Synthesis and Interfacial Properties of Aminosilane Derivative of Acrylated Epoxidized Soybean Oil

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ABSTRACT: In this study silanized acrylated epoxidized soybean oil (silanized-AESO), a multifunctional monomer, was synthesized by reacting acrylated epoxidized soybean oil with 3-Aminopropyltriethoxysilane via a Michael addition reaction using less than equivalent amount of the silane. The characterization of silanized-AESO was done by NMR and IR spectroscopy. Free radically initiated homopolymer of silanized-AESO was synthesized by using the residual acrylate groups. The silanized-AESO homopolymer was characterized by IR spectroscopy. The interfacial adhesion of the polymer on glass surface before and after moisture cure was measured according to ASTM D 4541 Pull-Off Adhesion Test. After moisture curing process, an approximate of eight-fold improvement was observed in the adhesion strength. Prolonged exposure to 92% humidity for 48 h caused to approximately 15% decrease in the adhesion strength. Silanized-AESO was copolymerized with styrene in 1 : 1 weight ratio via radical polymerization. The effect of increased crosslink density upon moisture cure on the mechanical and physical properties of silanized-AESO-styrene copolymer was analyzed by DMA (Dynamic Mechanical Analysis), swelling, and surface hardness tests. Upon moisture cure 35% improvement was observed in the storage modulus because of the increase in the crosslink density. According to tan δ curves and surface hardness tests, silanized-AESO-styrene copolymer shows heterogeneous morphology in crosslinked areas. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2244–2253, 2007

Key words: renewable resources; adhesion; mechanical properties; crosslinking; coatings

INTRODUCTION

The prevailing raw material used in the synthesis of polymeric materials has been petroleum for the last 50 years. The depletion in the reserves and the increasing price of petroleum has driven the chemical industry to search for new and renewable raw materials. Because of the wide variety of possibilities for chemical transformations, universal availability, and low price, oils, and fats of vegetable and animal origin are preferred by the chemical industry as an alternative.[1]

Acrylated epoxidized soybean oil (AESO), shown in Figure 1, is synthesized by reacting Epoxidized Soybean Oil (ESO) with acrylic acid. The mechanism of the reaction is a standard addition of the acrylate to the epoxy ring. Although acrylic acid in addition to being a nucleophile also acts as a partial catalyst, additional catalysts are used as well, such as *N,N*-dimethyl aniline and triethylamine.[2]

AESO used in this work contains 3.4 acrylate double bonds per molecule, on an average. These double bonds can be free radically polymerized or copolymerized with reactive diluents such as styrene, to give thermoset resins, which have mechanical properties similar to commercially successful polyester and vinyl ester resins.[3,4] Polymers with different moduli and glass transition temperatures (T_g) can also be produced by varying the amount of reactive diluent. The properties of the polymer can also be controlled by changing the functionality of the molecule. By the reaction of AESO with chemical species such as diacids, diamines, anhydrides, and isocyanates, the properties of the resulting polymers can be optimized. AESO when emulsion polymerized with methyl methacrylate gives polymers that are useful as pressure sensitive adhesives.[5]

Organofunctional silanes are generally used as adhesion promoters/coupling agents, surface modifiers, and crosslinking agents. When an organofunctional silane coupling agent is used in composite materials containing an inorganic filler and an organic polymer, improvement in adhesion and mechanical properties such as tensile strength, impact strength, and abrasion resistance is observed.[6,7] This technique is widely used in the glass fiber industry. Reaction of the silane with the substrate is believed to involve in two main steps. The first step is the formation of reactive silanol groups upon hydrolysis of the alkoxy groups. The second step is the condensation of the reactive silanol groups to

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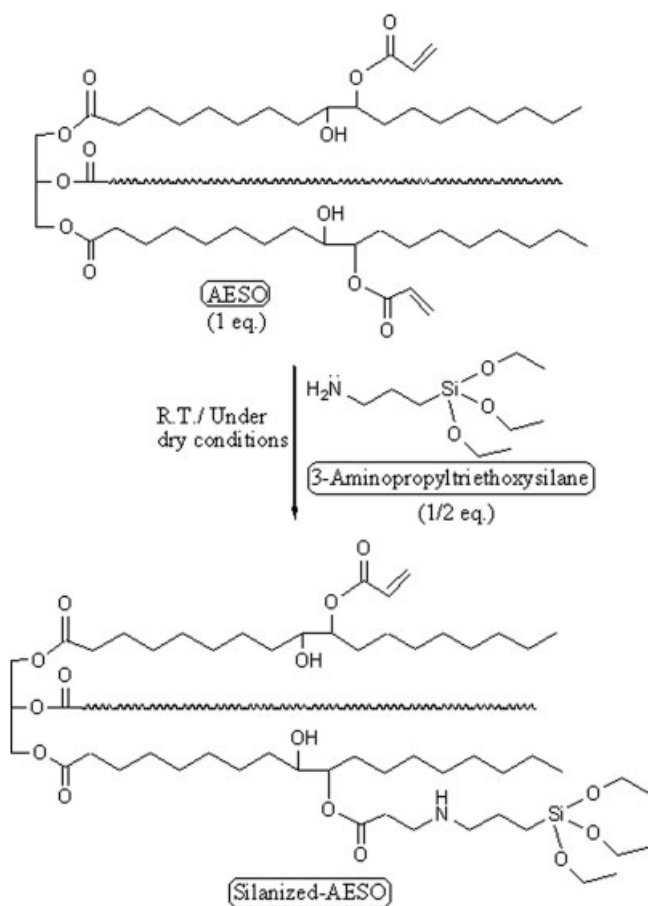
Figure 1 Synthesis of silanized-AESO.

form covalent bonds with the hydroxy sites of the substrate. During this step water is eliminated. Organofunctional silanes are used to modify surfaces by hydrophobation, give the surface an organophilic character, improve the processing properties, like dispersion behavior or viscosity by supplying compatibility between filler and polymer,[8] improve wetting of an inorganic substance by a polymer, and improve corrosion or scratch resistance by serving as a protective coating.[9] By a simple moisture-curing process, organofunctional silanes that are attached to the polymer are able to crosslink the polymer. After moisture cure hydrolized silanols are able to undergo condensation with other silanols in the medium, thus leading to crosslinks. Such a strategy is used in crosslinking in silicones, polyolefines, and polyacrylates[10] as observed in most commercial "heat-shrink" plastics.

