Synthesis of Benzoxazine Functional Silane and Adhesion Properties of Glass-Fiber-Reinforced Polybenzoxazine Composites

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ABSTRACT: A silane coupling agent with a benzoxazine functional group has been synthesized. A series of nonpolar solvents is found to favor benzoxazine monomer formation. Employing these nonpolar solvents, a high-purity benzoxazine functional silane coupling agent is obtained. The effectiveness of this silane coupling agent is evaluated by measuring the interlaminar short-beam shear strength of silane treated glass-fiber-reinforced polybenzoxazine composites. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2559–2567, 1998

Key words: benzoxazine; coupling agent; glass-fiber composite; heterogeneous synthesis; shear strength; phenolic

INTRODUCTION

Thermoset polymers such as phenolic resins are widely used in the form of composites. Among many fillers and fibers, glass fiber is one of the most frequently used reinforcement. The adhesion strength of the matrix to the fiber strongly affects the mechanical and physical properties of the composite. Consequently, it is a common practice to apply a silane coupling agent to silaceous fibers or fillers to enhance the adhesion at the interface. Various silane coupling agents are commercially available. For instance, amino-functional silanes are often used for phenolic and epoxy resins. The roles of silane coupling agents in promoting the adhesion between glass fiber and polymeric resin have been studied extensively.[1,2] Several factors contribute to the adhesion, such as chemical and physical compatibility, composite curing cycles, and the mismatch of the thermal expansion coefficient between the fiber and the matrix.

Polybenzoxazine is a novel class of phenolic resin. The chemistry of benzoxazine dates back to the early 1940s,[3] although it is only recently that the polymers with advantageous structural properties have been successfully synthesized.[4–6] The chemistry of benzoxazine synthesis offers a wide range of molecular design flexibility by using derivatives of phenol, primary amine, and aldehyde. Various combinations of amines and phenols have been used to synthesize benzoxazines. For example, bisphenol-A with aliphatic or cyclic amines has been used to synthesize difunctional benzoxazines. Halogenated benzoxazines have also been synthesized.[7] The objective of this work is to synthesize a silane coupling agent that is functionally compatible with benzoxazine resins.

A silane with a benzoxazine functional group may be synthesized employing the method of benzoxazine synthesis. There are 2 possible synthetic routes. The first entails synthesizing a benzoxazine with an allyl group. This can be done by using an allyl-terminated phenol or amine. Allylphenol and *tert*-butyl amine were used in this study. *tert*-Butyl amine was chosen because it favors oxazine ring formation due to the presence
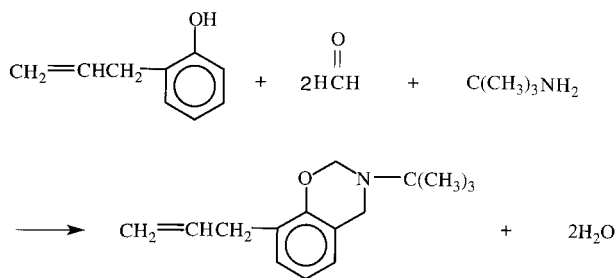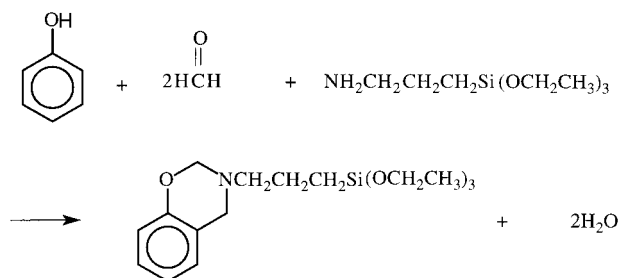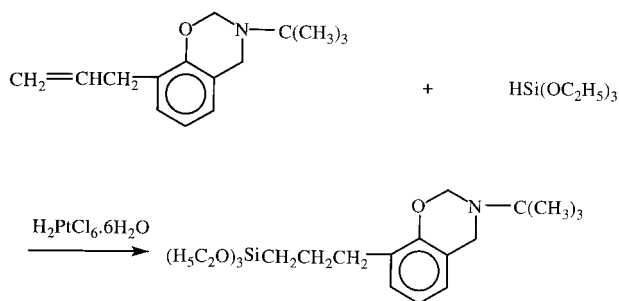
Scheme 1

Scheme 3

of inductive effects.[8] This synthesis procedure is shown in Scheme 1. The allyl group can then be used to couple with an alkoxy silane through hydrosilylation, as shown in Scheme 2. Hydrosilylation of an allyl group is well documented.[2]

The second method is the direct synthesis of the benzoxazine functional silane. This can be done by using an amino-functional silane as the primary amine for benzoxazine synthesis. This synthesis is shown in Scheme 3. However, one potential problem is that the water molecules, which are produced during the benzoxazine synthesis, can hydrolyze the alkoxy portion of the amino-silane, since it is readily hydrolyzed by water.[2] Once the alkoxy group is hydrolyzed, the stoichiometry is disturbed, and gelation of the reaction mixture may occur as silane oligomers are formed. If the water molecules can be separated from the reacting mixture upon formation, the hydrolysis reaction may be minimized.

