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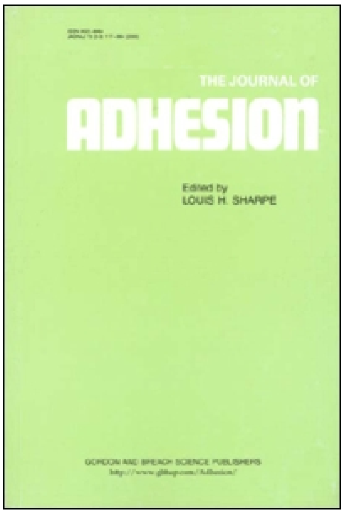

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Improved Matrix-Filler Adhesion

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Improved Matrix-Filler Adhesion

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Enhanced matrix-filler adhesion is realized after filler treatment with a surface treatment process. The hydrosol/coupling agent treatment was applied to a wide range of inorganic and organic fillers, and adhesion to a variety of matrix resins was improved. Scanning Electron Microscopy (SEM) was used to determine the locus of failure in the filled systems. The locus of failure shows the relative degree of adhesion between the filler and the polymer matrix. Significant improvement in adhesion in humid environments is also observed.

KEYWORDS: Adhesion, Composite materials, Filler-matrix adhesion, SNS treatment, Treatment of fillers, Wet stress exposure.

INTRODUCTION

Surface treatment of filler particles before incorporation into a polymer matrix results in improved filler-matrix adhesion and in improved physical properties of the composite material. Silane coupling agents have been studied extensively, and their ability to improve composite properties is well known.[1–4] Improved composite properties have been reported with the use of titanate coupling agents.[5] Other methods of surface modification of fillers include plasma discharge,[6] chemical reaction,[7] and grafting of polymer onto the filler particle surface.[8]

A treatment has been developed (SNS Process) that imparts improved matrix-filler adhesion, not only under ambient conditions, but also under conditions of high humidity and elevated temperature. The process involves treatment of the filler particle with a wetting metal oxide hydrosol, followed by treatment with an organic coupling agent. An improvement in properties is seen in numerous matrix-filler combinations, compared to untreated fillers and fillers treated by commercial processes.

The fillers used in this work are sodium borosilicate glass beads, alumina powder, quartz powder, copper powder, barium titanate powder, hollow spheres (sodium borosilicate, ceramic, and silica), and Kevlar® fiber. The resins used include various epoxies (rubber-modified and unmodified), silicones, polystyrene, polyimide, and polyetherimide.

MATERIALS AND METHODS

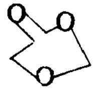
SNS treatment

The SNS Treatment Process involves a wetting hydrosol and a coupling agent.[9] For example, a wetting tin hydrosol[10] that deposits a mixed valence hydrous tin oxide can be used with an amino-functional silane coupling agent. The wetting hydrosol is prepared[10] by first dissolving 1.0 wt% stannic chloride monohydrate in water. Stannous chloride was then added to the resulting solution in two steps: 1) 2.5 wt%, then 2) 1.0 wt%. The solution is prepared at ambient temperature with stirring to aid dissolution before proceeding to the next step. The silane coupling agent is applied by immersing the sample in a 1 wt% aqueous solution of the amino-functional trimethoxysilane.

Only aqueous processing is required; no organic solvents are used, and all aspects of the treatment are nonpolluting as well. Treated surfaces are thermally stable (to 150°C) and resist corrosion.

Coupling agent preparation

The coupling agent solutions are prepared immediately before treatment of the filler, and are 1 wt% coupling agent in deionized water for the silanes. The silane coupling agents (Petrarch Systems, Inc.) studied are *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AEPS) and *p*-aminophenyltrimethoxysilane (APS). The titanate coupling agent solutions were also prepared immediately before filler treatment; the solutions are 1 wt% titanate in a suitable solvent (2-propanol or toluene) as suggested by Kenrich Petrochemicals, Inc., the supplier. The titanates studied are 2-propyltriisostearoyltitanate (KR TTS), suggested as an adhesion promoter for thermoplastics, 2-propyltri(*N*-2-ethylamino-2-ethylamino)titanate (KR 44), also suggested to promote adhesion, es-