3-Aminopropyltriethoxysilane is a bifunctional compound that possesses both organic reactive and inorganic reactive ends. The amino end of the molecule is capable of reacting with many organic polymers, especially those containing a carbonyl group such as polyesters and polyamides. Thus the molecule acts as a coupling agent between an organic polymer and an inorganic surface or filler.[11] Ethoxy

silane ends of the molecule can be hydrolyzed to silanols which will react with hydroxyl bearing inorganic surfaces such as glass, glass fibers, glass wool, mineral wool, quartz, sand, mica, aluminum hydroxide, kaolin, talc, metal oxides, and most metals.

We describe here a simple procedure for reacting AESO with 3-Aminopropyltriethoxysilane such that only one half of the acrylate groups are consumed. The resulting product is a multifunctional silane which provides acrylate groups for radical polymerization, a large triglyceride skeleton for rendering the interface hydrophobic and a triethoxysilane group for interaction with an inorganic surface.

EXPERIMENTAL

Reagents and instruments

Acrylated Epoxidized Soybean Oil (AESO) was obtained from Sartomer Company. (Exton, PA) and was used as obtained. 3-Aminopropyltriethoxysilane was obtained from Hüls-Degussa (Darmstadt, Germany) and was used as obtained. Styrene was purchased from Fluka (AG, Switzerland) and was used as received. CDCl$_3$ obtained from Aldrich (Milwaukee, WI) was used for ^{1}H-NMR and ^{13}C-NMR analysis. The radical initiators benzoyl peroxide and 2,2′-azobis (isobutyronitrile) (AIBN) were obtained from Fisher (New Jersey, USA) and Fluka (AG, Switzerland), respectively, and they were recrystallized from methanol prior to use. Epoxy adhesive "404" was produced by Cuhadaroglu (Istanbul, Turkey). The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Varian 400 MHz NMR operating at a frequency of 399.986 MHz for proton and 100.587 MHz for carbon. The spectra were reported as ppm (δ). The IR analysis was performed with Genesis FT-IR spectrometer using KBr window. The dynamic mechanical thermal analysis of the polymer samples were performed by using Dynamic Mechanical Analyzer (DMA). DMA measurements were done with TA Instrument Q800. Temperature scans were run from room temperature to 160°C at a heating rate of 3°C/min with a frequency of 1 Hz and strain 0.01%. The adhesion strength of silanized-AESO styrene homopolymer was tested with DVT G-21 type of tensile strength machine according to the ASTM D 4541 Pull-Off Adhesion Test. The surface hardness of the polymers was analyzed with a Zwick/Roell Durometer according to ASTM D 2240 test. The swelling behavior of silanized-AESO-styrene copolymer was tested in CCl$_4$ by using a Geartner 7109-46 traveling microscope.

Silanization of acrylated epoxidized soybean oil

In a N$_2$ purged flask to which a drying tube was attached 2.402 g (6.8068 mmol in acrylate) acrylated

epoxidized soybean oil and 0.758 g (3.4028 mmol) 3-Aminopropyl triethoxysilane were stirred magnetically for 60 min. The reaction was followed by IR and NMR spectroscopy, and loss of vinyl protons was observed in NMR. The product is a viscous liquid.

^{1}H-NMR (CDCl$_3$) δ: 0.61 (—CH$_2$—Si—); 0.87 (—CH$_3$); 1.20 (—CH$_2$—); 1.23 (—Si—O—CH$_2$—CH$_3$); 1.605 (—NH—CH$_2$—CH$_2$—CH$_2$—Si—); 2.3 (—O(C=O)CH$_2$—); 2.6 (—NH—CH$_2$— —CH$_2$—CH$_2$—Si—); 2.87 (—O(C=O)CH$_2$—CH$_2$—NH—); 3.79 (—Si—O—CH$_2$—CH$_3$); 3.99 (—CH(OH) —CH(C=O)CH$_2$); 4.11 (—O—CH$_2$—CH(O—) —CH$_2$—O—); 5.24 (—O—CH$_2$—CH(O—) —CH$_2$—O—); 5.84 (—O(C=O)CH=CHaHb); 6.11 (—O(C=O)CH=CHaHb); 6.41 (—O(C=O)CH=CHaHb).

^{13}C-NMR (CDCl$_3$) δ: 7.68, 8.08 (—CH$_2$—Si—), 14.07, 14.13, 14.18 (CH$_3$—CH$_2$—CH$_2$—), 18.39, 18.52 (—Si—O—CH$_2$—CH$_3$), 22.59, 22.69, 22.76, 22.86, 22.96, 23.24, 23.29 (—CH$_2$—), 24.90, 24.95 (—NH—CH$_2$—CH$_2$—CH$_2$—Si—), 31.93, 31.98, 31.99 (—CH$_2$—), 34.06, 34.12, 34.22 (—O(C=O)CH$_2$—CH$_2$—CH$_2$—), 34.83, 34.99 (—O(C=O)CH$_2$—CH$_2$—NH—), 44.69, 44.91, 44.99 (—O(C=O)CH$_2$—CH$_2$—NH—), 52.18, 52.26, 52.51 (—NH—CH$_2$—CH$_2$—CH$_2$—Si—), 58.31, 58.43, 58.44 (—Si—O—CH$_2$—CH$_3$), 62.17(—O—CH$_2$—CH(O—) —CH$_2$—O—), 69.04(—O—CH$_2$—CH(O—) —CH$_2$—O—), 77.06, 77.38, 77.58, 77.70 (—CH(OH)CH—O(C=O)—), 80.53, 81.32, 81.42, 81.79, 81.89 (—CH(OH)CH—O(C=O)—), 127.81, 128.67(—O(C=O)—CH=CH$_2$), 132.23(—O(C=O)—CH=CH$_2$), 165.56, 165.72, 165.90, 166.13 (—O(C=O)—CH = CH$_2$), 172.19, 172.25, 172.48, 172.64, 172.81, 173.21 (—O(C=O)CH$_2$—CH$_2$—NH—).

