UCLA

UCLA Previously Published Works

Title

Monodisperse SiC/vinyl ester nanocomposites: Dispersant formulation, synthesis, and characterization

Permalink

<https://escholarship.org/uc/item/1r72r9w3>

Journal

Journal of Materials Research, 24(4)

Authors

Yong, Virginia

Hahn, H. Thomas

Publication Date

2011-01-31

Peer reviewed

Monodisperse SiC/vinyl ester nanocomposites: Dispersant formulation, synthesis, and characterization

Virginia Yong

Department of Materials Science and Engineering, University of California—Los Angeles, Los Angeles, California 90095

H. Thomas Hahn^{a)}

Department of Materials Science and Engineering, University of California—Los Angeles, Los Angeles, California 90095; and Department of Mechanical and Aerospace Engineering, University of California—Los Angeles, Los Angeles, California 90095

(Received 30 November 2008; accepted 6 January 2009)

A novel dispersant “mono-2-(methacryloyloxy)ethyl succinate” was formulated for dispersing 30-nm SiC nanoparticles in vinyl ester resin. The eight carbon rule was used as the guideline to achieve a particle–particle separation of 20 to 60 nm for colloid stability. Fourier transform infrared spectroscopy was performed to characterize the SiC particle surfaces. Only a negligible amount of oxidized layer was observed; which illustrates that the SiC surface is basic. Thus, the Lewis base–Lewis acid reactions make the functional group –COOH an effective adsorbate to the SiC nanoparticle surface. The organofunctional group “methacrylates,” which exhibits the best wet strength with polyester copolymerizes with styrene monomers in the vinyl ester during cure. Hence, this novel dispersant also acts as an efficient coupling agent that reacts with both SiC and vinyl ester. The monolayer coverage dosage of 62 fractional wt% of the dispersant was used to attain the minimum filled resin viscosity. The multicomponent compositional imaging using atomic force microscopy confirmed the monodisperse SiC nanoparticles in vinyl ester. The 3 vol% SiC reinforced vinyl ester achieved a 75% increase in modulus, 42% increase in strength, and 75% increase in toughness as compared with the neat resin without nanofiller reinforcement.

I. INTRODUCTION

Polymer nanocomposites are hybrid structures where one phase has at least one dimension in the nano-size range (usually defined as 1–100 nm). Compared to particles with sizes in the micrometer 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.^{2,3} A good dispersion of nanofiller in the polymer matrix coupling with a strong interface between the two phases is essential to achieve enhanced mechanical properties.^{4,5}

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

inertness (oxidation and corrosion resistance), and thermal stability at high temperatures. The low viscosity, coupled with 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. 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.⁶ Here, we report a novel dispersant formulation approach for monodisperse SiC/vinyl ester nanocomposite synthesis. The stated formulation methodology could be deployed to other polymer nanocomposite material systems as well.

II. EXPERIMENT

The vinyl ester resin used was Derakane momentum 411-350 (Dow Chemical Co., USA), 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

^{a)}Address all correspondence to this author.

e-mail: hahn@seas.ucla.edu

DOI: 10.1557/JMR.2009.0176

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. A 0.3 wt% of cobalt naphthenate (CoNap) promoter was added to promote the decomposition of the catalyst during room temperature cure. A 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), was the majority phase as specified by the manufacturer.

Particle morphology (size and shape) were characterized on a JEOL transmission electron microscope (TEM; JEOL TEM-2010) (Fig. 1). TEM sample preparation was carried out by diluting the SiC nanoparticles with isopropyl alcohol (IPA) and sonicating the suspension at 40 W for 10 min. A drop of the sonicated suspension was then put on the Prod. #01800 Ted Pella 200 mesh specimen support film grids (USA). Only SiC nanoparticles were

left for TEM examination on the support film after the evaporation of IPA solution. A Fourier transform infrared (FTIR) spectrometer (FTIR 420; Jasco Corp., Tokyo, Japan) in absorbance mode under dry nitrogen flow ($10 \text{ cm}^3 \text{ min}^{-1}$) was used to study the surface chemical composition of SiC nanoparticles. The SiC sample was mixed with IR grade KBr powder, ground, and compressed into a pellet.