The course of a synthesis is often governed by the choice of solvent. Solvent may stabilize or destabilize certain species in the reacting pool, thus directly affecting the course of reaction. Ning and Ishida[4] have synthesized difunctional benzoxazines in solvents of varying polarity. They reported that the less polar solvents gave a higher yield of benzoxazine monomer; namely, 1,4-dioxane gave a higher yield of monomer than tetrahydrofuran (THF) or methanol. The effect of solvents was also studied by Liu in the synthesis of fluorinated

Scheme 2

benzoxazine.[7] They concluded that it was the dielectric constant, rather than the polarity, that governed the yield of benzoxazine. They also concluded that 1,4-dioxane gave the highest yield of benzoxazine monomer. In an attempt to obtain benzoxazine with higher yield, a new solvent system is employed in this study.

EXPERIMENTAL

Synthesis of 3-*tert*-Butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine

Allyl-phenol, *tert*-butyl amine, and formaldehyde were purchased from Aldrich (Milwaukee, WI) and used as received. All other chemicals were purchased from Fisher (Pittsburgh, PA). The ratio of the allyl-phenol-to-formaldehyde-to-amine was 1 : 2 : 1. For synthesis in 1,4-dioxane, a portion of 0.1 mol of formaldehyde in 4 mL of solvent was cooled to below 10°C in a three-neck flask, at which point 0.05 mol of *tert*-butyl amine in 2 mL of solvent was added dropwise into the cooled formaldehyde with continuous stirring. The mixture was allowed to react for 10 min before the solution of 0.05 mol of allylphenol in 4 mL of solvent was added. The mixture was then warmed up to room temperature, (21 ± 1°C) and allowed to react for 4 h. The solvent was removed by vacuum distillation at room temperature in order to avoid unnecessary heating of the product.

For synthesis in nonpolar solvents, paraformaldehyde was used rather than formaldehyde. A mixture of amine and paraformaldehyde was stirred for 10 min at 80°C, after which allylphenol was added. The resulting mixture was then stirred for another 4 h. The purification procedure, when necessary, was performed by washing the product in diethyl ether with 3*N* NaOH, followed by distilled water. Finally, the solvent was separated using a rotary evaporator.

Hydrosilylation of the Allyl Group of 3-*tert*-Butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine

In a 100-mL three-neck flask were added hexa-chloroplatinic acid (5×10^{-5} mol) in 3 drops of isopropanol. Next, 3-*tert*-butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine (0.1 mol) in 2 mL of carbon tetrachloride was added to the three-neck flask. The mixture was then refluxed at 75°C in a pre-heated oil bath. Excess triethoxysilane in carbon tetrachloride was added to the three-neck flask while stirring. The mixture was allowed to react overnight at 75°C. The solvent and unreacted trie-thoxysilane were separated by vacuum distilla-tion.

Synthesis of 3-(Triethoxysilyl-)*n*-propyl-3,4-dihydro-2H-1,3-benzoxazine

A 50-mL three-neck reaction flask was purged with argon gas for several minutes. A portion of paraformaldehyde (0.6322 g, 0.02 mol) in 3 mL of chloroform was measured into the 50-mL three-neck flask, with continuous stirring. Next, γ-aminopropyltriethoxysilane (2.2137 g, 0.01 mol) in 2 mL of chloroform was added to the paraform-aldehyde solution, which was heated to 85°C in a preheated oil bath. The mixture of paraformalde-hyde and γ-aminotriethoxysilane was allowed to react for 10 min. Next, phenol (0.9411 g, 0.01 mol) in 4 mL of chloroform was added into the reaction flask and allowed to react for 3 h. The product was vacuum-distilled to eliminate the solvent and unreacted starting materials.

Fourier transform infrared (FTIR) spectra were taken on a Bomem Michelson MB FTIR spectrometer. A sample of 3-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine was cast from acetone solu-tion on a KBr plate, while a thin film of 3-(tri-ethoxysilyl-)*n*-propyl-3,4-dihydro-2H-1,3-benzo-xazine was sandwiched between 2 KBr plates. A liquid-nitrogen-cooled mercury-cadmium-tellu-ride (MCT) detector with a specific detectivity, D^*, of 1×10^{10} cm Hz$^{1/2}$ W^{-1} was used. Size exclu-sion chromatography (SEC) was employed to de-termine the extent of reaction. A Waters 510 high-pressure liquid chromatography (HPLC) pump equipped with an U6K Universal injector was used. The detector was a Waters 440 ultraviolet (UV) detector fixed at a wavelength of 254 nm. The columns were packed with μ-Styragel™ (1000, 100, and 50 nm) and connected in series. Proton nuclear magnetic resonance (¹H-NMR) spectra were obtained from a Varian XL-200-H spectrometer at a proton frequency of 200 MHz

Table I   Molding Condition for Glass-Reinforced Polybenzoxazine Composites

Temperature (°C)	Applied Load (lb)	Duration (min)
80	—	15
100	2500	60
125	2500	60
175	5000	90
190	5000	90
200	7500	60

and operated at a fixed field of 4.2 T. Samples were dissolved in deuterated chloroform con-taining 0.05% of tetramethylsilane (TMS), in which TMS served as an internal standard.