IR (Film) υ (cm^{-1}): 3436 (br, O—H), 2929 (s, CH), 2855 (s, CH), 1738 (s, C=O), 1463 (m, CH$_2$, Def.), 1406 (m, =CH$_2$, Def.), 1295–1283 (s, C—O— Def.; O—H, Def.), 1192 (m, CO, Def.; C—O—C, Def.), 1103 (s, Si—O, Def.), 1079 (s, C—N, Def.), 809 (m, =CH$_2$, Def.), 1636, 959 cm^{-1}(m, =CH, Def., characteristic for vinyl group conjugated with carbonyl).

Radical homopolymerization of silanized-AESO

In a sample procedure, under absolutely dry conditions 3.15 g of silanized-AESO was mixed with 0.048 g (1.5% in weight) benzoyl peroxide. Reagents were stirred for 12 h under N$_2$ atmosphere at 70°C to give a soft, clear, insoluble polymer. Characterization of the homopolymer was done by IR spectroscopy, and the disappearance of the acrylate double bond peak was observed.

IR (Film) υ (cm^{-1}) (Before Moisture Cure): 3452 (br, O—H), 2920 (s, CH), 2853 (s, CH), 1731 (m, C=O), 1456 (m, CH$_2$, Def.), 1378 (m, =CH$_2$, Def.), 1294-1251 (s, C—O— Def.; O—H, Def.), 1184 (m, CO, Def.; C—O—C, Def.), 1096 (s, Si—O, Def.), 831 (m, =CH$_2$, Def.).

IR (Film) υ (cm^{-1}) (After Moisture Cure): 3490 (br, O—H), 2930 (s, CH), 2853 (s, CH), 1746 (s, C=O), 1730 (s, C=O), 1715 (s, C=O), 1453 (m, CH$_2$, Def.), 1384 (m, =CH$_2$, Def.), 1253 (b, C—O— Def.; O—H, Def.), 1153 (b, Si—O, Def.), 830 (m, =CH$_2$, Def.).

Radical copolymerization of silanized-AESO with styrene

In a sample procedure, 2.09 g of silanized-AESO was mixed with 2.13 g styrene under dry conditions for 10 min. N$_2$ was purged to the flask. Then, 0.029 g (1.5% in weight) of AIBN was added to the mixture. The mixture was stirred for 12 h at 70°C.

Moisture curing of polymers

Moisture curing process was done after radical polymerization was complete. Polymer samples were prepared as a thin film on glass and were then exposed to water vapor for 12 h. The coupling process was done at 125°C for 12 h.

Radical curing process for adhesion tests

For adhesion tests mixture prepared for homopolymerization was applied on a glass surface at a thickness of ∼ 80 μm. The polymerization was done under N$_2$ atmosphere to prevent any moisture present in the medium at 70°C for 12 h on the glass surface.

Moisture curing process for adhesion tests

Moisture cure process was done by keeping the polymer in ambient conditions for 24 h to allow enough time needed for hydrolysis of ethoxysilane groups, followed by keeping at 125°C for 12 h.

Adhesion test

The adhesion properties of the silanized-AESO homopolymer on glass, before and after moisture cure were measured by the ASTM D 4541-85 pull-off adhesion test. In the pull-off test a loading fixture, commonly called a metal dolly or stub, is affixed by an adhesive to a coating. By use of a portable pull-off adhesion tester, a load is increasingly applied to the surface until the metal dolly is pulled off. The force required to pull the metal dolly off yields the tensile strength in kilo Pascals (KPa). Figure 2 shows a general representation of the instrumentation used for the test.

Prior to any further application surface of the polymer was wiped with wipes soaked in acetone to remove any impurities. Then, metal dollies having 1.833 cm^2 surface areas were adhered on the surface of the polymer with an epoxy adhesive. After the metal dollies were attached on the polymer, a cut was made along the circumference of the dolly so
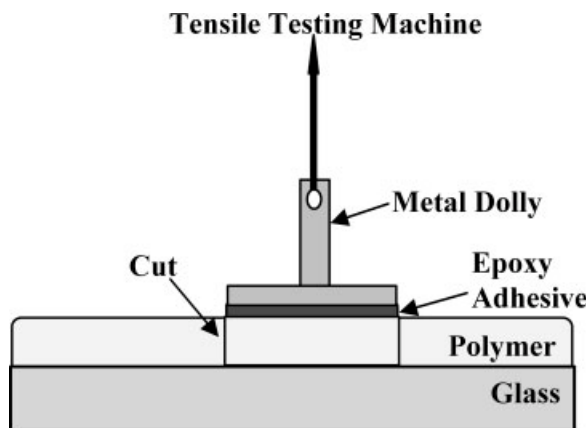
Figure 2 Adhesion Pull-Off Testing setup.

that only the area under the dolly would be pulled off during the test.

Swelling tests

For the swelling test polymer samples were cut into rectangular pieces of dimensions about $1 \times 5 \times 10$ mm^3. The tests were carried on 4 different samples for each polymer and the average of the results was taken. The swelling tests were done in CCl$_4$. The initial values of the sample lengths were recorded. The samples were then put into closed containers, which contain solvent. The increase in the lengths was measured within one hour time interval until solvent uptake ceased.

RESULTS AND DISCUSSIONS

Synthesis and characterization of silanized-AESO

Acrylate double bonds of AESO are very susceptible towards nucleophilic attack, which makes them good Michael acceptors. In the presence of a good Michael type of nucleophile the addition reaction can easily take place.[12]

Silanized-AESO was synthesized by the Michael Reaction of 3-Aminopropyltriethoxysilane on AESO by using less than equivalent amount of the aminosilane, so that some of the acrylate groups will be left intact to provide the radical polymerization sites. The synthesis and the chemical structure of the silanized-AESO are shown in Figure 1.

