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## ABSTRACT

In-situ filling through hydrolysis and condensation of silicon alkoxides has been utilized to generate nanocomposites in which the filler phase can be intimately associated with the polymer on relatively small length scales. One problem of the method has been achieving useful fill volumes without bulk phase separation of the reacting silicon monomer from the polymer. In this paper, we describe the preparation of a new class of nanocomposite materials in which the inorganic filler phase is pre-assembled before copolymerization with an organic species. Maleimide monomers, prepared from alkoxysilylpropyl amines and maleic anhydride, were protected against side reactions by forming the oxonorbornene Diels-Alder adduct with furan. The monomers were then reacted under sol-gel conditions to form oligomers or polymers-the filler phase. The material was activated by thermal deprotection of the maleimide and reacted with organic monomers or polymers to form the filled nanocomposite.

## INTRODUCTION

Reinforcing fillers are used in composite chemistry primarily to improve the mechanical properties of the final product and to reduce the cost of manufacture. The most common reinforcing fillers used are carbon black and silica. The latter has been especially applied to synthetic rubbers and is usually used by mechanical mixing of the filler into the rubber formulation. Many of the problems associated with this technique, including silica aggregation and phase separation are caused by the incompatibility of the inorganic filler with the organic polymer.

Methods of improving the compatibility of the inorganic/organic system have been developed. Silane coupling agents containing functional groups capable of bonding to the silica (e.g., alkoxysilyl) and to the diene polymer (e.g., mercapto) are used to chemically bond the filler to the polymer [1]. In situ filling by sol gel polymerization of tetraethoxysilane (TEOS) within the rubber formulation has been used to couple the formed filler with the polymer [2].

In this paper we describe the preparation of inorganic/organic hybrid nanocomposites, in which the inorganic and organic components are interweaved on a molecular level. We have prepared a series of alkoxysilylmaleimide monomers which were polymerized along the alkoxysilane by a sol-gel reaction to form an inorganic silica network. Due to the hydrolytic instability of the maleimide, the monomer was first protected by reaction with furan to form the oxonorbornene adduct, prior to sol-gel polymerization. The furan protecting group was removed after polymerization by a retro Diels-Alder reaction. The functionalized silica was then copolymerized with styrene to form a filled styrene-maleimide nanocomposite.

## EXPERIMENT

**N-(triethoxysilylpropyl)maleimide (1).** Compound 1 (Figure 1) was prepared according to Toru's method for preparing other maleimides [3]. Because of the hydrolytic instability of the ethoxysilyl- groups, workup was modified to avoid the aqueous washing step. 3-aminopropyltriethoxysilane (90 g, 0.40 mol) in benzene (100 mL) was added dropwise to a solution of maleic anhydride (40 g, 0.40 mol) dissolved in benzene (1800 mL). The reaction was

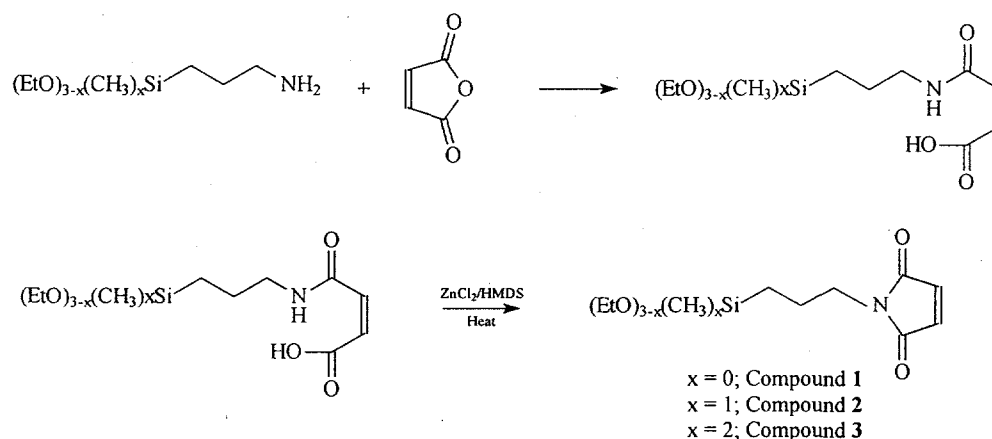
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stirred for 2 h at room temperature.  $\text{ZnCl}_2$  (56 g, 0.40 mol) was added in bulk, the mixture stirred for 30 min and then a solution of hexamethyldisilazane (HMDS, 98 g, 0.60 mol) in benzene (100 mL) was added dropwise. After complete addition of the HMDS, the reaction was refluxed for 2 hours, cooled to room temperature, filtered and filtered again through silica gel. The volatiles were removed under reduced pressure and the product flash distilled at  $90\text{ }^\circ\text{C}/100\text{ mtorr}$  (yield: 78 g, 64 %).