Preparation of Glass-Fiber-Reinforced Composites

E-glass cloth was used as the reinforcement. All glass cloth was heat-treated in a furnace at 500°C for 24 h in order to eliminate any sizing materials. The glass fibers were treated with the following commonly used silane coupling agents: γ-metha-cryloxypropyltrimethoxysilane (γ-MPS), γ-amino-propyltrimethoxysilane (γ-APS), and *N*-vinyl-ben-zyl-*N*-2(trimethoxysilylpropylamino) ethyl, NH_4Cl (*N*-VBA). Silane solutions at a concentration of 0.1% by weight were prepared. γ-APS was hy-drolyzed in deionized and distilled water, while γ-MPS and *N*-VBA were hydrolyzed in a mixture of a 90 : 10 ratio of methanol and deionized–distilled water. Glass cloth of 70×100 mm was immersed in the hydrolyzed silane solution for 15 min and air-dried at room temperature overnight. Bisphenol-A and methylamine-based benzoxazine was used as the matrix. This resin was synthesized according to a previous article.[4] The composites were molded using a 30-ton Carver compression molder. The curing conditions are presented in Table I. The fiber volume content was determined by thermal diges-tion of the composites.

Glass-fiber-reinforced novolac was also pre-pared for comparison purpose. The novolac resin with catalyst was supplied by Rogers Corporation (Rogers, CT). The composites were cured in the compression molder using the curing conditions suggested by the manufacturer.

Interlaminar short-beam shear tests were con-ducted according to ASTM D2344-84, with sample dimensions of $21 \times 6 \times 3$ mm. The tests were performed at room temperature. Interlaminar

short-beam shear tests were also conducted for composites boiled in water for 12 h. The interlaminar short-beam shear tests were performed at BF
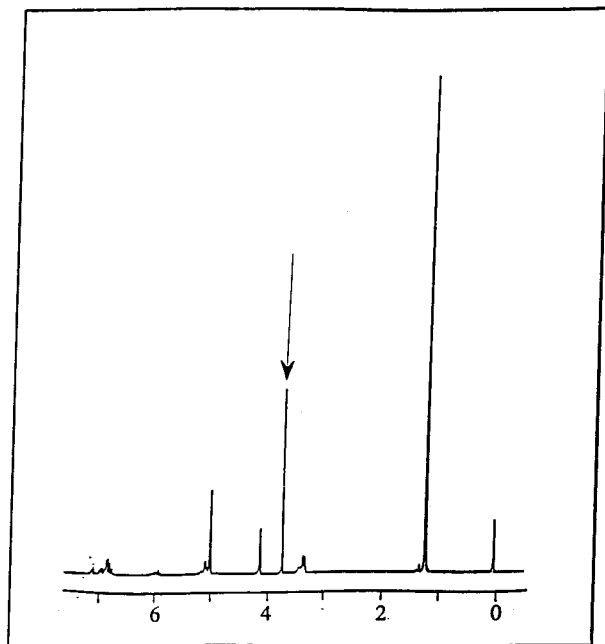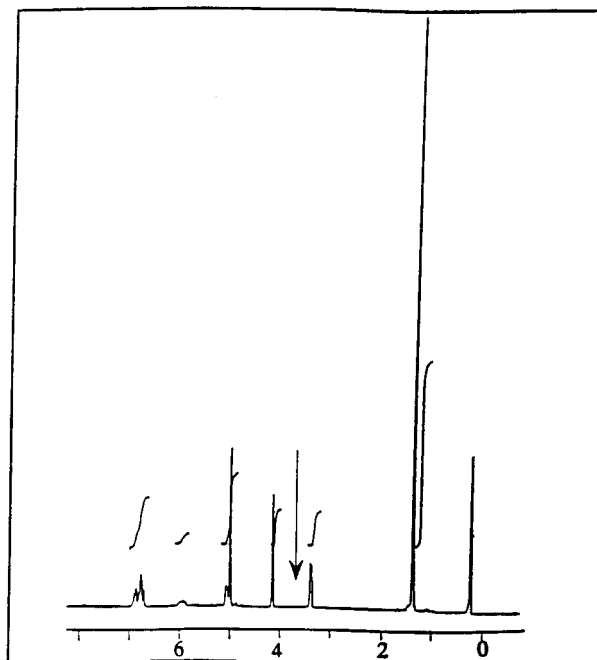