The silanized-AESO contains three important functional groups. It contains long hydrophobic carbon chains, reactive acrylate double bonds, and hydrolyzable ethoxy silane groups. The acrylate double bonds are very reactive and can be easily radically polymerized. The ethoxy silane groups can be easily hydrolyzed to yield hydroxysilane groups. Hydroxysilane groups are capable of self-condensing or reacting with other inorganic substrates containing hydroxyl functional groups and the fatty acid provides a thick and hydrophobic interface.

Figure 3 shows the ^{1}H-NMR the silanized-AESO. The peaks appearing at 5.84 ppm (—O(C=O) CH=CHaHb); 6.11 ppm (—O(C=O)CH=CHaHb); and 6.41 ppm (—O(C=O)CH=CHaHb), indicate the presence of unreacted acrylate double bond in the

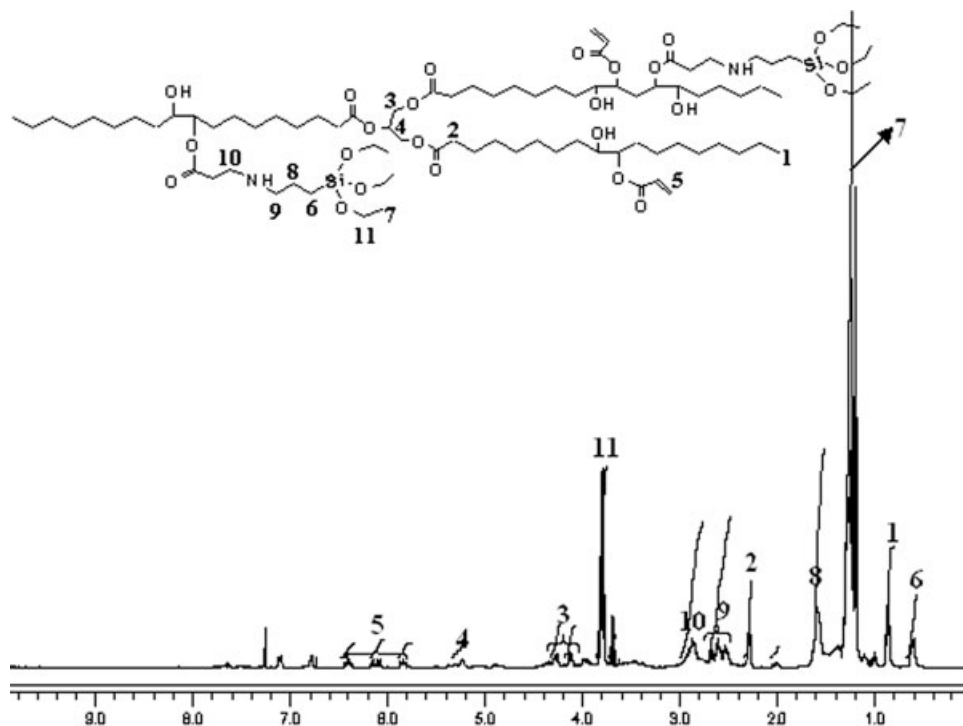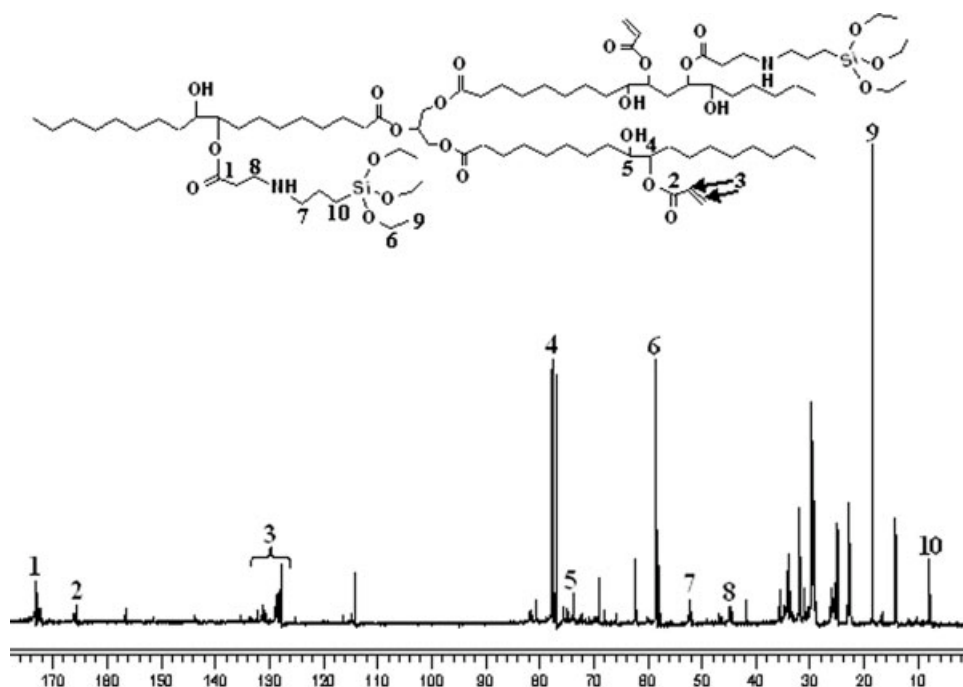**Figure 3** ^{1}H-NMR spectrum of partially silanized-AESO.

Figure 4 ^{13}C-NMR spectrum of partially silanized-AESO.

monomer. ^{1}H-NMR of the product shows that there are 1.7 acrylate groups and 1.7 aminosilane groups per triglyceride on an average.

The ^{13}C-NMR spectrum, Figure 4, shows that carbonyl carbons of the acrylate ester shift to lower field from 165.90 ppm (—O(C=O)—CH=CH$_2$) to 172.48 ppm (—O(C=O)CH$_2$—CH$_2$—NH—) after addition of 3-Aminopropyltriethoxysilane to the double bond.

