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Towards Tailored Interphase Formation Utilizing Surface-Active Benzylsulfonium Salts as Cationic Initiators

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Introduction

The bonding between reinforcement and matrix in a composite involves a microscopic interphase region that is generally composed of a polymer network formed by multilayer buildup of a coupling agent attached to the surface of the fiber into which the matrix can propagate and bond. The main purpose of the interphase is to provide a structural lattice that will allow for good energy transfer from the matrix to the reinforcement.[1] The interphase plays a dominant role in the fracture toughness properties of composites and in their response to aqueous and corrosive environments. Being able to develop tailored interphases will allow control of composite properties to optimize strength, modulus, and toughness.

Our conceptual approach is based on being able to tailor the formation of the interphase by covalently attaching compounds to the surface of glass that are capable of initiating the polymerization of various monomers. Here we report the synthesis of novel benzylsulfonium salts capable of initiating the polymerization of cationically active monomers. Similar salts have been extensively explored as thermal cationic initiators of spiro orthocarbonates and bicyclo orthoesters,[2] epoxy resins,[3] styrene,[4] and vinyl ethers.[5,6,7] The general structure of the surface active initiator investigated is shown in Figure 1.

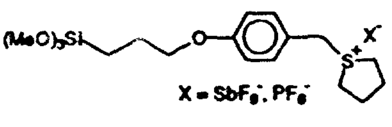


Figure 1: Surface-active benzylsulfonium salt

Experimental

The general procedure for the synthesis of the benzylsulfonium salt initiators (surface active (7), surface inactive (6)) is outlined in Scheme 1. Isolated yields on intermediates 1-6 were all above 90 %. ^{13}C NMR spectra of the products are shown in Figure 2. Surface coupling of 7 with silica gel (surface area ≈ 500 m^2/g) gave 25 % by weight (TGA) add-on of sulfonium salt. ^{13}C CPMAS and ^{29}Si CPMAS solid state NMR confirmed the presence of 7 on the surface (Figure 3).

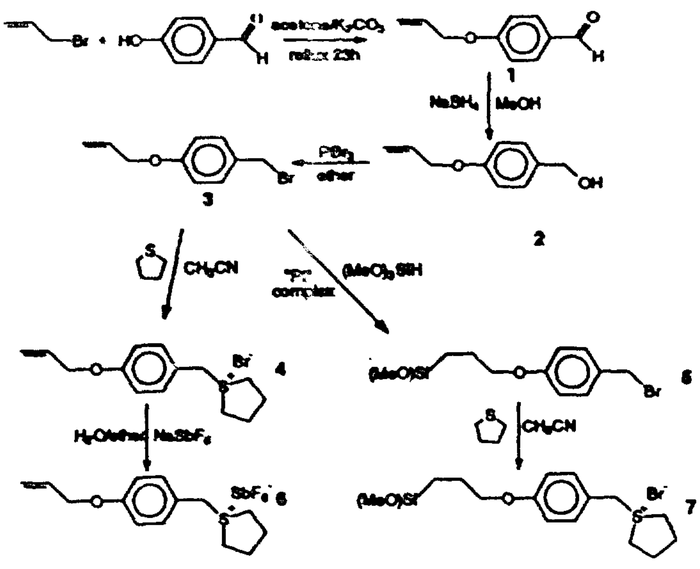
Characterization

Thermal analysis was preformed using a TA Instruments SDT 2960 (TGA) and DSC 2920, controlled using a TA Thermal Analyst 2100. TGA's were run at a heating rate 20 °C/min in air or N_2. DSC's were run at 10 °C/min with nitrogen purge. Solution ^{13}C NMR were preformed on a Bruker AC-200 while solid state ^{13}C CPMAS, and ^{29}Si CPMAS were run on a Bruker MSL-400.

Results and Discussion

The ability of un-bound (6) and silica-bound sulfonium salt (SbF_6-silica) to initiate polymerization of epoxy compounds was investigated by DSC. The epoxy resin used was Dow's DER 324 resin (DGEBA based). Figure 4 shows the DSC thermograms for DER 324 with 1.0 wt% 6. Heating the sample to 300 °C gave two exotherms, one at 100 °C, the other at 240 °C with roughly equal heat liberated (DER 324 showed no transitions when run without initator). The first exotherm is believed to be due to the cationic initiation and partial polymerization of the epoxy groups. As the sample vitrifies and the temperature increases, the cationic mechanism is terminated and no more reaction occurs. At higher temperature, further reaction can take place through etherification to complete the conversion of the epoxy groups.

