Rheology of Silicon Carbide/Vinyl Ester Nanocomposites

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ABSTRACT: Silicon carbide (SiC) nanoparticles with no surface treatment raise the viscosity of a vinyl ester resin much more intensely than micrometer-size SiC particles. An effective dispersant generally causes a reduction in the resin viscosity attributed to its surface-active properties and thereby increases the maximum fraction of particles that can be introduced. This article assesses the rheological behavior of SiC-nanoparticle-filled vinyl ester resin systems with the Bingham, power-law, Herschel–Bulkley, and Casson models. The maximum particle loading corresponding to infinite viscosity has been determined to be a 0.1 volume fraction with the $(1 - \eta_r^{-1/2})$–ϕ dependence (where η_r is the relative viscosity and ϕ is the particle volume frac-

tion). The optimum fractional weight percentage of the dispersants (wt % dispersant/wt % SiC) is around 40% for 30-nm SiC nanoparticles, which is much higher than 1–3% for micrometer-size particles. SiC nanoparticles at a concentration of 9.2 wt % (0.03 volume fraction) cause a fourfold increase in the resin viscosity. The addition of a dispersant at the optimum dosage lowers the viscosity of SiC/vinyl ester suspensions by 50%. The reduction in the viscosity is substantial to improve the processability of SiC/vinyl ester nanocomposites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4365–4371, 2006

Key words: nanocomposites; nanoparticles; rheology

INTRODUCTION

Covalent, ceramic materials such as silicon carbide (SiC) have been recognized as potential candidates for structural applications because of their superior mechanical properties (strength, stiffness, and hardness), chemical inertness (oxidation and corrosion resistance), and thermal stability at high temperatures. The low viscosity, coupled with the rapid curing rate at room temperature and the relatively low cost of vinyl ester resins, has led to their extensive use as matrix materials for reinforced composites. Compared with SiC particles with sizes in the micrometer range, SiC nanoparticles with no surface treatment have a strong negative influence on the rheology,[1] causing a lower maximum particle content and a higher viscosity. The SiC nanoparticles, because of their high surface energy coupled with the high surface area, attract the hydrophilic polar portion of vinyl ester molecules, resulting in a mobility reduction of the polymer molecules. The large surface-to-volume ratio of the hydrophilic SiC surface also acts as the driving force for SiC aggregate network formation in the hydrophobic resin.[2–4] These particle–resin and particle–particle interactions lead to

increased viscosity. Also, the viscosity of a suspension increases as the particle concentration increases.[5] This increase is caused by stronger particle–particle interactions, which become attractive with decreasing distance between the particles.[6] With higher particle contents, the distance between the particles decreases, and the short-range van der Waals attractive forces dominate. This article studies the effects of the dispersant type and concentration on the rheological properties of SiC-nanoparticle-filled vinyl ester resin systems.

EXPERIMENTAL

Materials

The vinyl ester resin used in this study was Derakane Momentum 411-350 (provided by Dow Chemical, Midland, MI), which is a mixture of 55 wt % bisphenol A epoxy based vinyl ester and 45 wt % styrene monomers. The hybrid molecular structure of epoxies and polyesters contributes to its excellent mechanical strength and chemical and solvent resistance. The aromatic rings provide good mechanical properties and heat resistance. The ether linkage contributes to good chemical resistance. The ester group and the C=C double bond located at each end of the polymer chain lead to the high reactivity of the resin.