The ester functionality of the triglyceride in the presence of an amine can undergo an undesirable amidation reaction. To prove that reaction proceeds only trough the Michael Addition, AESO was reacted with 3-Aminopropyltriethoxysilane in 1 : 1 ratio so that all the double bonds were depleted in the reaction. The reaction was completed in 90 min. Figure 5 shows ^{1}H-NMR spectrum of fully silanated molecule. Complete disappearance of the peaks cor-
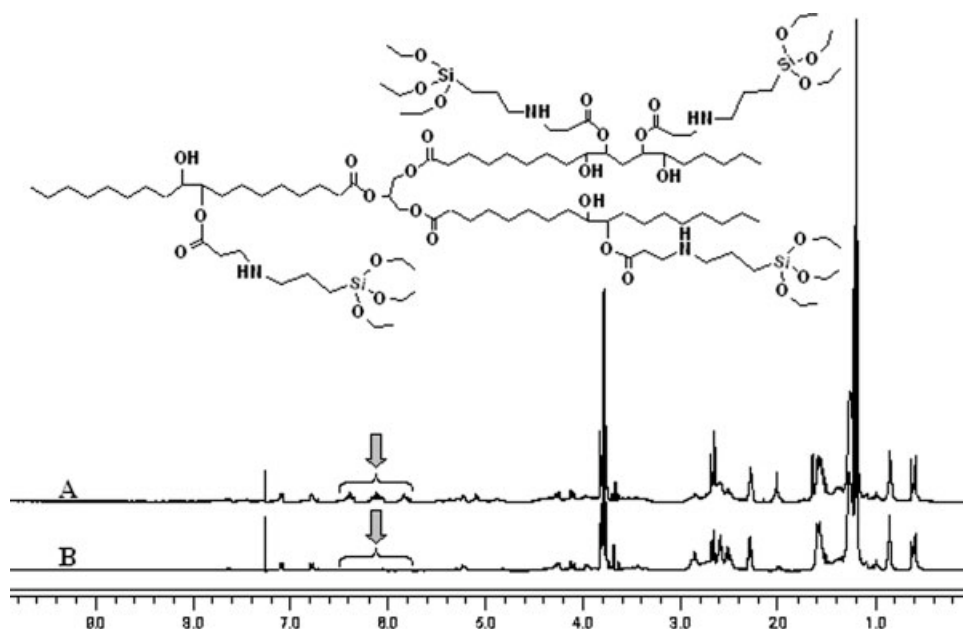

Figure 5 ^{1}H-NMR spectrum of fully silanized-AESO; (A) beginning of the reaction and (B) end of the reaction.

responding to —CH=CH₂ protons of the acrylate esters indicated that the reaction proceeded via Michael reaction.

At higher temperatures aminosilane is capable of adding to two acrylate groups.[13] This leads to undesirable over consumption of the acrylate groups and gels the sample. However, when the reaction is carried out at room temperature there was no evidence of a second Michael addition by the secondary amine.

Adhesion properties

Soucek and his coworkers studied the effect of moisture cure on the adhesion strength of isocyanurate coatings. In this study, aminosilane functionalized 1,6-hexamethylene diisocyanate was used to formulate a coating. The effect of moisture cure was investigated, and it was reported that moisture curing process dramatically enhances the adhesion and increases the crosslink density.[14] In another study isocyanate-free moisture cure coatings were prepared from epoxidized soybean oil. ESO was used to prepare polyols, which then were used for synthesizing a urethane prepolymer. Prepolymer was then treated with aminosilane which added to the isocyanate end of the prepolymer. It was concluded that aminosilanes treated samples show better adhesion properties.[15]

Figure 6 shows the IR spectra of the silanized-AESO monomer and homopolymer under dry conditions and after moisture curing process. The disappearance of the peak corresponding to the acrylate double bonds at 959 cm^{-1} after polymerization can be clearly observed. Subsequent to the polymerization, the presence of three different carbonyl groups, namely acrylate ester carbonyl groups, (—O(C=O)—CH₂—CH₂) and (—O(C=O)CH₂—CH₂—NH—), and fatty acid ester carbonyl group, in the polymer structure becomes more pronounced. The wide peak occurring in both spectra in 1000–1200 cm^{-1} region is because of the overlapping of the peaks corresponding to —C—Si—O—, —Si—O—Si—, and —Si—O—C— stretchings.

To study the improvement in the adhesion strength adhesion strength was measured before and after moisture cure. Before moisture cure the silanol groups are still protected as ethoxy groups. Therefore only weak Van der-Waals type attractions exist at the polymer-glass interface, and the adhesive strength should be low. After moisture cure the ethoxy groups are hydrolyzed and new silyl ether bonds (—Si—O—Si—) are formed at the interface. These are covalent bonds of about 799.6 ± 13.4 kJ/mol[16] bond strength and the adhesive strength at the interface should be much higher. To observe full benefits of the hydrolysis/condensation steps, the
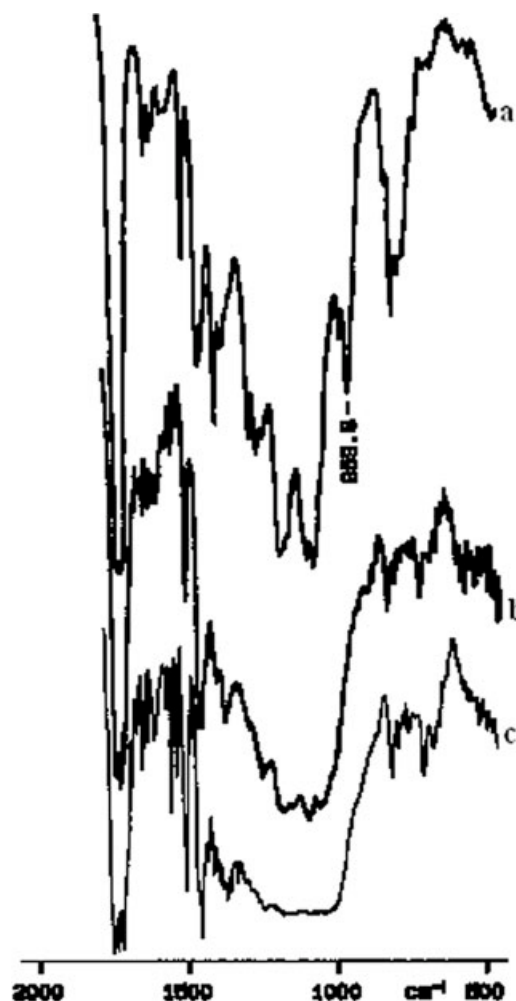