AEPS	$NH_2(CH_2)_2NH(CH_2)_3Si(OCH_3)_3$
APS	p-$NH_2C_6H_4Si(OCH_3)_3$
KR 38S	$(CH_3)_2CHO$-$Ti(OP(O)(OH)OP(O)(OC_8H_{17})_2)_3$
KR 138S	$Ti(OP(O)(OH)OP(O)(OC_8H_{17})_2)_2$
KR 44	$(CH_3)_2CHO$-$Ti(O(CH_2)_2NH(CH_2)_2NH_2)_3$
KR TTS	$(CH_3)_2CHO$-$Ti(OOCC_{17}H_{35})_3$

FIGURE 1 Silane and titanate coupling agents.

pecially with epoxies, 2-propyltri(dioctylpyrophosphato)titanate (KR 38S), suggested as an adhesion promoter, and titanium di(dioctylpyrophosphate)oxyacetate (KR 138S), a cheating titanate. The structures of the coupling agents used for comparison are given in Figure 1.

Successful filler treatment was verified by X-ray Photoelectron Spectroscopy (XPS). The spectra were obtained on fillers before and after treatment. Routine samples were run on the DuPont 650B, and high resolution analyses were performed on a Perkin-Elmer Model 549.

Resins

A variety of resins, both thermoplastic and thermosetting, were used. The epoxy resin systems are: Epon® 828 (a diglycidyl ether of bisphenol A, Shell)-diethylenetriamine-benzyldimethylamine (828-DTA-BDMA); DEN® 438 (an epoxy novolac, Dow)-bisphenol A-BDMA (438-BPA-BDMA); Epon® 828-nadic methyl anhydride-BDMA (828-NMA-BDMA); and Hycar® CTBN1300X8 (a carboxy-terminated butadiene-acrylonitrile copolymer, B.F. Goodrich)-828-piperidine (X8-828-PIP). The other resins are polystyrene (MW ~ 2 × 10^6), polyetherimide (PEI, Ultem,® General Electric), Dow Corning 648 semiconductor junction coating (DC 648, a methylphenyl polysiloxane), and thermoplastic polymide (LARC-TPI), a NASA-developed material marketed by Gulf.

The formulation and cure schedule for the 828-DTA-BDMA system are 100 parts by weight (pbw) 828, 5 pbw DTA, and 0.5 pbw BDMA; the epoxy and DTA are combined, the filler is added and mixed, then BDMA is added with thorough mixing, and the system is cured at 170°C for 1 h. The formulation and schedule for the 828-NMA-BDMA system are 15 pbw 828, 13.5 pbw NMA, and 0.14 pbw BDMA; 828, NMA, and the filler are combined and mixed, then BDMA is added with mixing, and the sample cured at 120°C for 1 h, then at 200°C for 4 h. The formulation and schedule for the 438-BPA-BDMA system are 59 pbw 438, 37 pbw BPA, and 0.5 pbw BDMA; 438 and BPA are combined and heated until mixed at 110°C, the filler is added and stirred 30 min, then the BDMA is added with mixing, a sample cast, and cured at 170°C for 2 h. The X8-828-PIP system has been described by Bascom.[11] The formulation and schedule are 81 pbw, 15 pbw X8, and 4 pbw piperidine; X8, 828, PIP, and the filler are combined and mixed thoroughly for 30 min, then a sample is cured at 120°C for 16 h.

Two of the other resins are supplied as solutions, DC 648 in xylene. and LARC-TPI in diethylene glycol dimethyl ether (diglyme). Solutions were made of the remaining resins, both thermoplastics, polystyrene in toluene and PEI in chloroform. LARC-TPI, PEI and polystyrene are thermoplastics, and the filled systems are processed as described below. The DC 648 is a reactive system (condensation to make a polysiloxane); the filled system is cured in a four step process: ambient temperature for 1 h after preparation of the sample, 120°C for 2 h, 140° for 2 h, and 230° for 16 h.