**Figure 1.** Synthesis of compounds 1, 2 and 3.

**Diels-Alder Adduct of 1 (4, Figure 2).** Compound 1 (77 g, 0.25 mol) and furan (52 g, 0.75 mol) were placed in a Carrius tube, freeze-pump-thaw degassed, sealed and then heated in an oil bath at  $70\text{ }^\circ\text{C}$  for 24 hours. The reaction mixture was cooled to room temperature and the excess furan removed under reduced pressure. The desired product was purified by reprecipitation from hexanes (yield: 45 g, 49 %). The diethoxymethyl- (5) and ethoxydimethyl- (6) compounds were prepared in an analogous manner. NMR data for compounds 4 and 5 are as follows. Compound 4:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 5.58 (d, 2H), 4.88 (d, 2H), 3.74 (q, 6H), 3.50 (t, 2H), 2.04 (d, 2H), 1.91 (m, 2H), 1.12 (t, 9H), 0.68 (m, 2H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 175.8, 136.2, 81.0, 58.5, 47.4, 41.4, 21.8, 18.5, 8.0.  $^{29}\text{Si}$  NMR (neat,  $\delta$ ): -46.5. Compound 5:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 5.59 (d, 2H), 4.89 (d, 2H), 3.63 (q, 4H), 3.59 (t, 2H), 2.05 (d, 2H), 1.78 (m, 2H), 1.09 (t, 6H), 0.60 (m, 2H), 0.05 (s, 3H).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $\delta$ ): 175.8, 136.2, 81.0, 58.1, 47.4, 41.5, 21.7, 18.6, 11.3, -4.3.  $^{29}\text{Si}$  NMR (neat,  $\delta$ ): -6.6.

**Sol-gel polymerization.** In a typical sol-gel polymerization, 0.1 N HCl (0.135 mL, 0.75 equiv.  $\text{H}_2\text{O}$ ) was added to a solution of compound 4 (3.7 g, 0.01 mol) in THF. The solution was then diluted to 10 mL with THF. After 24 hours, excess ethoxytrimethylsilane was added and then the volatiles removed under vacuum. Molecular weight measurements of the oil (determined by GPC) indicated a  $M_w$  value of 2000 and  $M_n$  of 1600. Molecular weight data were determined using a Polymer Labs PL-GPC210 equipped with 2 mixed bed 5-micron Polymer Labs columns in series, a refractive index detector, and a Precision Detectors' PD2040 dual-angle ( $15^\circ$  and  $90^\circ$ ) laser light scattering detector. The instrument was calibrated using a 50,000 g/mol narrow polystyrene standard. The mobile phase was THF at a flow rate of 1.0 mL/min.

**Deprotection.** The siloxane oil was deprotected by heating at  $150\text{ }^\circ\text{C}$  under vacuum for 30 minutes. Deprotection was verified by  $^1\text{H}$  NMR (see Results and Discussion section).

**Copolymerization with styrene.** Styrene (0.18 g, 1.7 mmol) and AIBN (0.001 g, 0.006 mmol) were added to the deprotected maleimide (0.39 g) in about a 1:1 molar equivalent ratio. The compounds were mixed, degassed under argon and heated to  $70\text{ }^\circ\text{C}$  to initiate radical

polymerization. An insoluble clear, colorless, homogenous solid, conforming to the geometry of the reaction flask, formed within 15 minutes.