Figure 6 IR spectrum of silanized-AESO (a) homopolymer after radical polymerization (b) homopolymer after radical and (c) moisture cure.

sample has to be heated to a temperature which is high enough to push the silanol-silyl ether equilibrium to the right by allowing ethanol and water to evaporate from the interface.

The adhesion on the glass surface was studied according to the ASTM D 4541-Pull Off Adhesion Test (Fig. 2). To perform the test, a metal dolly was adhered on the polymer surface by using epoxy adhesive resin. Then it was pulled with a tensile testing machine to measure the force at which adhesive failure at the polymer glass interface was observed.

The adhesion before moisture cure was studied on the sample immediately after the radical polymerization process. Then, adhesion strength after moisture cure was measured.

Considerable experimental difficulties were encountered during testing. For the test to yield valid results it is necessary to obtain a clean and complete adhesive failure at the polymer-glass interface. Any other type of failure such as partial adhesive–cohesive failure or failure at the dolly-epoxy adhesive or
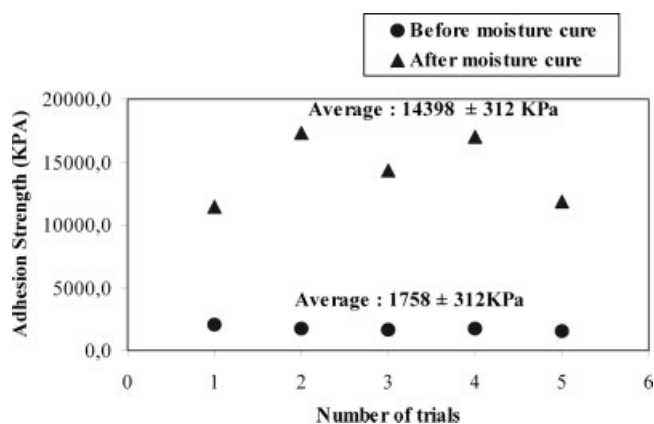
Figure 7 Adhesion strength before and after moisture cure.

at the epoxy adhesive-polymer interfaces is not acceptable. Tests where the metal dollies fail to lift vertically and shear off to one side or tests that result in overstressing and breaking of the glass substrate are also not acceptable. To get valid results at high adhesive strength it was necessary to decrease the polymer-glass interfacial area while keeping the dolly-polymer interfacial area the same, so that adhesive failure at the polymer-glass interface took place exclusively.

The adhesion strength results before and after moisture cure are shown in Figure 7. It was observed that upon moisture cure the average adhesion strength of the homopolymer increases from 1758 ± 312 KPa to 14,398 ± 312 KPa, a remarkable eight-fold increase indicating that with the moisture curing process —Si—O—Si— bond formation took place at the polymer-glass interface.

It is known that the formation of —Si—O—Si— bonds is reversible. With prolonged exposure to moisture or humid air, —Si—O—Si— bonds can hydrolyze back to silanol groups. This reversible bond formation will cause a decrease in adhesion strength of the polymer with time. This has an important practical importance in the use of silane coupling agents in moist media, such as marine and automotive applications. In general the more hydrophobic the coupling agent is the less susceptible, it is to reversal in wet media. Here, the three large alkyl groups on the triglyceride should make silanized-AESO uniquely successful.

The effect of humidity on the adhesion strength of the homopolymer was therefore studied. The moisture cured polymer was kept in a humidity chamber for 48 h. At room temperature a 92% constant humidity was supplied by keeping the sample within a closed space with a saturated aqueous solution of $Na_2CO_3 \cdot 10H_2O$.[17] Figure 8 shows the decrease in the adhesion upon exposure to humidity.

It was concluded that average adhesion strength decreases from 14,398 ± 312 KPa to 12,154 ± 312 KPa, an average of 15% decrease. Samples that were kept dry showed no change in adhesion strength within experimental error.

From the results it can be concluded that humidity causes a decrease in the adhesion strength. But the decrease is very small compared to the increased adhesion after moisture cure. The moisture treated interface is still sevenfold stronger than the original surface before the activation of the silanol groups. We conclude that the presence of the very hydrophobic triglyceride on the silanized-AESO does in fact protect the interface against water ingress quite successfully.

Improvement in the mechanical and physical properties of the copolymer upon moisture cure

Silanized-AESO is capable of free radical polymerization through its acrylate functionality and is also capable of condensation polymerization after the deprotection of its ethoxysilane groups. Under dry conditions and with a free radical initiator only the former mechanism takes place. If the resulting polymer is now moisture cured in the absence of an inorganic surface such as glass, the silanol groups that are produced will self condense and lead to higher connectivity, cross-linking, and increased modulus.