Thirty-nanometer SiC powder (Fig. 1) with a composition of more than 95% SiC, 1–1.5% oxygen, and 1–2% carbon was used. β-SiC, a cubic zinc blende structure, or 3C–SiC, with a stacking order of A, B, and C (where
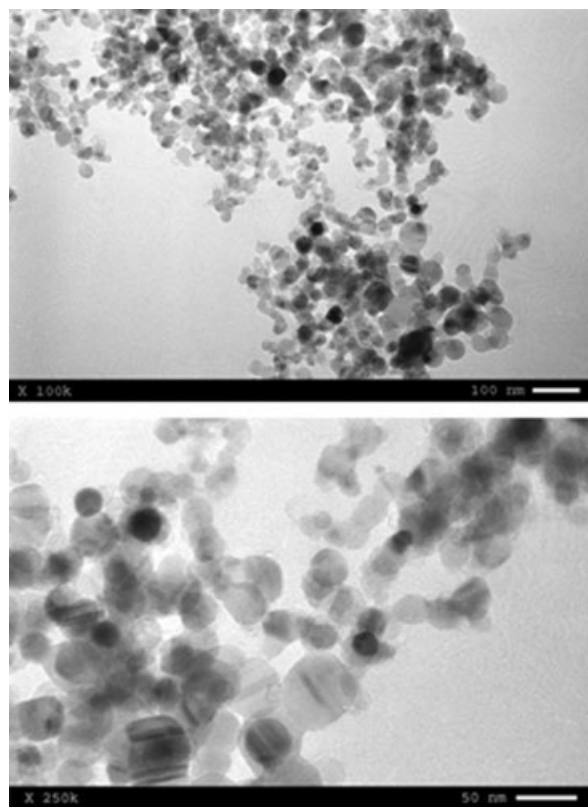
Figure 1 Transmission electron micrographs (100,000 and 250,000×) showing the particle morphology of the SiC nanoparticles used in this study.

A, B, and C denote the three distinct layers), was the majority phase, as specified by the manufacturer.

A nonionic, methacrylate ester functional silane, γ-methacryloxypropyl trimethoxysilane (MPS), was chosen as the coupling agent. The coupling mechanism depended on a stable link between the organofunctional group (Y, chosen for its chemical reactivity with the vinyl ester resin) and hydrolyzable groups (X, intermediates in the formation of silanol groups for bonding to SiC surfaces) in compounds of the structure X_3SiRY. The best wet-strength retention was obtained with three hydrolyzable groups on silicon. Although there were three reactive silanols ($\sim$Si—OH) per molecule, the reactive sites on the SiC particle surface were so spaced that not more than one silanol group per MPS molecule could bond to the SiC surface. The remaining silanol groups could condense with adjacent silanols to form a siloxane layer (Si—O—Si) or remain partly uncondensed at the surface. The organofunctional group methacrylates exhibited the best wet strength with polyester, and the functional group —$(CH_2)_3Si(OMe)_3$ of the methacrylate additive exhibited the highest flexural strength of polyester glass laminates.[7] The functional group —$(CH_2)_3Si(OMe)_3$ reacted with hydroxylated SiC surfaces through hydrogen bonding and through covalent siloxane (Si—O—Si) bonds.[8] In addition, the organofunctional

group methacrylates could copolymerize with styrene monomers in the vinyl ester during the cure.[9] Therefore, MPS could act as a bridge to bond SiC to the vinyl ester resin with a chain of covalent bonds. This could lead to the strongest interfacial bond.

BYK-W966 (registry number 223251-74-9) consists of salts of alkylamides and esters. The specific chemical identity of the proprietary ingredients is a trade secret. It has a relatively low molecular weight and high acid numbers and may be classed as an unsaturated polymeric ester. This wetting and dispersing additive improved the dispersion and reduced the compound viscosity so that a higher filler loading in the resin was possible. Its function was to encapsulate the filler, and this resulted in an entropic dispersion that achieved 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, reacted chemically with the polyester resin during curing. Hence, the hydrophobic wetting agent also acted as an efficient coupling agent that reacted with both the filler and resin. When silane coupling agent MPS and dispersant W966 were used together in 1 : 1 ratio, a synergistic performance (viscosity reduction and flexural strength enhancement) could be obtained.[10,11]

A flushing operation using 1-octanol was employed to disperse the SiC nanoparticles in the vinyl ester resin.[12,13] R—OH denotes nonionic molecules relying on hydrogen bonding primarily and van der Waals forces secondarily to attach themselves to the SiC particle surfaces and serve as dispersants. The chain length was a factor in the dispersion, and a separation of 20–60 nm was necessary to overcome the van der Waals forces for colloid stability, but the eight-carbon rule (the oleophilic–hydrophilic balance point) was generally a workable guide for the dispersant design.