The mechanical properties of the fabricated nanocomposites were evaluated by three-point bending tests following the American Society for Testing and Materials Standard (ASTM, Standard D790) using an Instron 5544 testing machine. Five to seven specimens per sample were tested. An optical microscope (OM; Olympus BX41) and a scanning electron microscope (SEM; JEOL field-emission scanning electron microscope, JSM-6700F) were used to examine the fracture surfaces. The SEM specimens were prepared by sputter coating a thin gold layer $\sim 3 \text{ nm}$ thick on a nanocomposite sample.

The atomic force microscope (AFM; Dimension 3100, Veeco Company, USA) operated in tapping mode was used to investigate the dispersion quality of the SiC nanoparticles within the vinyl ester resin matrix. The probes used were TappingMode etched antimony-doped silicon probes with nominal tip radius $< 10 \text{ nm}$, resonant frequency about 320 kHz, and spring constant of around 42 N m^{-1} .

III. RESULTS AND DISCUSSION

All SiC nanoparticles were pretreated by vacuum baking at 200°C for 24 h to remove the moisture, which was adsorbed due to the hydrophilic SiC surface.^{3,7} Water increases one particle surface's affinity for another, which excludes organic molecules within agglomerates. Furthermore, water is difficult to remove from particle surfaces once these are immersed in organic liquids, as illustrated by the considerably higher heat of wetting by water compared to organic liquids.⁸

For SiC with an average diameter of 30 nm, specific surface area is $62.5 \text{ m}^2 \text{ g}^{-1}$. Powder with a specific surface area $\geq 10 \text{ m}^2 \text{ g}^{-1}$ is considered suitable for FTIR surface analysis,^{9,10} and FTIR spectroscopy has been used for distinguishing the presence of an oxidized layer on the particle surfaces for pure SiC and oxidized SiC nanopowders.¹¹ It has also been used for surface analysis of other nano-sized particles, such as diamond nanoparticles,¹² titanium oxide,¹³ and tin oxide nanopowders.^{14,15} Figure 2 shows the IR spectrum of pretreated SiC nanoparticles over the range of 4500 to 400 cm^{-1} . An intense absorption band at $\sim 800 \text{ cm}^{-1}$ [the transverse-optical (TO) phonons] with a shoulder at 912.5 cm^{-1} was observed, which is attributed to the Si–C stretching vibration mode in crystalline cubic β -SiC.¹⁶ The band at 2340 cm^{-1} was assigned to CO_2 gas.

FIG. 1. TEM micrographs at 100 and 250 kX showing the particle morphology of the SiC nanoparticles.

FIG. 2. FTIR spectrum of pretreated SiC nanoparticles. The inset in the figure corresponds to an enlarged view of a strong characteristic absorption peak at $\sim 800\text{ cm}^{-1}$, which is attributed to the transverse optical phonons of Si-C bonds in 3C-SiC.

FIG. 3. Molecular structure of mono-2-(methacryloyloxy) ethyl succinate.

FIG. 4. Copolymerization of methacrylate and styrene.

The absorption band in the range from 3550 to 3300 cm^{-1} is commonly assigned to hydroxyl group vibrations.¹⁷ Additionally, the absorption band at 1100 to 1070 cm^{-1} is due to the Si-O stretching vibrations of the different silicon oxycarbide, SiO_2C_2 and SiO_3C , species. These species have been reported to be the first layers of oxidation of SiC.¹⁸ The small $1100 - 1070$ and $3550 - 3300\text{ cm}^{-1}$ band absorbance indicates that the degree of SiC surface oxidation is negligible.

A novel dual-functional coupling and dispersing agent “mono-2-(methacryloyloxy)ethyl succinate” was formulated for dispersing 30-nm SiC nanoparticles in vinyl ester resin (Fig. 3). Pure SiC surface is basic, whereas an oxidized SiC surface contains a layer of silica, which causes the surface acidic. Thus, the Lewis base-Lewis acid reactions (electron donor-acceptor interactions) make the functional group $-\text{COOH}$ an effective adsorbate to the SiC nanoparticle surface.¹¹ The organofunctional group “methacrylates,” which exhibits the best wet strength with polyester copolymerizes with styrene monomers in the vinyl ester during cure (Fig. 4). Hence, this novel dispersant also acts as an efficient coupling