Copolymerization was done by mixing the silanized-AESO and styrene in 1 : 1 weight ratio. AIBN was used as radical initiator. Polymerization was done under dry conditions to prevent hydrolysis of ethoxysilane groups of the silanized-AESO. As a result a polymer which contains hydrolyzable ethoxysilane groups was synthesized. The styrene-silanized-AESO copolymer was then moisture treated to hydrolyze the ethoxysilane groups and then heated to self-condense the silanol groups. As this experiment was done on the neat copolymer in the absence
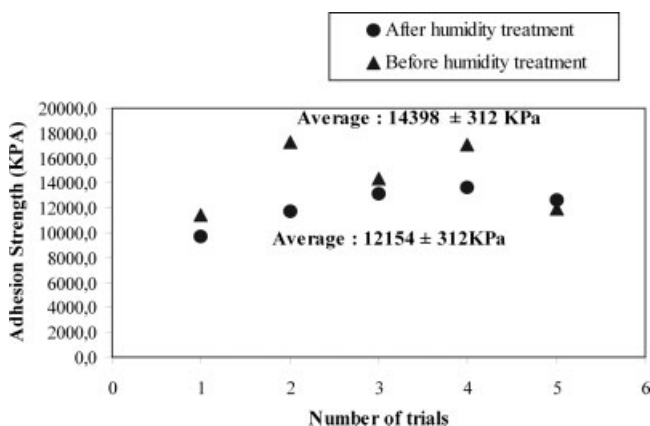
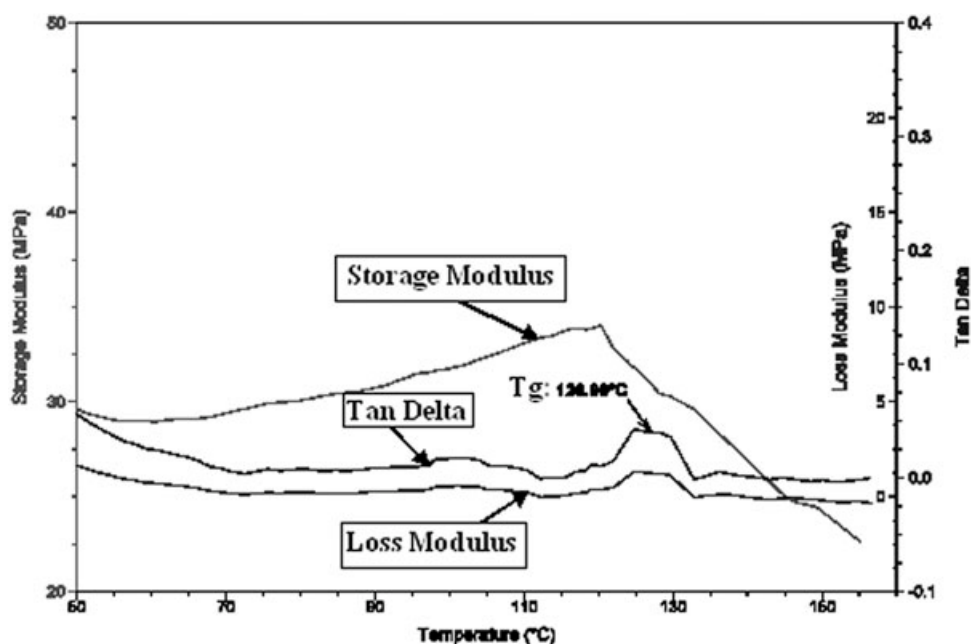**Figure 8** Decrease in the adhesion strength upon exposure to humidity.

Figure 9 DMA traces for silanized-AESO-styrene copolymer before moisture cure.

of an inorganic surface or filler the silanol groups could only self-condense and give a highly crosslinked network.

The polymer samples for dynamic mechanical analysis were prepared to dimensions of $25 \times 5 \times 0.5$ mm^3. DMA scans were run from room temperature to 160°C at a heating rate of 3°C/min at a frequency of 1 Hz and strain 0.01%. Figure 9 shows the dependence of the storage modulus E′, loss modulus

E″, and the loss factor tan δ for the copolymer after radical polymerization under dry conditions, and Figure 10 shows the results after moisture curing and condensation of the same polymer.

The silanized-AESO-styrene copolymer samples show rubbery behavior in dynamic medium. The effects of self-condensation cause an increase in the crosslinking density and were clearly observed with DMA analysis. The free radically polymerized sam-
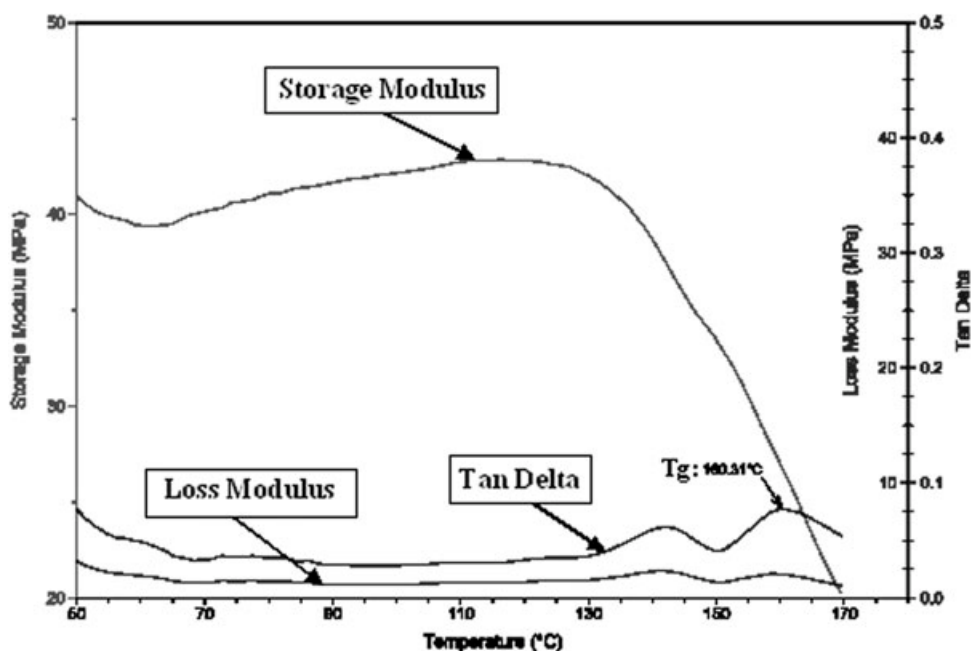

Figure 10 DMA traces for silanized-AESO-styrene copolymer after moisture cure.