Rheological measurements

The neat resin and suspensions were tested for viscosity with a shear-rate sweep at 25°C on a Haake cup and cone rheometer, which was reported to be the appropriate instrument for viscosity measurements in comparison with a Brookfield rheometer.[6] The rheological

TABLE I
Newtonian, Bingham-Plastic, and Power-Law Fluids as Special Cases of the Herschel–Bulkley Model

Fluid	K	n	τ_0
Newtonian	>0	1	0
Bingham plastic	>0	1	>0
Power law			
Shear thinning (pseudoplastic)	>0	$0 < n < 1$	0
Shear thickening (dilatant)	>0	$1 < n < \infty$	0
Herschel–Bulkley	>0	$0 < n < \infty$	>0
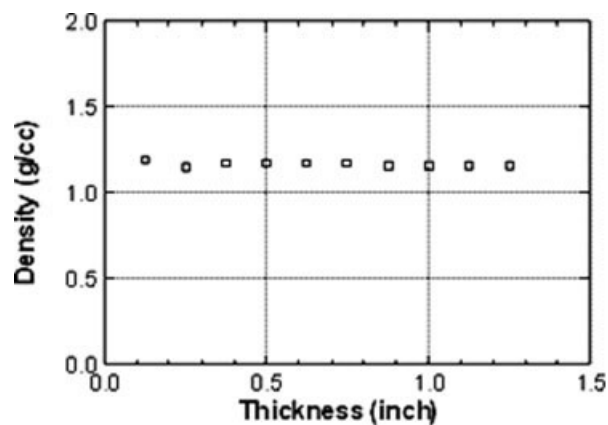
Figure 2 Sedimentation test for the SiC nanoparticles (6 wt %).

Figure 4 Viscosity curves of SiC/vinyl ester resin systems with and without SiC nanoparticles. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

behavior was visualized as a plot of the shear stress (τ) versus the shear rate ($\dot{\gamma}$). The resulting curve was mathematically modeled with various functional relationships. A general relationship to describe the behavior of non-Newtonian fluids is the Herschel–Bulkley model:[14]

$$\tau = K(\dot{\gamma})^n + \tau_0$$

where K is the consistency coefficient, n is the flow behavior index, and τ_0 is the yield stress. Newtonian, Bingham-plastic, and power-law (shear thinning at $0 < n < 1$ or shear thickening at $1 < n < \infty$) behaviors are considered as special cases (Table I). With the Newtonian and Bingham-plastic models, K is commonly called the viscosity coefficient and plastic viscosity, respectively. The Casson model was evaluated as well:[15]

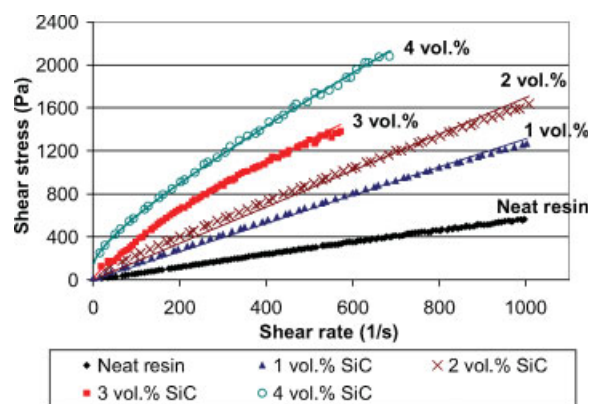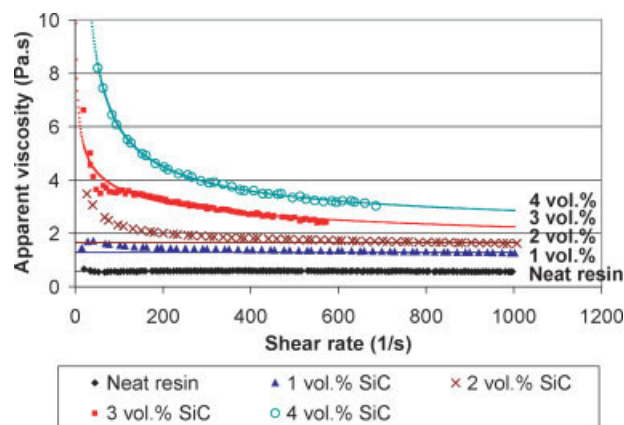$$\tau^{0.5} = K(\dot{\gamma})^{0.5} + (\tau_0)^{0.5}$$