Dispersion of filler into the resin

The filler is dispersed into the matrix by one of two methods, depending on whether the matrix is a thermoplastic or a thermoset. With thermoplastic resins, a viscous solution of the resin in a suitable solvent is prepared. A suitable solvent possesses appropriate acid-base properties that allow the acid-base interactions between the resin and the filler to predominate over interactions between the solvent and the filler (*vide infra*). The filler is added to the viscous solution, the mixture stirred 30 min at ambient temperature, and a sample is cast, or a film is prepared by draw down techniques, with a usual film thickness of 25–75 μm. Evaporation and heating are used to remove the solvent, with a final heating step of 16 h at 20° above the boiling point of the solvent.

With thermosetting resins, the filler is added to the liquid resin (heated if required to liquify) and the mixture stirred 30 min. The curing agent is added, mixed thoroughly, a sample is cast, and the system cured.

Fracture and failure analysis

Matrix-filler adhesion is evaluated under two conditions—dry (exposure to ambient conditions after sample preparation, then fractured under tension), and wet (after sample preparation, immersion in water at 70°C for 24 h, then immediately fractured under tension while still wet). The locus of failure in the fractured specimens was determined by Scanning Electron Microscopy. The SEM photomicrographs were obtained on an AMR Model 1000 scanning Electron Microscope, equipped with a Tracor Northern TN 2000 energy dispersive x-ray analysis system and a Kevex-ray Model 3205-1000V detector. A series of photomicrographs were taken of each specimen to ensure that the failure mechanism reported was consistent throughout the sample. The failure is categorized into three regimes: cohesive within the resin matrix (C), interfacial at the resin-filler interface (I), and an intermediate regime where both cohesive and interfacial failure mechanisms are observed, but < 50% interfacial (C/I).

RESULTS AND DISCUSSION

Effect of treatment, matrix, and filler

Sodium borosilicate glass beads, obtained from Ace Scientific Supply Co. (nominal diameter of 29 μm) were used as the filler in most of the

TABLE I
Effect of treatment on locus of failure sodium borosilicate glass beads in 438-BPA-BDMA

	Locus of failure	
Treatment	Dry	Wet
Untreated	C	I
APS	C	C
AEPS	C	C
SNS	C	C
KR 38S	C	C
KR 138S	C	I
KR 44	C	I
KR TTS	C	I

experiments. All fillers were used as received, stored under ambient conditions, and no attempt at cleaning or drying the surface was made. The beads were treated as discussed above with the SNS process, according to supplier's recommendations (titanates), or accepted literature practice (silanes).[1] The effect of a variety of surface treatments on locus of failure in the epoxy system 438-BPA-BDMA is seen in the data in Table I.

For fracture under ambient conditions (dry), all treatments, and no treatment, resulted in cohesive failure in the epoxy matrix. On stressing the samples (wet), the difference in the effectiveness of the treatments becomes apparent. The two silane coupling agents, the SNS process, and the titanate treatment KR 38S result in cohesive failure in the matrix, where the other treatments now yield interfacial failure. The silane treatments possess amine groups that are capable of reacting with the epoxy matrix during cure—resulting in a good filler-matrix bond. The corresponding titanate (KR 44) also has amine groups, but no improvement in adhesion is observed. The titanate that did give improvement is reported to improve adhesion by reaction with the acidic protons on both the filler and the resin;[12] and since hydroxyl groups are present on the surface of the glass and in the curing epoxy, this is a plausible explanation. Treatment with SNS yields similar results to the silanes and KR 38S titanate.

Table II contains data from which one can compare the effect of AEPS and SNS treatments of glass beads in five different resin systems.

TABLE II
Effect of resin and treatment on locus of failure for sodium borosilicate glass beads

Resin	Treatment	Locus of failure Dry	Locus of failure Wet
438-BPA-BDMA	Untreated	C	I
438-BPA-BDMA	AEPS	C	C
438-BPA-BDMA	SNS	C	C
Polystyrene	Untreated	I	
Polystyrene	AEPS	I	
Polystyrene	SNS	C	
PEI	Untreated	I	
PEI	AEPS	I	
PEI	SNS	C	
DC 648	Untreated	I	I
DC 648	AEPS	C/I	I
DC 648	SNS	C	C
LARC-TPI	Untreated	I	
LARC-TPI	AEPS	C	
LARC-TPI	SNS	C	

Treatment with SNS always results in improved filler-matrix adhesion, even in matrices where chemical reaction between the treated filler and the matrix is impossible (polystyrene, polyetherimide (PEI), and LARC-TPI). An improvement over AEPS treatment is seen in three matrices, polystyrene, PEI, and the silicone DC 648. Figure 2 shows SEM photomicrographs of untreated and SNS-treated glass beads in 438-BPA-BDMA exposed to both dry and wet conditions. SEM photomicrographs of untreated and SNS-treated glass beads in DC 648 exposed to both dry and wet conditions are shown in Figure 3.