## RESULTS AND DISCUSSION

**Monomer synthesis.** The maleimide functionalized alkoxyisilane monomers were prepared by the reaction of the alkoxyisilylpropylamine with maleic anhydride at room temperature to form the amic acid. Thermal ring closure of the amic acid to form the imide results in formation of water which can react with the alkoxyisilane. Therefore, the imidization reaction was done in the presence of zinc chloride and hexamethyldisilazane, as described by Toru for the synthesis of alkyl and aryl maleimides [3]. The reaction was modified to eliminate the aqueous workup step. The monomers were isolated by filtration through silica gel followed by distillation. Sol-gel polymerization of the alkoxyisilylmaleimide in the presence of water could result in inadvertent addition of water to the maleimide, which is a Michael acceptor. To eliminate this possibility, the maleimide was reacted with furan (Diels-Alder reaction) to form the oxonornornene adduct which is not a Michael acceptor and, therefore, is considerably more stable (Figure 2). A single crystal of compound 4 was obtained from hexanes and the X-ray diffraction structure determined (Figure 3). The molecule exhibits *exo* geometry at the maleimide-oxonornornene junction.

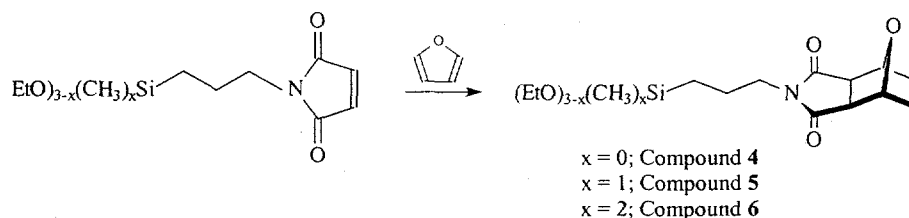


Figure 2. Preparation of compounds 4, 5 and 6.

**Sol gel polymerization.** Sol gel polymerization of the protected compounds 4, 5 and 6 yields siloxane networks with a variety of microstructures (Figure 4). For example, compound 4, the triethoxysilyl substituted monomer, can form branched, crosslinked and silsesquixane type arrangements. The molecular weight (and solubility) can be controlled by varying the amount of water. When 0.75 equivalents of water were used for the condensation reaction, the product was a soluble low molecular weight oil ( $M_w = 2000$ ). With

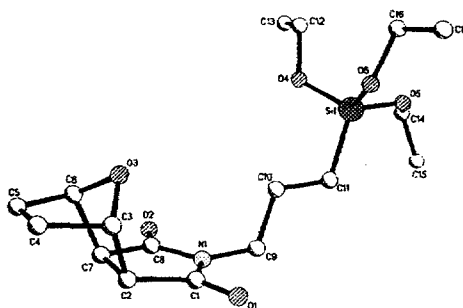
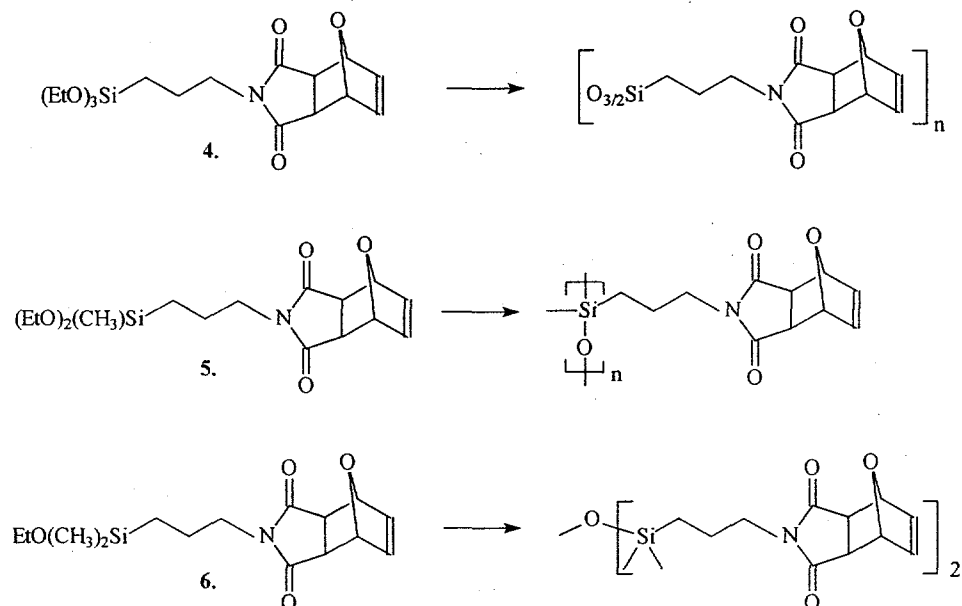


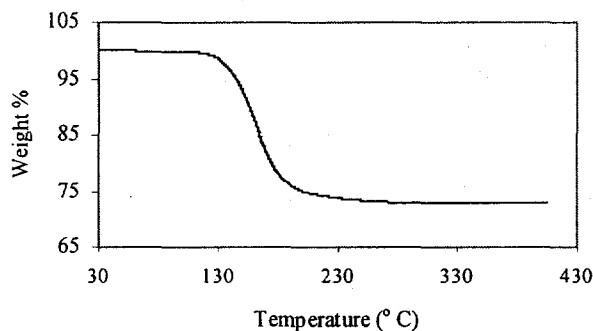
Figure 3. Crystal structure of 4.

