimal dosage of MPS and W966 in a 1:1 ratio are in agreement with the literature [6]. With an optimal dosage of MPS and W966, a small amount of SiC in 0.5 wt% results

in 8% increase in strength and 14% increase in modulus. It confirmed the high potential of nanoparticle reinforcement in enhancing the mechanical properties of composites.

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