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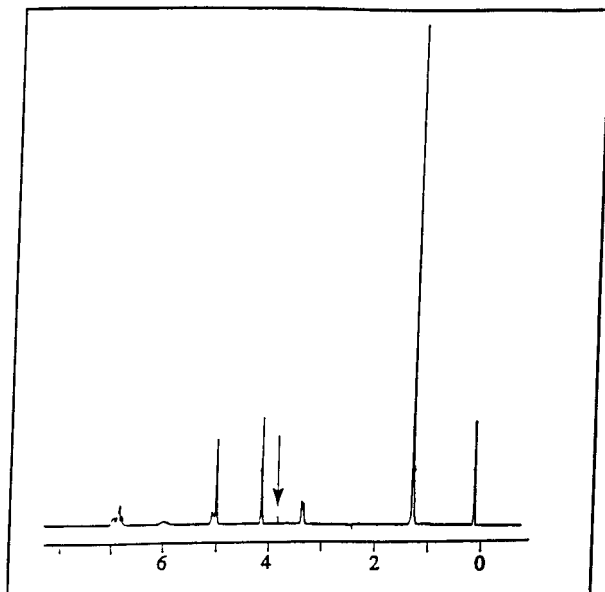
(b)

Figure 1   (a) ¹H-NMR spectrum of the crude reaction product from benzoxazine synthesis in 1,4-dioxane. The arrow indicates the peak due to methylene protons of Mannich base. (b) ¹H-NMR spectrum of the purified benzoxazine from synthesis in 1,4-dioxane. (c) ¹H-NMR spectrum of the purified benzoxazine after treatment in chloroform overnight.

(c)

Figure 1   (*Continued*)

Goodrich Co. All tests were carried out on an Instron Model 1125 universal testing apparatus, at a crosshead speed of 1.3 mm/min.

RESULTS AND DISCUSSION

### Synthesis of Benzoxazine-Functional Silane

Synthesis of 3-tert-Butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine

The as-synthesized product from 1,4-dioxane was a slightly yellow liquid at room temperature. The ¹H-NMR of the as-synthesized benzoxazine is shown in Figure 1(a). The methylene protons of the Mannich base were assigned according to a previous study.[4] The open benzoxazine ring protons give rise to a resonance at approximately 3.6 ppm, which is indicated by the arrow in Figure 1(a). This resonance may be shifted depending on the type of amine used. The concentration of dimers or oligomers is higher than that of the monomer. The ¹H-NMR spectrum of the purified product is shown in Figure 1(b). The intensity of the methylene protons at 3.6 ppm is significantly reduced, but the monomer content is only 88%. Further purification was not attempted due to the possibility of oxazine ring opening by the alkaline solution.

The purified benzoxazine was dissolved in chloroform and left to stand overnight. The ^{1}H-NMR of the chloroform-treated benzoxazine is shown in
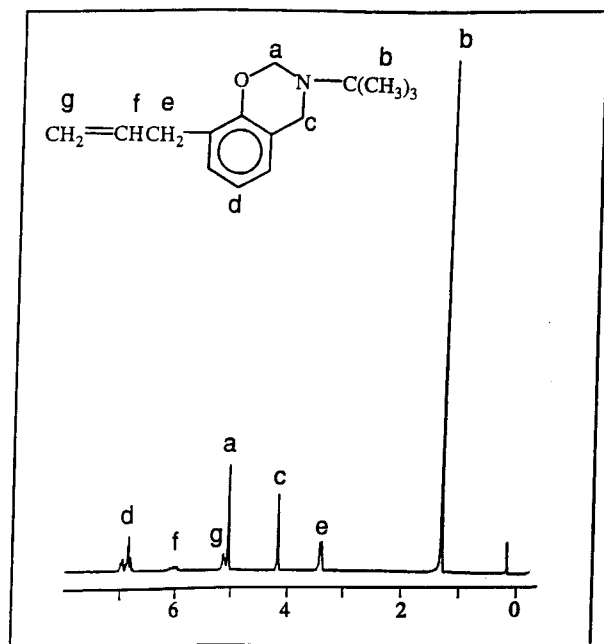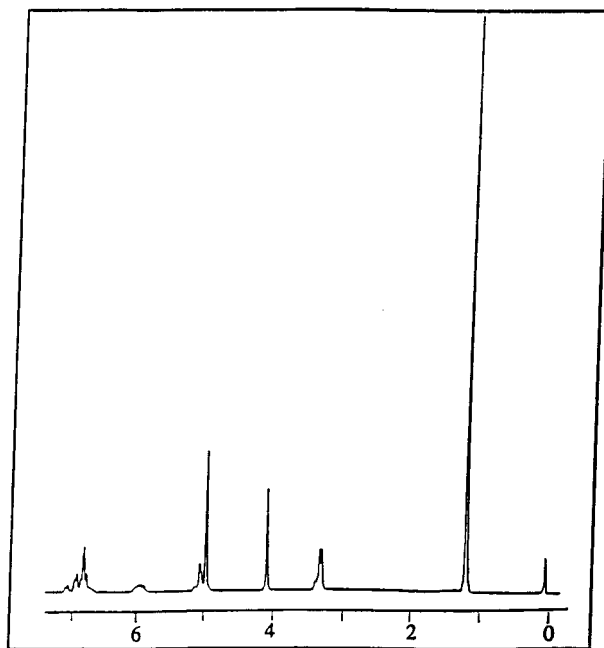