1.5 equivalents of water, an insoluble glassy solid polymer resulted. The diethoxysilyl monomer, 5, formed linear and cyclic polymers and the ethoxysilyl, 6, formed the dimer.



**Figure 4.** Sol-gel polymerization of 4, 5 and 6.

**Deprotection.** Once formed and isolated, the maleimide functionality (protected) of the siloxane resin can be activated by a thermally induced retro Diels-Alder process to remove the oxornobornene. This occurs at temperatures greater than 120 °C and can be observed by TGA (Figure 5) and by  $^1\text{H}$  NMR spectroscopy (Figure 6) of the polymer (before and after thermolysis). The TGA reveals a 27 % weight loss beginning at about 120 °C corresponding to quantitative removal of the furan (calculated to be 26 % weight loss). The  $^1\text{H}$  NMR spectra show disappearance of the peaks centered at 5.7, 5.0 and 2.3 ppm (loss of furan) and appearance of peaks at 5.9 ppm (vinyl hydrogens of the deprotected maleimide).



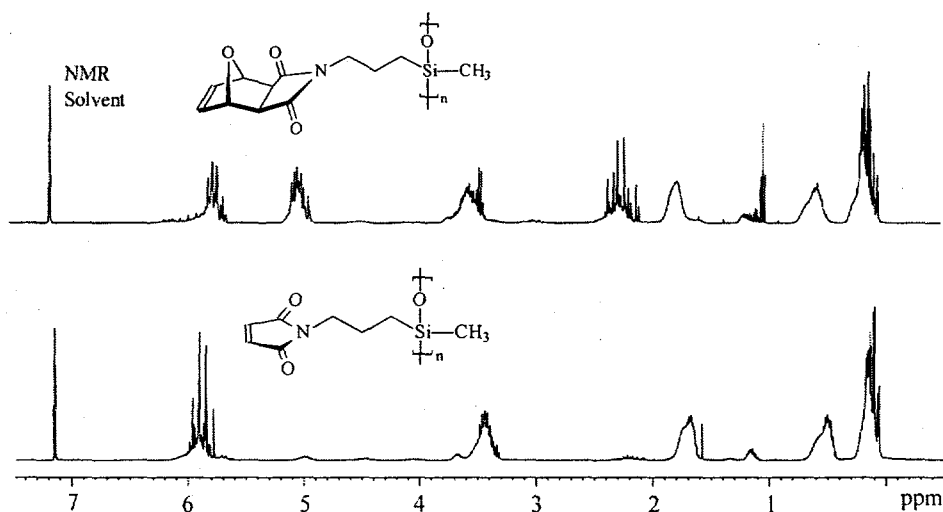
**Figure 5.** TGA of protected maleimide-siloxane polymer.

**Filled hybrid composite.** The siloxane polymers described above represent organically functionalized silica particles. In macroscale composite chemistry, where silica filler is added for reinforcement purposes, the filler is bonded to the organic polymer with coupling agents. In our system, the filler is built on a nanoscale and is functionalized. The functionalized silica can then be reacted with an unsaturated polymer or a monomer. Heating of a mixture of the silica and an unsaturated polymer results in coupling of the maleimide with the polymer at sub

vulcanization temperatures (by an Alder-ene or a radical process). The siloxane system functions as both filler and coupling agent. This work will be described elsewhere.