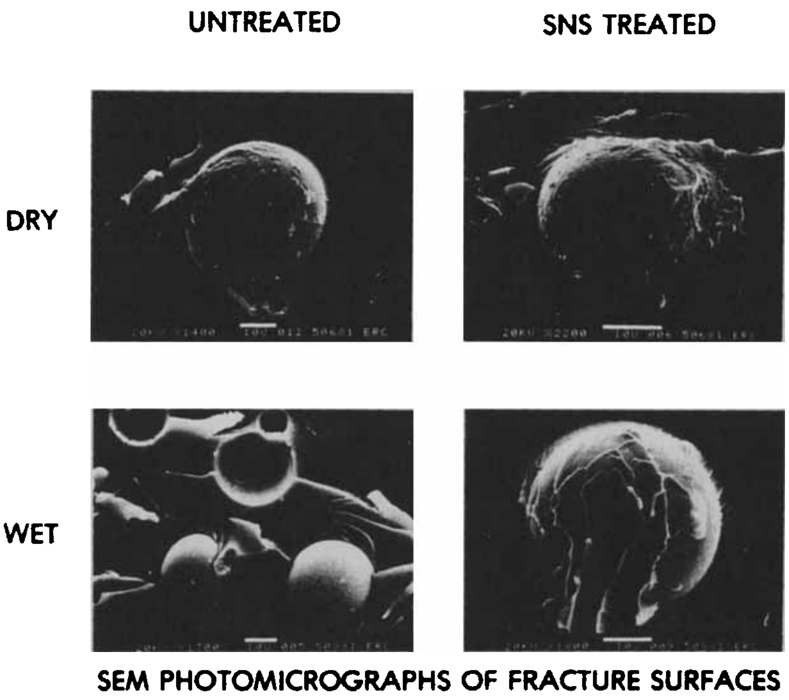
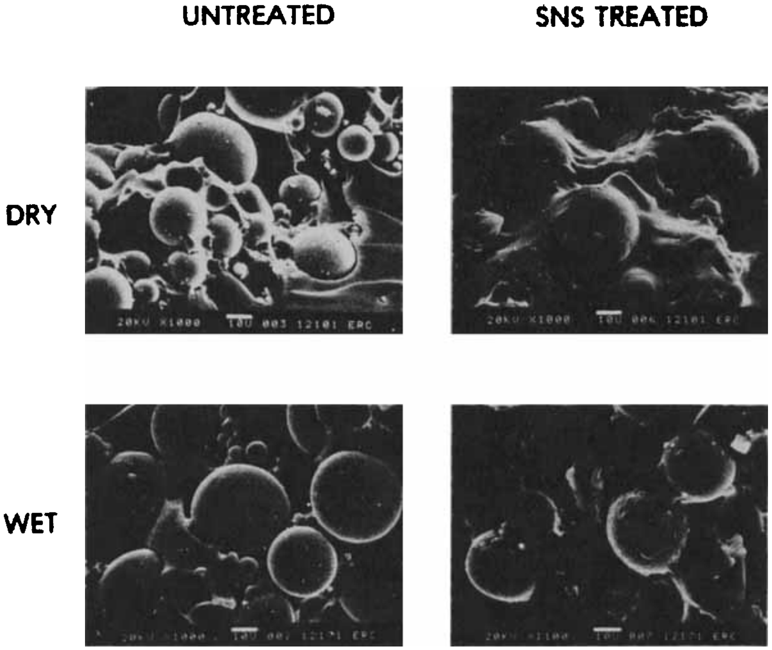


FIGURE 2 Photomicrographs of glass beads in 438-BPA-BDMA.

A comparison of the effect of treatment (untreated, AEPS, SNS) on locus of failure in 438-BPA-BDMA for a variety of fillers is given in Table III.