RESULTS AND DISCUSSION

Particulate sedimentation

Small particles with diameters smaller than 1 μm are maintained in a suspension by Brownian motion,[16] but this agitation also promotes particle collisions, which often lead to aggregation, followed by gelation or by gravitational settling of the particle clumps. The rheology of flocculating suspensions is difficult to measure because the flocs tend to settle during the measurement and produce an inhomogeneous composition in the measurement cell. Nanoparticles of SiC exhibit no appreciable tendency for sedimentation when mixed with a low-viscosity resin of vinyl ester, in contrast to the case of micrometer-size particles (Fig. 2).[1] As gravitational sedimentation pulls particles downward to the bottom and Brownian motion distributes particles throughout the suspension, the observed phenomenon could be explained by the ratio of gravitational forces to Brownian forces:[17]

$$\frac{a^4 \Delta \rho g}{k_B T} = \frac{(15nm)^4 (3200 - 1046)kg/m^3 (9.8m/s^2)}{(1.3807 \times 10^{-23} J/K)(300K)}$$

$$= 2.6 \times 10^{-7}$$

Figure 3 Flow curves of SiC/vinyl ester resin systems with and without SiC nanoparticles. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

TABLE II
Summary of the Rheological Behavior of SiC/Vinyl Ester Resin Systems

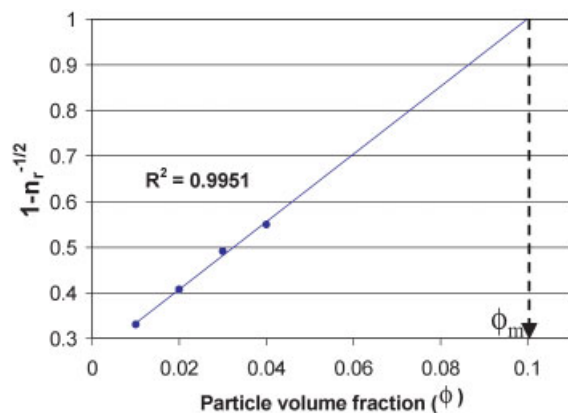| SiC (vol %)	Model	K	n	τ_0	Viscosity at 1000 s^{-1}
0	Newtonian	0.5793	1	0	0.5793
1		1.3116	1	0	1.3116
2		1.6941	1	0	1.6941
3	Power Law	9.8796	0.7851	0	2.2389
4	Casson	1.3441	—	120	2.8582

Figure 5 $(1 - \eta_r^{-1/2})$–ϕ dependence for the determination of ϕ_m. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Flow curves of SiC/vinyl ester resin systems with and without 1-octanol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

where a is the particle radius, $\Delta\rho$ is the density difference between the particle and liquid, g is the acceleration due to gravity, k_B is Boltzmann's constant, and T is the absolute temperature. Because the ratio is much lesser than 1, Brownian diffusion dominates, and no sedimentation is expected when the particles are fully dispersed.

Rheological behavior

The flow characteristics of the SiC/vinyl ester resin systems were evaluated in terms of the Bingham, power-law, Herschel–Bulkley, and Casson models. The Bingham model was used to estimate the apparent yield stress value.[16] The method of regression analysis was used to determine the best fitted model. The results are summarized in Figures 3 and 4 and Table II.

The neat resin and 1 and 2 vol % SiC suspensions exhibited a Newtonian flow, as illustrated by the
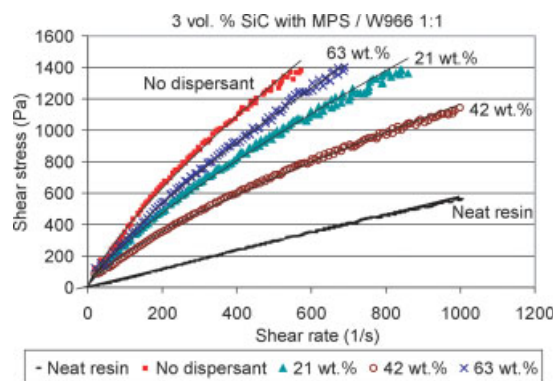
fairly linear $\tau - \dot{\gamma}$ relationship. As the particle loading increased further to 3 and 4 vol %, the suspension $\tau - \dot{\gamma}$ relationship deviated pronouncedly from linearity, revealing a non-Newtonian flow behavior. The flow behavioral change indicated a higher resistance to flow due to the SiC floc formation with increasing SiC loading.