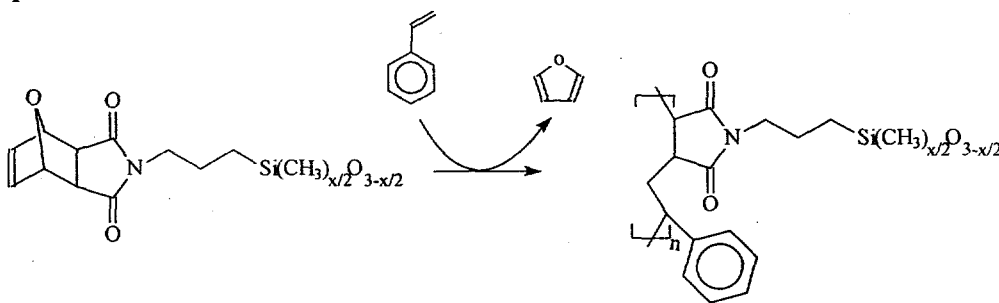
Alternatively, the functionalized silica can be copolymerized with an organic monomer such as styrene. In this process, a styrene-maleimide copolymer was formed in which the polymer and silica were interweaved resulting in formation of a filled nanocomposite. Figure 7 shows the reaction process.

The composite, which was prepared as described in the experimental section, was a clear colorless insoluble material that did not exhibit phase separation between the inorganic and organic components (on a macroscopic scale).



**Figure 6.**  $^1\text{H}$  NMR spectra of protected (top) and deprotected (bottom) siloxane polymers.

The infrared spectrum of the filled composite is shown in Figure 8 and reveals the expected absorbances, in particular, CO ( $\nu = 1703\text{ cm}^{-1}$ ), SiO ( $\nu = 1078\text{ cm}^{-1}$ ) and C-N ( $\nu = 1402\text{ cm}^{-1}$ ). The absorbance frequencies of the vinylic group of unreacted styrene, i.e., C=C stretch ( $1630\text{ cm}^{-1}$ ), =C-H out of plane bending ( $992, 909\text{ cm}^{-1}$ ) [4] are not present in the spectrum of the composite.



**Figure 7.** Reaction of the maleimide functionalized silica polymer (filler) with styrene.

Further evidence that the styrene and the maleimide functional groups of the siloxane had reacted was provided by the  $^{13}\text{C}$  NMR. The  $^{13}\text{C}$  NMR spectrum of the deprotected siloxane monomer exhibits signals at 171 ppm (CO), 134 ppm (C=C) and several signals between 58 and 2 ppm, corresponding to the aliphatic carbons. In the solid state  $^{13}\text{C}$  NMR of the filled styrene-

maleimide copolymer the peak at 134 ppm disappears and a peak at 128 ppm appears, the former indicating loss of the vinylic maleimide carbons (i.e., reaction with styrene) and the latter indicating the presence of aromatic carbons (phenyl group of the styrene component).

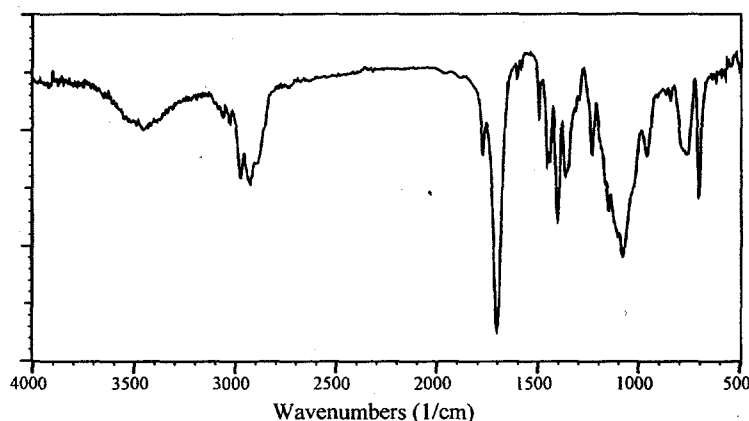


Figure 8. IR spectrum of the filled styrene-maleimide composite.

## SYMMARY

This paper describes the preparation of maleimide functionalized siloxane polymers. The polymers were prepared by the sol-gel polymerization of the corresponding alkoxysilane monomer. Prior to polymerization, the monomer was reacted with furan by a Diels-Alder reaction to protect the maleimide against Michael addition (e.g., of water, which was added during the sol-gel process). Subsequent to sol-gel polymerization, the maleimide was activated by thermal removal of the furan protecting group (retro Diels-Alder reaction). The maleimide functionalized silica was then copolymerized with styrene to form a filled styrene-maleimide nanocomposite.

Future work will focus on determining the effect of varying the size (molecular weight) of the inorganic component of the composite. Transmission Electron Microscopy will be used to determine domain size in the composite and the mechanical properties of the materials will be measured.

## ACKNOWLEDGMENTS

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