*** Vary chain length and dosage to give minimum viscosity.**

FIG. 5. Schematic diagram of the design of dispersants for SiC/vinyl ester nanocomposite synthesis.

agent that reacts with both SiC and vinyl ester. Chain length is a factor in dispersion and a separation of $20\text{--}60\text{ nm}$ is necessary to overcome the van der Waals forces for colloid stability.^{3,8} The eight carbon rule (oleophilic-hydrophilic balance point) was used as the guideline to achieve the particle-particle separation. A dispersant “hydroxypropyl methacrylate” with an alcohol head group $-\text{OH}$ acting as a Lewis base was also selected as a test vehicle. The schematic diagram of the design of dispersants is shown in Fig. 5.

Because the energy of wetting must exceed the interparticle binding energy and the process is liquid diffusion limited, mechanical force is required (we used ultrasonic disperser and magnetic stirrer) to separate the agglomerates of particles and permit the dispersant to adsorb onto the unwet portions of the SiC surface. SiC/vinyl ester nanocomposites were mixed under the following conditions: (i) resin (Derakane momentum 411-350): 100 mL ; (ii) sonication (24 W) + magnetic stirring (cooled with compressed air): 1 h ; (iii) degassing in vacuum for 1 h ; (iv) Trigonox (catalyst): $2.0\text{ wt\%}$; (v) CoNap (promoter): $0.3\text{ wt\%}$; and (vi) post-cure at 85°C for 1 h .

The calculation of the amount of mono-2-(methacryloyloxy)ethyl succinate dosage was as follows:

$$m_f = \frac{M_f m_s A_{sp}}{A_f} + M_f \text{CMC}_f V_l$$

with m_s = mass of SiC nanoparticles = $1\text{ wt\%}$ of 15 mL of vinyl ester = $0.156/1000\text{ kg}$; A_{sp} = specific surface area of SiC (diameter of 30 nm) = $62500\text{ m}^2\text{ kg}^{-1}$; M_f = molar mass of mono-2-(methacryloyloxy)ethyl succinate = $230.21/1000\text{ kg mol}^{-1}$; A_f = molar area coverage of mono-2-(methacryloyloxy)ethyl succinate = $10^5\text{ m}^2\text{ mol}^{-1}$. This corresponds to 6 molecules adsorbed per nm^2 (or $100\text{ \AA}^2$) of surface. V_l = volume of liquid [m^3]; CMC_f = saturated solubility of mono-2-(methacryloyloxy)ethyl succinate in resin = assume

FIG. 6. Stress versus strain curves, SiC/vinyl ester nanocomposites with mono-2-(methacryloyloxy)ethyl succinate and hydroxypropyl methacrylate, respectively. Mixing without dispersant was investigated as a control.

0 mol m⁻³. Therefore, a monolayer coverage dosage (m_f) of 62 fractional wt% of the mono-2-(methacryloyloxy)ethyl succinate (wt% dispersant/wt% SiC) was used to attain the minimum filled resin viscosity.^{3,6} Similarly, the dosage of hydroxypropyl methacrylate with a molar mass of 144.17/1000 kg mol⁻¹ was determined to be 39 fractional wt%.

Three-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 (Fig. 6). As Young’s modulus of β -SiC (3C) in the $\langle 100 \rangle$ direction is 392–694 GPa,¹⁹ which is a hundred times stiffer than the vinyl ester matrix, modulus increases when the SiC volume fraction increases. A change in the nature of interface and dispersion quality at constant volume fraction does not have a significant influence on the modulus, but is essential in determining both the strength and toughness of the composite.^{20,21}

With dispersant “mono-2-(methacryloyloxy)ethyl succinate”, both modulus and strength increase when the SiC volume fraction increases. The 3 vol% SiC reinforced vinyl ester achieved a 75% increase in modulus, 42% increase in strength, and 75% increase in toughness (area under the stress–strain curve) as compared with the neat resin without nanofiller reinforcement. Fracture surfaces were devoid of any particle agglomerates (Fig. 7). However, with dispersant “hydroxypropyl methacrylate,” both modulus and strength decrease when the SiC volume fraction increases. The observed foams/microvoids are presumed to be responsible for the limited improvement on flexural properties for hydroxypropyl

FIG. 7. Fracture initiation sites: (a) with dispersant “mono-2-(methacryloyloxy)ethyl succinate” and (b) without dispersant.