For the 3 vol % SiC suspension, $n = 0.7851$, a value significantly less than 1, indicated a shear-thinning effect. This behavior corresponded to a progressive deformation and disruption of SiC flocs in the shear field.[18] The 4 vol % SiC suspensions exhibited a yield stress of 120 Pa. This behavior indicated that the suspension was flocculated and interparticle attractive forces prevented flow until sufficient energy was imparted to the suspension to overcome their resistance.[19]

The maximum particle volume fraction (ϕ_m) for the SiC/vinyl ester system was predicted with the following viscosity/particle-concentration relationship:[20]

Figure 6 Flow curves of SiC/vinyl ester resin systems with and without MPS/W966. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
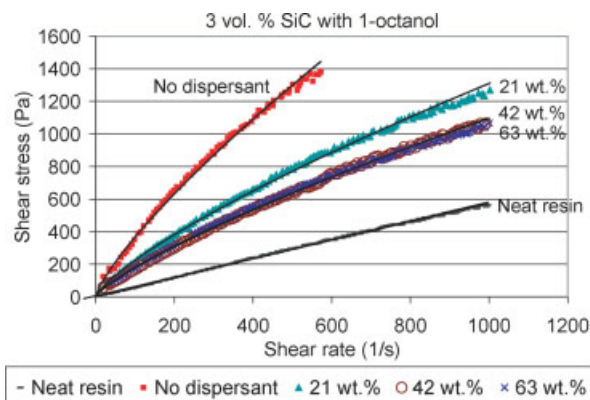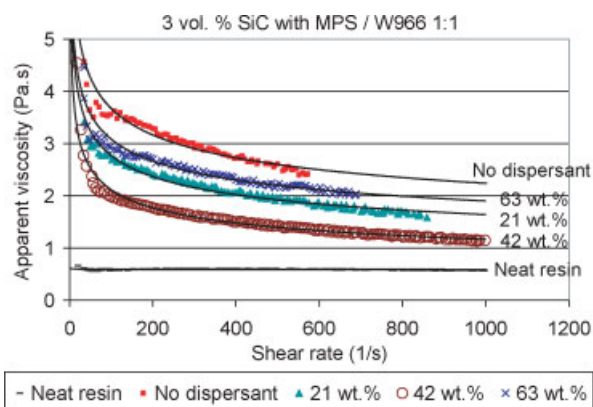

Figure 8 Viscosity curves of SiC/vinyl ester resin systems with and without MPS/W966. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
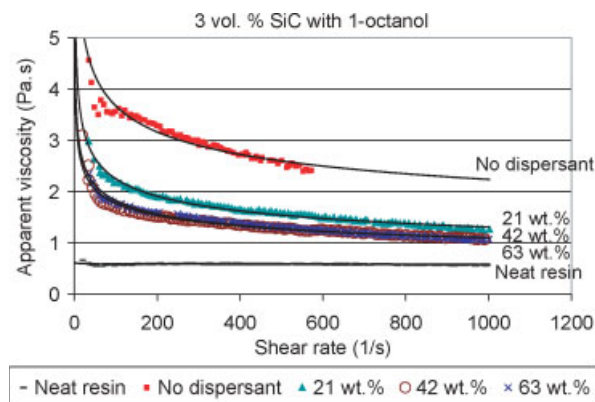
Figure 9 Viscosity curves of SiC/vinyl ester resin systems with and without 1-octanol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
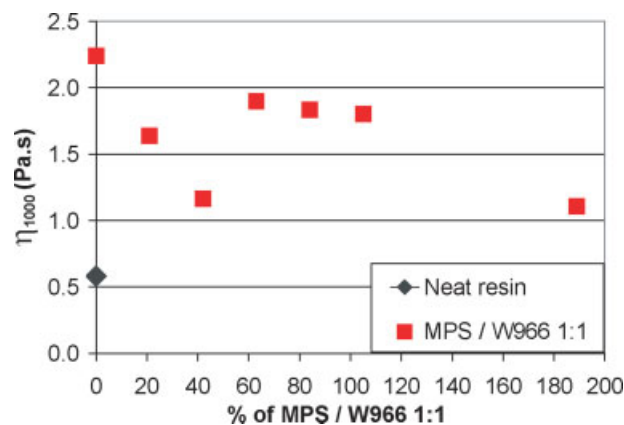