ple showed an average 30 MPa storage modulus. The same sample after moisture curing sample showed nearly a 35% improvement in the storage modulus, from 30 to 43 MPa. The effect of increased crosslink density upon moisture cure can also be observed in the glass transition temperatures of the polymer samples. The T_g of the copolymer increases from 127 to 160°C. This indicates that a higher temperature is required for the onset of large scale segmental motion in crosslinked polymer.
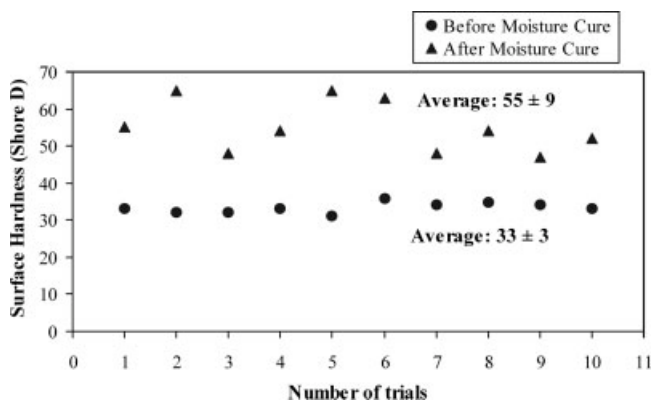
Tan δ curves of the silanized-AESO-styrene copolymer before and after moisture cure shows two maxima. This indicates an uneven crosslinking density of the polymer morphology. The effect is clearly observed after the moisture curing process. After the self-condensation of silanol groups some highly crosslinked areas are formed, while other regions remain lightly crosslinked. These two regions lead to two maxima on tan δ curve suggesting a polymer morphology that is heterogeneous. Such behavior known as "grainy morphology" has been observed in other crosslinked polymers such as polyesters before.[18]
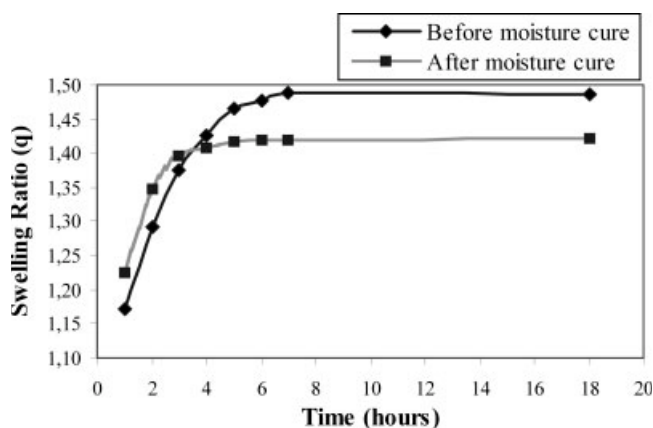
Surface hardness tests

The surface hardness of the polymers was measured by using a shore durometer according to the ASTM D-2240 test.

For the analysis 1 mm thick samples were prepared. The samples were protected from any possible mechanical stress before testing. The samples were tested at 10 different points on the same surface. Figure 11 shows the results for the surface hardness of the styrene copolymer before and after moisture cure.

After moisture curing process an increase in surface hardness from an average of 33 ± 3 to 55 ± 9 was observed as expected. The improvement in the surface harness can be attributed to the increase in the crosslink density.

Figure 12 Swelling behavior of styrene-silanized-AESO in CCl$_4$ copolymer before and after moisture cure.

Swelling test

Crosslinked polymers when placed in a good solvent absorb the solvent and swell. The extent of swelling represents a competition between two forces. During mixing the solvent penetrates in the polymer. As the polymer chains in the crosslinked polymer try to elongate, they generate a force in opposition to this deformation. The volumetric swelling reaches a steady state when two forces balance each other. The swelling behavior of crosslinked polymers is also a good indication for the crosslink density. Higher swelling indicates lower crosslink density.

The swelling behavior of the copolymer in CCl$_4$ was examined by using a traveling microscope. The samples were put in a closed container and the experiment was continued until the solvent uptake ceased. The swelling ratio (q) was obtained by the following equation:

$$q = \frac{V}{V_0} = \left(\frac{L}{L_0}\right)^3$$

where V_0 and V are the volumes of unswollen and swollen polymer samples, respectively; and L_0 and L are the unswollen and swollen polymer samples, respectively. Figure 12 shows the swelling behavior of the samples before and after moisture cure. The swelling ratio of moisture cured silanized-AESO-styrene copolymer is higher that the swelling ratio of only radically cured copolymer, indicating higher crosslink density.

CONCLUSIONS

A multifunctional monomer was synthesized by reacting acrylated epoxidized soybean oil with 3-Aminopropyltriethoxysilane. The characterization of the silanized-AESO was done by NMR and IR spectros-

Figure 11 Surface hardness results before and after moisture cure.

copy. Ethoxysilane groups of the silanized-AESO can easily be hydrolyzed, which makes them very sensitive to moisture. To prevent any possible hydrolysis silanized-AESO was used without any purification for further synthesis. Adhesive properties of the silanized-AESO homopolymer were studied on glass surface. An eightfold of increase was observed in the adhesion strength of the silanized-AESO homopolymer upon moisture cure. Exposure to 92% humidity for 48 h caused to a 15% decrease in the adhesion strength of the silanized-AESO homopolymer. The silanized-AESO monomer was copolymerized with styrene by using 2,2'-azobis (isobutyronitrile) (AIBN) as radical initiator. The mechanical and physical properties of the silanized-AESO-styrene copolymer were studied with DMA, swelling, and surface hardness tests. A 35% increase was observed in the storage modulus value of silanized-AESO-styrene copolymer after moisture cure treatment. Tan δ curves of polymers indicate that crosslinked areas of the polymer show heterogeneous morphology. The T_g of the silanized-AESO-styrene copolymer was found to be 127°C before moisture cure and 160°C after moisture cure. The effect of increasing crosslink density was clearly observed in the swelling test results. The use of the silanized-AESO in glass fiber sizing compositions is currently under study.

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