(a)
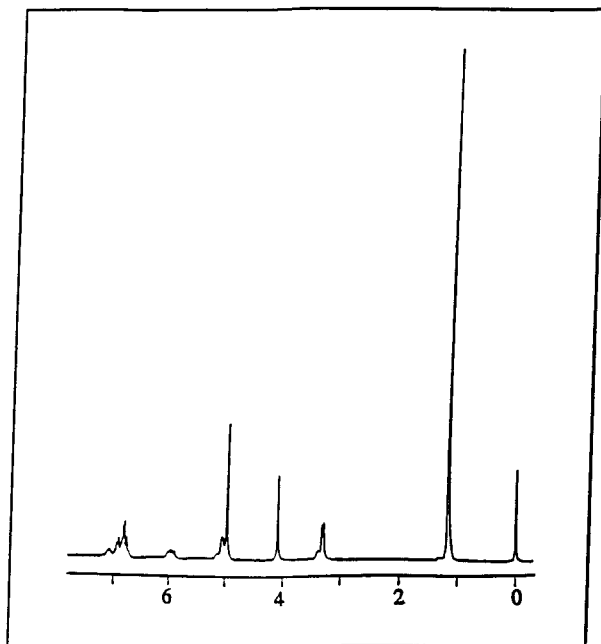
(b)

Figure 2   (a) ^{1}H-NMR spectrum of the crude reaction product from benzoxazine synthesis in carbon tetrachloride. (b) ^{1}H-NMR spectrum of the crude reaction product from benzoxazine synthesis in chloroform. (c) ^{1}H-NMR spectrum of the crude reaction product from benzoxazine synthesis in n-hexane.

(c)

Figure 2   (*Continued*)

Figure 1(c). It is apparent that the intensity of the peak at 3.6 ppm is further reduced. The monomer content was calculated to be 95%. This result implies that chloroform helps ring closure of the open Mannich base. In order to further verify and investigate the effects of the solvent on the ring closure of benzoxazine, the purified benzoxazine was dissolved in carbon tetrachloride overnight. Carbon tetrachloride is also a nonpolar solvent with dielectric constant of 2.238, while chloroform has a dielectric constant of 4.806. In the synthesis of fluorinated benzoxazines, Liu[7] reported that solvents with low dielectric constant favor ring closure. The result from ^{1}H-NMR (not shown here) of the carbon-tetrachloride-treated benzoxazine indicates a similar effect as that of the chloroform. Even though there are no set rules on how to select the best solvents, the dielectric constant and the solubility of solvents often dictate the course of a reaction by stabilizing certain species through solvation.[9] Therefore, the above results imply that chloroform and carbon tetrachloride are preferred solvents for benzoxazine stability.

As a result of the above, the synthesis of benzoxazine was repeated in carbon tetrachloride rather than with 1,4-dioxane as the solvent. Carbon tetrachloride was chosen as its dielectric constant (2.238) is almost the same as that of 1,4-dioxane (2.209). The ^{1}H-NMR of the as-synthe-

sized product is shown in Figure 2(a). The peak at 3.6 ppm is surprisingly difficult to detect within the noise level of the ^{1}H-NMR spectrum. Since carbon tetrachloride is immisible with water, the final product in the reaction flask showed the following 2 distinct phases: one of carbon tetrachloride and the other of water. The benzoxazine had limited solubility in water; therefore, the product was in the carbon tetrachloride phase. The experiment was repeated with chloroform and again the peak at 3.6 ppm is undetectable, as can be seen in Figure 2(b). From Liu's results, the yield of the fluorinated benzoxazine is 80% in 1,4-dioxane and 70% in diethyl ether. Diethyl ether has a dielectric constant of 4.2 (about twice as high as 1,4-dioxane). However, in the case of 3-*tert*-butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine, there was practically no difference in the yield of the benzoxazine synthesized in chloroform and carbon tetrachloride, even though the dielectric constant of carbon tetrachloride is about twice that of chloroform. A preliminary conclusion from these results is that when a nonpolar solvent was used in the synthesis, the dielectric constant effect becomes trivial. Conversely, if a polar solvent is used, the effect of dielectric constant on the benzoxazine yield is significant. Furthermore, in a nonpolar solvent, the water phase tends to be separated from the reaction phase, reducing the chances of ring opening and, subsequently, the formation of dimers or oligomers. According to the mechanism of the condensation reaction of methylolamine by phenol, a water molecule is produced as side product. Since water repels nonpolar solvents, the water molecule is pushed out of the reaction phase as it is formed, thereby driving the equilibrium towards ring formation.

Both of the previous solvents were halogenated. In order to verify the effect of a nonpolar solvent, the 3-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine was synthesized in n-hexane, a nonhalogenated, nonpolar solvent. The dielectric constant of n-hexane is 1.890 at room temperature. The ^{1}H-NMR of the as synthesized product is shown in Figure 2(c). The spectrum is practically identical to those synthesized in halogenated and nonpolar solvents. This approach has a potential in industrial applications as n-hexane is a non-toxic solvent.