Figure 10 Rheological profile showing the optimum dosage of MPS/W966. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\eta_r = [c(\phi_m - \phi)]^{-m}$$

where η_r is the relative viscosity (the suspension viscosity divided by the viscosity of the suspending medium), c is a constant, m is a flow-dependent parameter that is suspension-specific, and ϕ is the particle volume fraction. The term $\phi_m - \phi$ is physically interpreted as the effective space available for the particles to move in the matrix medium. When ϕ approaches ϕ_m, the available space disappears, and the viscosity of suspensions becomes infinite. The suspension hence ceases to flow and behaves like a solid. ϕ_m can be determined from the $(1 - \eta_r^{-1/m})$–ϕ relationship, which often follows a linear relationship over a broad range of particle volume fractions.[21] m generally falls in a range of 2–3.[20,21] Figure 5 shows the $(1 - \eta_r^{-1/m})$–ϕ dependence at $\dot{\gamma} = 1000 \text{ s}^{-1}$ by assuming m equals 2. The correlation is excellent, as illustrated by the large value of the coefficient of determination (0.9951). By the extrapolation of $1 - \eta_r^{-1/2}$ to 1, the theoretical maximum particle loading was determined to be a 0.1 volume fraction.

Viscosity measurements can provide useful information on the effectiveness and optimum dosage of a dispersant.[6,12,22] Figures 6–9 show the rheological properties of SiC/vinyl ester suspensions (3 vol %

SiC) in the presence of MPS/W966 and 1-octanol. The points in the figures are experimental data, whereas the lines represent the power-law models. The SiC/vinyl ester suspensions with dispersants exhibited a power-law shear-thinning behavior. The apparent viscosity was calculated as $\tau/\dot{\gamma}$ and plotted as a function of $\dot{\gamma}$ (Figs. 8 and 9). Both MPS/W966 and 1-octanol had a pronounced effect on reducing the suspension viscosity. The dispersing effect was due to the adsorbed dispersant on the SiC nanoparticle surface, resulting from the dispersant–surface affinity, which reduced the interparticle forces and the tendency for flocculation.[12]

Dispersion characteristics

The data shown in Table III and Figure 10 result from viscosity measurements attained at the $\dot{\gamma}$ value of 1000 s^{-1}. From the plot of the viscosity as a function of the weight percentage of the dispersants (wt % dispersant/wt % SiC), the optimum amount of the dispersant (dispersant adsorbed) could be obtained at the point at which a minimum viscosity occurred.[6,12] It was around 40% for MPS/W966. The minimum viscosity corresponded to the point of transition from attractive

TABLE III
SiC Suspension Viscosity in the Presence of MPS/W966

SiC (vol %)	MPS/W966 dosage (wt %)	K	n	Viscosity at 1000 s^{-1}
0	—	0.6077	0.9937	0.5818
3	0	9.8796	0.7851	2.2389
	21	7.9155	0.7720	1.6386
	42	6.9607	0.7412	1.1648
	63	8.1225	0.7896	1.8988
	84	11.126	0.7390	1.8337
	105	12.510	0.7195	1.8020
	189	6.9337	0.7342	1.1055

TABLE IV
SiC Suspension Viscosity in the Presence of 1-Octanol

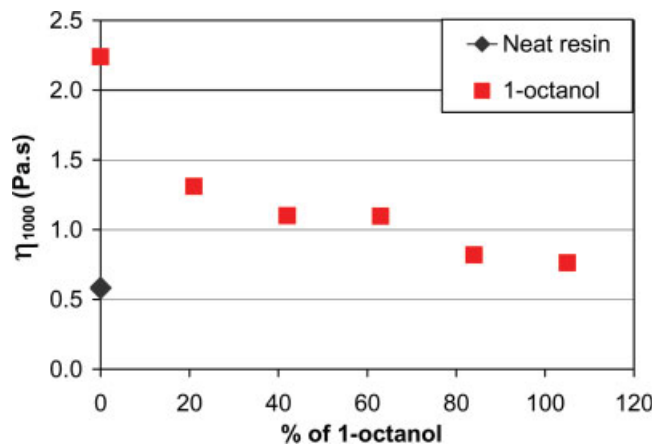| SiC (vol %)	1-Octanol dosage (wt %)	K	n	Viscosity at 1000 s^{-1}
0	—	0.6077	0.9937	0.5818
3	0	9.8796	0.7851	2.2389
	21	6.6379	0.7651	1.3102
	42	4.5900	0.7932	1.1001
	63	5.0657	0.7784	1.0961
	84	3.5469	0.7877	0.8184
	105	3.0537	0.7991	0.7623