SEM PHOTOMICROGRAPHS OF FRACTURE SURFACES

FIGURE 3 Photomicrographs of glass beads in DC 648.

TABLE III
Effect of treatment on locus of failure for various fillers in 438-BPA-BDMA

	Locus of failure					
	Untreated		AEPS		SNS	
Filler	Dry	Wet	Dry	Wet	Dry	Wet
Glass beads	C	I	C	C	C	C
Ceramic ECS$	I	I			C	C/I
Silica ECS$	C	C/I	C	C/I	C	C
Borosilicate ECS$	C/I	I	C/I	I	C	C
Alumina powder	C	C			C	C
Quartz powder	C/I	C/I			C	C
Barium titanate	C	C			C	C
Kevlar® fiber	C	I	C/I	C/I	C	C

*ECS-Eccospheres® (Emerson and Cuming)-hollow microspheres.

The data show that SNS treatment yields improved adhesion compared to no treatment in all but two systems, and in those systems, the locus of failure is cohesive in the matrix under both conditions, SNS-treated and untreated. Comparing the data for AEPS and SNS treatments shows improved adhesion in the SNS-treated fillers in three instances, Silica Eccospheres®, Borosilicate Eccospheres®, and Kevlar® Fiber. Comparable adhesion is observed in the treated glass bead systems.

Effect of solvent

Fowkes and Mostafa[13] and Manson[14] have described the importance of acid-base interactions on the properties of filled polymer systems. Maximum adsorption of a basic polymer onto an acidic filler particle is obtained when the solvent is less acidic than the surface of the filler; if it is more acidic, then adsorption is prevented. The effect of solvent on the locus of failure in the polystyrene—SNS treated glass bead system is evident from the data in Table IV.

The SNS-treated surface is mildly acidic.[15] Maximum adsorption of polystyrene onto the treated filler surface is obtained when the polymer/solvent system possesses appropriate acid-base characteristics. The acid-base characteristics of polystyrene and the solvents listed in Table IV have been determined.[16] Thus, the acidic methylene chloride will interact with the basic polystyrene, inhibiting adsorption. The strongly basic DMF preferentially interacts with the acidic filler surface, preventing adsorption. Only when the acid-base characteristics are balanced, weakly basic polymer and solvent with an acidic surface, does adsorption occur to any extent.

TABLE IV
Effect of solvent on dry locus of failure SNS treated glass beads in polystyrene

Solvent	Locus of failure	Acid-base characteristics
Toluene	C	Weak base
Methylene chloride	C/I	Acid
N,*N*-Dimethylformamide	I	Strong base
Polystyrene		Weak base

Treatment of copper powder

Copper powder is successfully treated by the SNS process, as determined by XPS analysis. Interfacial failure is observed with untreated copper powder in 828-NMA-BDMA. The locus of failure is shifted to cohesive in the epoxy matrix when the filler surface is treated with the SNS process.

Treatment of Kevlar®

Kevlar® filled composites are an area of intense interest, for electronic as well as structural composite applications.[7] It has been reported that sized fiber yields better adhesion than unsized fiber.[17] Successful treatment of unsized Kevlar® fiber is achieved with the SNS process. The fiber was dispersed in several resin systems, the locus of failure determined, and compared to the untreated and AEPS treated systems. The results are listed in Table V.

TABLE V
Effect of treatment on locus of failure Kevlar® filled systems

	Locus of failure					
	Untreated		AEPS		SNS	
Resin	Dry	Wet	Dry	Wet	Dry	Wet
828-DTA-BDMA	C	I	C	C	C	C
828-NMA-BDMA	C/I	C/I			C	C
438-BPA-BDMA	C	I	C/I	C/I	C	C
Polystyrene	C/I	C/I	C/I	C/I	C	C
DC 648	C	I	C	C	C	C

SNS treatment results in improved adhesion in three epoxy systems, polystyrene, and silicone, as compared to no surface treatment. Improvement over AEPS treatment is observed in polystyrene and one epoxy system; comparable results are obtained in the silicone system and another epoxy system. Thus, this process may have a place in the manufacture of Kevlar® composites.