The Tg of this sample was found on the second run to be 82 °C, and did not increase after repeated heating cycles to 300 °C. FTIR analysis of the DSC sample indicated a high degree of conversion as indicated by disappearance of the epoxy stretch at



Scheme 1: Synthesis of benzylsulfonium salts

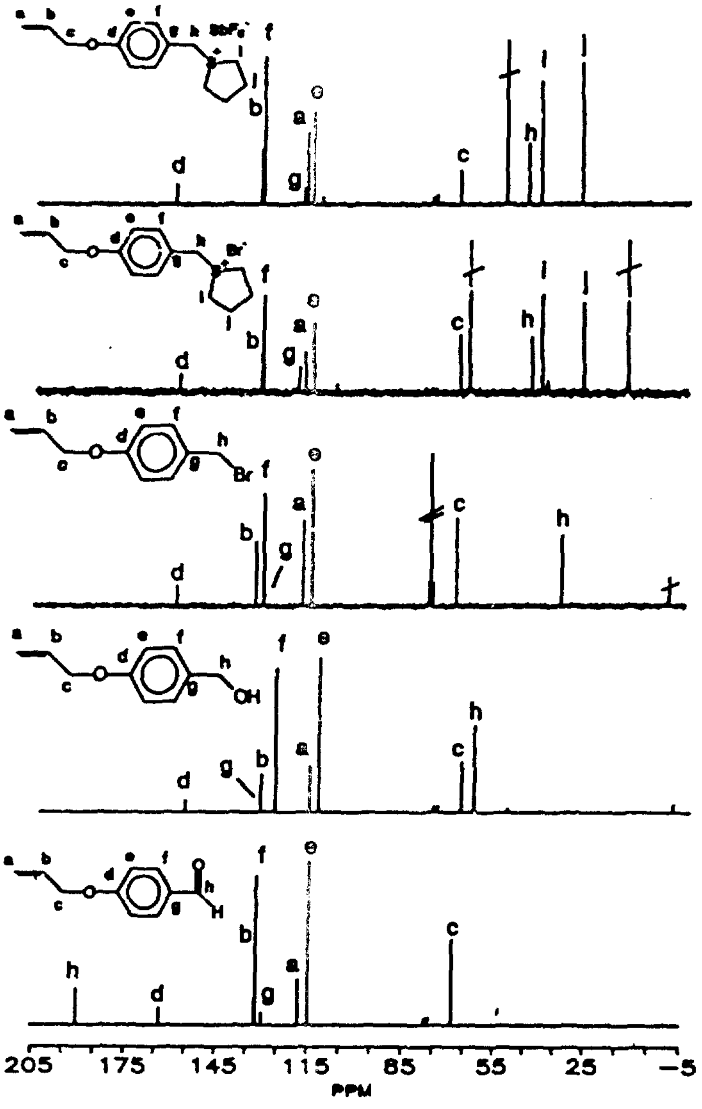


Figure 2: ^{13}C NMR of products in Scheme 1. All spectra run in $CDCl_3$ except 4 (H_2O, D_6-DMSO insert).

915 cm^{-1}.

Anion exchange to give a non-nucleophilic counterion is necessary in order to have an active initiator. Exchange of the bromide form of the salt on the surface (Br-silica) was done in a manner similar to that by 4. Figure 5 shows the DSC thermograms for Br-silica and SbF_6-silica with DER 324 (38 % and 40 % silica, wt/wt respectively). SbF_6-silica with DER 324 showed one major exotherm centered at 215 °C and a broad, shallow exotherm at 145 °C liberating a total heat of 391 J/g epoxy (correcting for the weight of the silica in the sample). FTIR analysis of this sample indicated high conversion. The Br-silica only showed the lower, broad exotherm and the absorption for the epoxy ring was still observable in the IR spectrum of this sample.

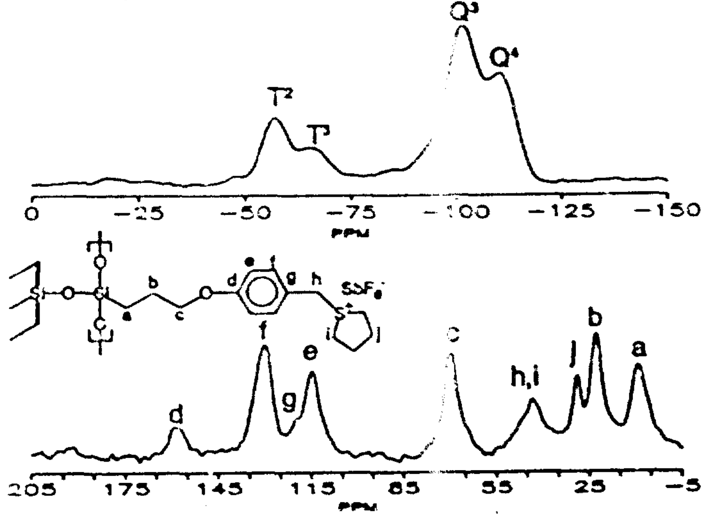


Figure 3: Solid state ^{13}C CPMAS (bottom) and ^{29}Si CPMAS (top) NMR of surface-bound sulfonium salt.