Hydrosilylation of the Ally Group of the 3-tert-butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine

Hydrosilylation of the 3-*tert*-butyl-3,4-dihydro-2H-1,3-benzoxazine was found to be difficult be-
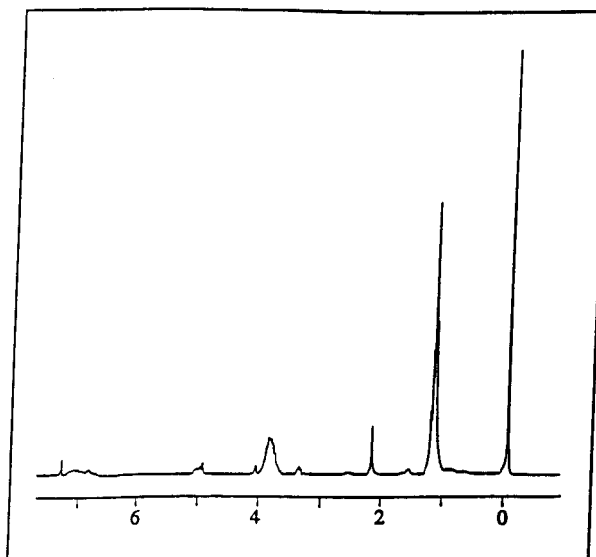
Figure 3 ^{1}H-NMR spectrum of the hydrosilylation products.

cause the hydrosilylation condition is believed to favor ring opening of the oxazine ring. Hydrosilylation of an allyl group is normally carried out in the presence of a catalyst, such as chloroplatinic acid in propanol, at 80°C and above. Thermal exposure of the benzoxazine in the presence of a polar solvent will open the oxazine ring. This is evident in the ^{1}H-NMR of the product of the hydrosilylation reaction shown in Figure 3. The two oxazine protons at 4.2 and 5.0 ppm are significantly reduced, while the peak at 3.6 ppm appears, indicating the presence of methylene protons from either open ring or dimers. There are also peaks corresponding to impurities in this ^{1}H-NMR spectrum. Therefore, an alternative synthesis route for a silane with a benzoxazine functional group is necessary.

### Direct Synthesis of 3-(Triethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-benzoxazine

As mentioned earlier, a problem which that be encountered using this approach is that water produced during the synthesis can hydrolyze the alkoxy portion of the silane. However, using the proposed approach (synthesis of benzoxazine in nonpolar solvent), the water molecules produced will be automatically separated from the product phase. Since the benzoxazine portion of the product is insoluble in water, the alkoxy groups of the silane will be protected.

The product from the direct synthesis of the 3-(triethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-
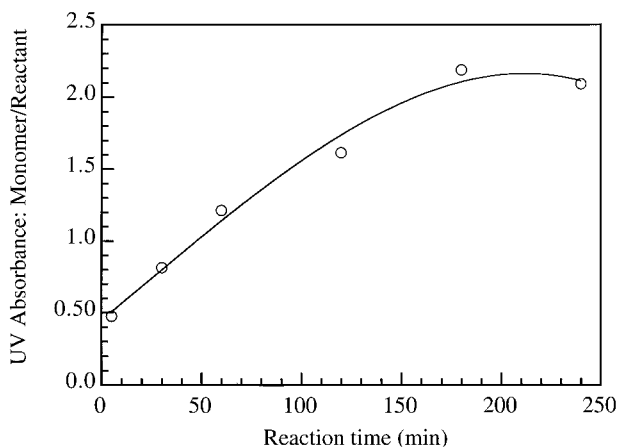
Figure 4 Ratio of product to reactants as a function of reaction time for the direct synthesis of benzoxazine silane in chloroform.

benzoxazine is a colorless liquid at room temperature. The ratio of the product to the reactants obtained from SEC analysis showed that the optimum reaction time was 3 h. At a reaction time beyond 4 h, a peak began appearing in the SEC, indicating the formation of dimers. Figure 4 shows the ratio of product to reactants as a function of reaction time. The ^{1}H-NMR of the as-synthesized product is shown in Figure 5. Peak assignment was done according to a previous study of benzoxazine[4] and with the help of the ^{1}H-NMR spectrum of γ-aminopropyltriethoxysilane. The ^{1}H-NMR spectrum of the as-synthesized product shows no trace of dimers or oligomers both from
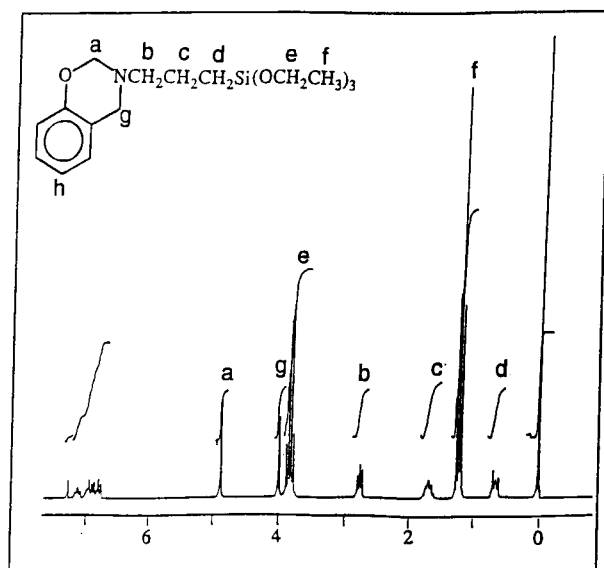

Figure 5 ^{1}H-NMR spectrum of the as-synthesized product from direct synthesis of benzoxazine silane.