FIG. 8. AFM images show a fully dispersed SiC in vinyl ester with mono-2-(methacryloyloxy) ethyl succinate: (a) 1 vol% SiC and (b) 3 vol% SiC. Inset in (a) shows the enlargement of one nanoparticle within the matrix. The bottom part of the figure is the corresponding three-dimensional images of (a) and (b) on top of them.

methacrylate dispersed SiC/vinyl ester nanocomposites. For mixing without dispersant, higher particle loading introduces larger and more loosely assembled nanoparticle agglomerates, which act as the stress concentrators causing a decrease in strength.

The phase contrast in atomic force microscopic phase images measured in tapping mode were investigated for distinguishing the interphase in several systems, such as E-glass fiber filled polypropylene and epoxy resin composites,²² carbon fiber filled epoxy resin composites,^{23,24} alumina nanoparticle filled polymeric nanocomposites,²⁵ and gold nanoparticle filled polymeric photoresists (PR).²⁶ Figure 8 shows the AFM phase images under tapping mode of the SiC nanoparticle filled vinyl ester nanocomposites. The different stiffnesses of the SiC and vinyl ester resin matrix are manifested by the two different signals with a phase difference, and SiC particles (stiffer component) were seen as locations with brighter contrast. The AFM confirmed the monodisperse SiC nanoparticles in vinyl ester, with mono-2-(methacryloyloxy)ethyl succinate. The SiC nanoparticles were observed to be around 30 nm, consistent with the TEM

observation and the average size of 30 nm specified by the manufacturer.

IV. CONCLUSIONS

Nanocomposites and nanoparticles are being used as nanostructured photovoltaic devices, high-performance catalysts, and as advanced energetic, electronic, photonic, magnetic, and biomedical materials. Here, we reported the formulation of a novel dual-functional coupling and dispersing agent for surface modification of a 30-nm SiC inorganic phase. The interparticle interaction was controlled by changing the length of the surface passivation molecules. The tailored inorganic–organic, SiC-vinyl ester, hybrid nanostructure exhibits a 75% increase in modulus, 42% increase in strength, and 75% increase in toughness. The increase in flexural properties is likely attributable to the monodisperse SiC nanoparticles in vinyl ester as observed under the AFM (Fig. 8), and a stronger interfacial bonding between the SiC nanoparticles and vinyl ester resin as a result of the mono-2-(methacryloyloxy)ethyl succinate addition. The stated

formulation methodology could be deployed to other polymer nanocomposite material systems as well. We demonstrated that with good dispersion, nanoparticles will improve mechanical properties of nanocomposite films, coatings, etc. This opens doors to the use of functional nanoparticles in multifunctional applications.

ACKNOWLEDGMENTS

The authors would like to thank the Air Force Office of Scientific Research (L. Lee) and the United States Army Natick Laboratory (J. Song and M. Sennett) for financial support through AFOSR Grant F49620-02-1-0414, and Dr. John W. Goodman for his advice.