Elastomer-modified epoxy matrices

Filled elastomer-modified epoxy systems were also studied. The effect of fracture temperature, elastomer-modification, and elastomer-epoxy prereaction were investigated. The results are presented in Table VI for both SNS-treated and untreated glass beads.

In the modified, but not prereacted system,[11] the effect of fracture temperature and treatment is clear. Even with SNS treatment, fracture at room temperature yields interfacial failure, indicating the strength of the matrix, relative to that of the interface. On cooling to liquid nitrogen temperature, the entire matrix becomes glassy (below the Tg of the rubber) and SNS treatment results in cohesive matrix failure. This analysis is supported by the results of the unmodified system, which exhibits cohesive failure with SNS-treated beads (both dry and wet), and some cohesive failure (C/I) with untreated beads in the dry condition. An explanation may be found by examining the results with a prereacted system. The epoxy and elastomer were prereacted by triphenylphosphine catalysis before incorporation of the filler and the piperidine. No change from the nonprereacted system is seen with untreated filler; however, SNS treatment results in excellent filler-matrix adhesion under both dry and wet conditions, even with room temperature fracture. One explanation for this result is migration of the elastomer to the filler surface before reaction in the nonprereacted system, thereby reducing the interaction between the SNS-treated surface and the matrix. In the prereacted system, such migration is unlikely; thus the full benefit of SNS treatment is realized.

TABLE VI
Glass beads in elastomer-modified systems effect of fracture temperature and prereaction

		Locus of failure			
		Untreated		SNS	
Resin	Fracture temp.	Dry	Wet	Dry	Wet
	−196°C	I	I	C	C
828-X8-PIP	23°C	I		I	
828-PIP	23°C	C/I	I	C	C
Prereacted (828-X8)-PIP	23°C	I	I	C	C

Mechanical and electrical properties

An improvement in mechanical properties is realized with SNS treatment of silica used in filled silicone composites.[18] A two-fold improvement in impact strength is seen, compared to both untreated silica and silane-coupling-agent-treated silica. Samples were prepared as 75 μm films and subjected to impact with increasing force until failure was observed. The results are listed in Table VII.

An improvement in cohesive strength in silica-filled composites as determined by a peel test is also observed with SNS treatment. A 90° peel test on metallized composite samples was used to determine the cohesive strength of the composite; failure is found to be cohesive in the composite, never interfacial. The results are presented in Table VIII.

TABLE VII
Effect of SNS treatment on impact strength silica filled silicones

Treatment	Impact strength (N-m)
Untreated	0.23–0.46
Silane	0.23–0.46
SNS	0.68–0.91

TABLE VIII
Effect of treatment on cohesive strength silica filled silicone composites

Treatment	Cohesive strength (N m^{-1})
Untreated	28
SNS	70–89

The effect of SNS treatment on other mechanical properties is under investigation. The electrical properties of SNS-treated, silica-filled composites are comparable to those of untreated composites.[18]

SUMMARY

Treatment of filler particles with the SNS process imparts enhanced filler-matrix adhesion in a variety of filler-matrix combinations, compared to no surface treatment, silane treatment, or titanate treatment. The enhancement is most pronounced under wet stress conditions. The combination of a wetting tin hydrosol and an organic coupling agent shifts the locus of failure from interfacial to cohesive in the polymer matrix. Enhanced adhesion is observed even with thermoplastic matrices which are incapable of covalently bonding to the filler surface. The interactions between the filler surface, the deposited hydrosol, and the coupling agent are critical for enhanced adhesion. Not only is matrix-filler adhesion improved, but composite material properties are improved as well with SNS treatment of the filler. Treatment of fillers with the SNS process always results in adhesion at least as good as that found with either silane or titanate treatment, and improved adhesion compared to silane treatment (AEPS) is found in several systems—glass beads in DC 648, glass beads in polystyrene, and hollow silica spheres in 438-BPA-BDMA. Improved adhesion compared to amino-titanate treatment is observed with glass beads in 438-BPA-BDMA.

A variety of fillers are successfully treated with the SNS process, and potential applications include reinforced composites, filled plastics and thermosets, metal-filled polymers and adhesives, molding and encapsulating compounds, and systems where polymer-inorganic (or organic) interfacial adhesion is important.

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