(a)

(b)
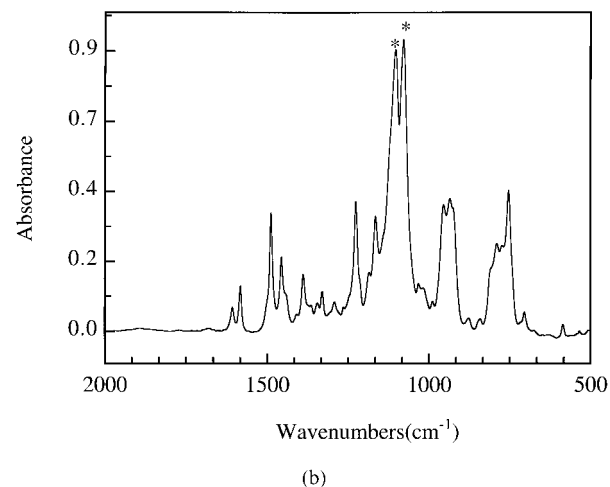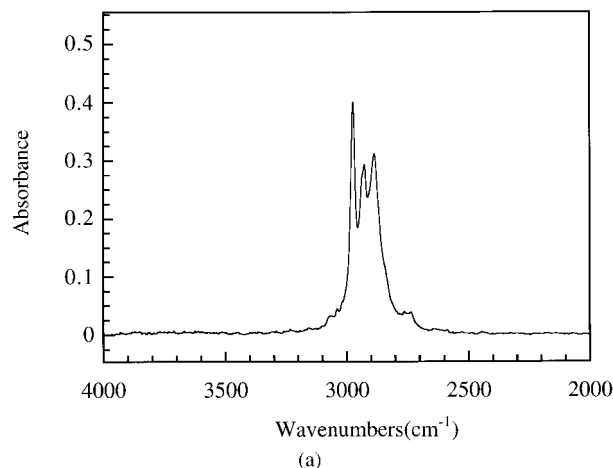
Figure 6 (a) FTIR spectrum of the as-synthesized benzoxazine silane. (b) FTIR spectrum of the as-synthesized benzoxazine silane.

either the benzoxazine or the silane groups. The integration correlated well with the theoretical number of the protons in the structure. The FTIR spectra of the as-synthesized product are shown in Figure 6. In Figure 6(a), there is neither a free hydroxyl group around 3600 cm^{-1}, nor a bonded hydroxyl group around 3400 cm^{-1} indicating that the alkoxy groups were not hydrolyzed during the synthesis. Also, it is concluded that there is no formation of dimers and oligomers from the benzoxazine group as such reactions lead to the formation of the phenolic OH group. The alkoxy groups have strong bands as a doublet at 1078 and 1104 cm^{-1}, as shown in Figure 6(b). The relative intensity of these bands with the aliphatic mode remained unchanged after the synthesis.

Silanes are beneficial only if they can be hydrolyzed. 3-(Triethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-benzoxazine was hydrolyzed in 40/60
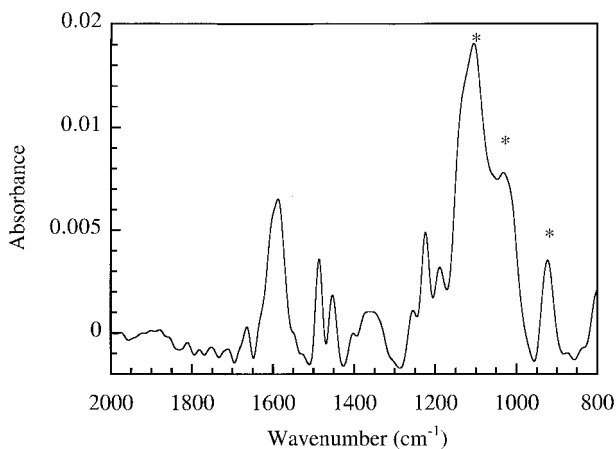
Figure 7 FTIR spectrum of the hydrolyzed benzoxazine silane.

w/w % of methanol–H_2O for 2 h. The FTIR spectrum of the hydrolyzate is shown in Figure 7. The region between the 1130 and 1000 cm^{-1} shows intense and broad bands, which are characteristic of siloxane. The siloxane can only be obtained if the alkoxy groups have been hydrolyzed. 3-(Triethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-benzoxazine will simply be referred to as benzoxazine silane in the following section.