REFERENCES

1. M.C. Roco: Nanoparticles and nanotechnology research. *J. Nanopart. Res.* **1**, 1 (1999).
2. V.M.F. Evora and A. Shukla: Fabrication, characterization, and dynamic behavior of polyester/TiO₂ nanocomposites. *Mater. Sci. Eng., A* **361**, 358 (2003).
3. V. Yong and H.T. Hahn: Processing and properties of SiC/vinyl ester nanocomposites. *Nanotechnology* **15**, 1338 (2004).
4. V. Yong and H.T. Hahn: Dispersant optimization using design of experiments for SiC/vinyl ester nanocomposites. *Nanotechnology* **16**, 354 (2005).
5. M.T. Ton-That, F. Perrin-Sarazin, K.C. Cole, M.N. Bureau, and J. Denault: Polyolefin nanocomposites: Formulation and development. *Polym. Eng. Sci.* **44**, 1212 (2004).
6. V. Yong and H.T. Hahn: Rheology of silicon carbide/vinyl ester nanocomposites. *J. Appl. Polym. Sci.* **102**, 4365 (2006).
7. H. Preiss, L.M. Berger, and M. Braun: Formation of black glasses and silicon carbide from binary carbonaceous/silica hydrogels. *Carbon* **33**, 1739 (1995).
8. R.F. Conley: *Practical Dispersion* (Wiley, New York, 1996).
9. E. Kissa: *Dispersions* (Marcel Dekker, New York, 1999).
10. Surface analysis of semiconducting nanoparticles by FTIR spectroscopy, in *Nanocrystalline Metals and Oxides: Selected Properties and Applications*, edited by P. Knauth and J. Schoonman (Springer, Kluwer Academic, Boston, 2002), pp. 165–187.
11. M. Okuyama, G.J. Garvey, T.A. Ring, and J.S. Haggerty: Dispersion of silicon-carbide powders in nonaqueous solvents. *J. Am. Ceram. Soc.* **72**, 1918 (1989).
12. Q.S. Yu, Y.J. Kim, and H.B. Ma: Plasma treatment of diamond nanoparticles for dispersion improvement in water. *Appl. Phys. Lett.* **88**, 231503 (2006).
13. M.I. Baraton and L. Merhari: Surface chemistry of TiO₂ nanoparticles: Influence on electrical and gas sensing properties. *J. Eur. Ceram. Soc.* **24**, 1399 (2004).
14. C. Drake, S. Deshpande, and S. Seal: Determination of free-carrier density and space charge layer variation in nanocrystalline In³⁺ doped tin oxides using Fourier transform infrared spectroscopy. *Appl. Phys. Lett.* **89**, 143116 (2006).
15. F.M. Liu, B.F. Quan, L.H. Chen, L.X. Yu, and Z.Q. Liu: Investigation on SnO₂ nanopowders stored for different time and BaTiO₃ modification. *Mater. Chem. Phys.* **87**, 297 (2004).
16. Y. Sun and T. Miyasato: Infrared absorption properties of nanocrystalline cubic SiC films. *Jpn. J. Appl. Phys.* **37**, 5485 (1998).
17. H. Kamiya, M. Mitsui, H. Takano, and S. Miyazawa: Influence of particle diameter on surface silanol structure, hydration forces, and aggregation behavior of alkoxide-derived silica particles. *J. Am. Ceram. Soc.* **83**, 287 (2000).
18. T. Merlemejean, E. Abdelmounim, and P. Quintard: Oxide layer on silicon-carbide powder: A FT-IR investigation. *J. Mol. Struct.* **349**, 105 (1995).
19. G.L. Harris: *Properties of Silicon Carbide (EMIS Datareviews Series No. 13)*, IEE, INSPEC, London, UK, 1995).
20. L.E. Nielsen and R.F. Landel: *Mechanical Properties of Polymers and Composites* (Marcel Dekker, New York, 1994).
21. R.P. Singh, M. Zhang, and D. Chan: Toughening of a brittle thermosetting polymer: Effects of reinforcement particle size and volume fraction. *J. Mater. Sci.* **37**, 781 (2002).
22. S.L. Gao and E. Mader: Characterisation of interphase nanoscale property variations in glass fibre reinforced polypropylene and epoxy resin composites. Compos. Part A: *Appl. Sci. Manuf.* **33**, 559 (2002).
23. S.L. Gao, E. Mader, and S.F. Zhandarov: Carbon fibers and composites with epoxy resins: Topography, fractography and interphases. *Carbon* **42**, 515 (2004).
24. B. Mader, S.L. Gao, and R. Plonka: Enhancing the properties of composites by controlling their interphase parameters. *Adv. Eng. Mater.* **6**, 147 (2004).
25. Z.H. Guo, T. Pereira, O. Choi, Y. Wang, and H.T. Hahn: Surface functionalized alumina nanoparticle filled polymeric nanocomposites with enhanced mechanical properties. *J. Mater. Chem.* **16**, 2800 (2006).
26. X.P. Zhang, B.Q. Sun, R.H. Friend, H.C. Guo, D. Nau, and H. Giessen: Metallic photonic crystals based on solution-processible gold nanoparticles. *Nano Lett.* **6**, 651 (2006).