Figure 11 Rheological profile showing the optimum dosage of 1-octanol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

particle interactions to repulsive particle interactions (i.e., just dispersed).[23] An excess of the dispersant beyond the optimum dosage might have caused reflocculation (an overdispersed state), which increased the viscosity.[16] A plateau value was observed at a higher concentration of approximately 60%, which dropped slightly with an increasing amount of the dispersant because of an oversaturated effect (dispersant dissolved).[19]

Table IV and Figure 11 show the reduction of the viscosity with increasing amounts of 1-octanol. The decrease took place in two steps instead. At first, the viscosity decreased gradually. Then, it stayed constant up to a value of 60% and finally decreased with higher amounts of the dispersant. The optimum amount of the dispersant could be obtained at the point at which the curve leveled out,[6] which was around 40%.

MPS/W966 and 1-octanol exhibited different dispersion characteristics (Figs. 10 and 11). 1-Octanol appeared to be more effective than MPS/W966 in dispersing SiC nanoparticles as there was no reflocculation.[16] The better dispersing capability of 1-octanol is likely attributable to the linear molecular structure of its head group[12] and the Lewis base/Lewis acid reactions (electron-donor/electron-acceptor interactions),[13,19] which make it an effective adsorbate to the SiC nanoparticle surface and explain the observed difference in its rheological profile and that of MPS/W966.

CONCLUSIONS

The incompatibility between hydrophilic SiC and a hydrophobic vinyl ester resin, coupled with the strong particle–particle interactions associated with the large specific surface area of the SiC nanoparticles, acted as the driving force for the network formation of SiC aggregates. This stabilized the suspension even at a very low particle loading (<0.04 particle volume fraction), resulting in very high viscosities. The theoretical

maximum particle loading corresponding to infinite viscosity was determined to be a 0.1 volume fraction with the $(1 - \eta_r^{-1/2})$–ϕ dependence.

The rheological behavior of the SiC-nanoparticle-filled vinyl ester resin systems was evaluated in terms of the Bingham, power-law, Herschel–Bulkley, and Casson models. The flow behavior of the neat vinyl ester resin and low volume percentage SiC suspensions was fairly Newtonian. However, a further increase in the volume of the SiC nanoparticles induced a pseudoplastic characteristic, which revealed that the SiC nanoparticle suspensions were flocculated and had a structure dependent on particle–particle interactions.[19]

A general guideline for the optimum fractional weight percentage of dispersants (wt % dispersant/wt % SiC) for dispersion stabilization is 1–3% for particles in the 0.1–3-μm range.[24] The optimum concentrations of the various dispersants (MPS/W966 and 1-octanol) giving the minimum viscosity were in the same range and were determined to be around 40% (a quantity much higher than 1–3%). This was in close agreement with the theoretically calculated monolayer coverage dosage of 67%.[2] The difference between the experimental and theoretical optimal values could be associated with the particle agglomeration, which reduced the effective surface area of the nanoparticles. Both MPS/W966 and 1-octanol had a pronounced effect on the rheological behavior of the SiC/vinyl ester suspension systems. 1-Octanol appeared to be more effective than MPS/W966 in dispersing the SiC nanoparticles. The better dispersing capability of 1-octanal is likely attributable to the linear molecular structure of its head group[12] and the Lewis base/Lewis acid reactions (electron-donor/electron-acceptor interactions),[13,19] which make it an effective adsorbate to the SiC nanoparticle surface. A 50% decrease in the suspension viscosity was observed at the optimal dispersant dosage. The amount of viscosity reduction was substantial to improve the processability of the SiC/vinyl ester nanocomposites.

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