Properties of Glass-Fiber-Reinforced Polybenzoxazine Composites

The color of the composites is rather interesting. Novolac–glass composites are opaque and dark brown, while polybenzoxazine–glass composites are a pale yellow–green and translucent. The degree of color and translucence are different for glass fibers with different treatments. This is an interesting observation because when reinforcements are incorporated into a polymeric matrix, the usual mismatch in refractive index results in opaque composites. The fact that the polybenzoxazine–glass composite is translucent means that the polybenzoxazine may have a refractive index close to that of the glass fiber. This could potentially lead to a new application for composite materials. With the rich molecular design flexibility of the benzoxazine-based phenolic resin, the refractive index of the resin can be designed to match that of the fiber. This is important from an aesthetic point of view since surface roughness and optical flatness are often the subjects of industrial interest. The fiber content obtained from the burnout tests indicates that all composites contain roughly 60% fiber by volume.

Interlaminar Short-Beam Shear Tests

Interlaminar short-beam shear (ILSS) is one of the most widely used characterization techniques to assess the overall adhesion properties of fiber-reinforced composites. One shortcoming of ILSS is that shear modulus cannot be determined accurately[10]; however, ILSS is still widely used as a screening method for evaluating fiber–matrix adhesion.

Results from interlaminar short beam shear tests of polybenzoxazine and novolac composites are presented in Table II. As can be seen, the ILSS strength of the glass-cloth-reinforced polybenzoxazine composite is significantly higher than that of the novolac composite when no surface treatment of the glass fiber was applied. When glass fibers were surface-treated with 0.1% by weight of γ-APS aqueous solution, the ILSS strength of the polybenzoxazine composite is comparable to that of novolac composite. γ-APS has been known to be a good coupling agent for phenolic resin. Treatment of γ-APS increases the ILSS dry strength of the novolac composite by 80%, while there is only a 35% increase for the polybenzoxazine composite. This means that γ-APS is not as effective on polybenzoxazine as it is on novolac. Yet, the absolute shear strength of polybenzoxazine composites are comparable with novolac composites. The high shear strength of polybenzoxazine composites is due to a better wetting of the glass fiber by the low viscosity of the benzoxazine resin. This is an advantage in terms of processing.

An important reason for applying silane coupling agents to glass-reinforced composites is to improve hydrothermal stability. The wet strength retention of the composites after immersion in boiling water can be used to investigate the effects of water on the ILSS strength. The wet strength and wet strength retention of polybenzoxazine composites and novolac composites are presented in Table III. Wet strength retention is calculated

Table II Interlaminar Short-Beam Shear Stress (MPa) of Glass-Fiber-Reinforced Composites

Coupling Agent	Polybenzoxazine	Novolac
N/A	39	24
0.05% γ-APS	52	—
0.1% γ-APS	58	53
VBA	51	—
γ-MPS	39	—
Benzoxazine silane	43	32

Table III   Interlaminar Short-Beam Shear Stress of Water-Boiled Glass-Fiber-Reinforced Composites

Coupling Agent	S_H (MPa)		Wet Strength Retention (%)	
	Polybenzoxazine	Novolac	Polybenzoxazine	Novolac
N/A	18	19	47	81
γ-APS (0.05% wt)	41	49	80	93
γ-APS (0.1% wt)	43	49	73	93
VBA	41	—	9	—
Benzoxazine silane	43	28	100	97

as the percentage of the ILSS strength, after immersion in boiling water for a period of 12 h, to the ILSS dry strength of the corresponding composite. The untreated polybenzoxazine composite suffers a 53% loss in the ILSS strength, while the untreated novolac composite shows only 19% reduction in ILSS strength after treatment in boiling water. It was reported that bisphenol-A-methylamine-based polybenzoxazine has a lower water absorption compared to epoxy and conventional phenolic resins.[5] Therefore, the lower wet strength retention of the untreated polybenzoxazine composite most likely originates from the weak interface. However, when the benzoxazine silane coupling agent is used to treat the glass fiber, the polybenzoxazine composite retained 100% of its strength even after treatment in boiling water. This effect clearly indicates the importance of chemical compatibility. Interestingly, the treatment of the benzoxazine silane coupling agent also gives the highest wet strength retention on the novolac composite. It should be mentioned that the structure and role of the benzoxazine silane at the interface is not fully understood, and the treatment condition has not been optimized. This reason also explains the lower ILSS dry strength of the benzoxazine-silane-treated composite in comparison to those treated with amino silane.

CONCLUSIONS

Nonpolar solvent systems have been employed in the synthesis of benzoxazine. These solvents resulted in a high yield of high-purity benzoxazine. Because of the high purity of the as-synthesized product, the tedious purification process can be avoided. Using the same solvent system, 3-(tri-ethoxysilyl-)n-propyl-3,4-dihydro-2H-1,3-benzoxazine was also successfully synthesized. The as-synthesized benzoxazine silane had a purity greater than 99%. This silane coupling agent has been shown to improve the ILSS strength of the glass-fiber-reinforced polybenzoxazine and novolac composites, despite the fact that the hydrolysis and treatment condition have not been optimized. A surprisingly high wet strength retention of 100% (after boiling for 12 h in distilled water) was obtained with this silane treatment on the polybenzoxazine composite.

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