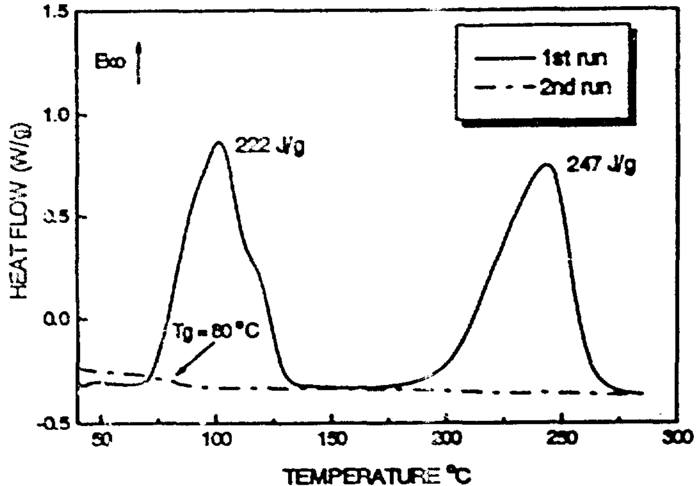


Figure 4: DSC thermograms for DER 324 with 1.0 wt% 6.

The reduction of the lower exotherm for SbF_6-silica/DER 324 relative to that seen for un-bound initiator indicates interference by the silica with the cationic mechanism of polymerization. FTIR and ^{29}Si solid state NMR indicate the presence of surface Si-OH. The influence that surface hydroxyls have on the ability of the sulfonium salts (bound and un-bound) to polymerize epoxies was investigated by DSC with samples of unmodified silica gel 30% wt/wt (dried 24h at 120 °C under vacuum) and DER 324 with 1.0 wt. % 6. Two exotherms (DSC not shown) were seen but both transitions liberated less heat than expected for complete conversion (225 J/g epoxy vs. 470 J/g epoxy from Figure 4). The lower temperature transition showed the greatest reduction (33.4 J/g epoxy in the presence of unmodified silica vs 222 J/g epoxy, Figure 4). It is assumed that either absorbed moisture not removed in the drying process and/or surface hydroxyls interfere with the initial reaction, killing the cationic polymerization (as indicated by the reduction in the lower transition). However, enough epoxies react initially to allow for the higher temperature reaction. The Br-silica doesn't allow for either propagation mechanism to occur. Finally, unmodified silica with resin (no initiator) has a DSC thermogram similar to the Br-silica showing no upper exotherm, and no reduction in the epoxy stretch at 915cm^{-1} after heating to 290 °C.

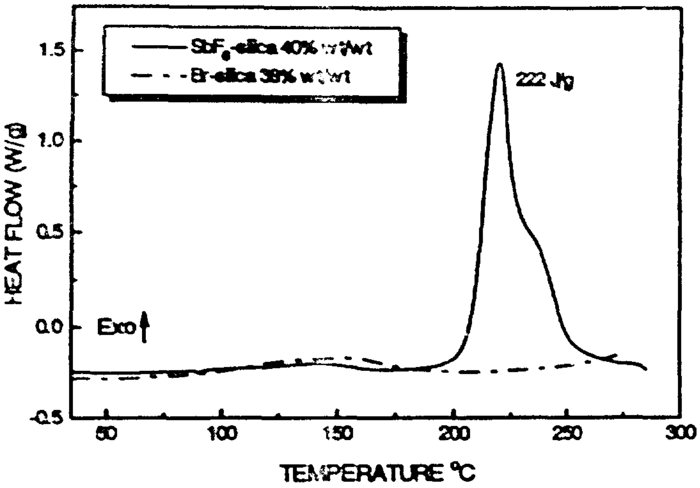


Figure 5: DSC thermograms for DER 324 and surface-bound sulfonium salts.

Conclusions

The sulfonium salt initiator (6) has been shown to cure the DGEBA resin to high conversion upon heating to 300 °C. In addition, the surface bound initiator with SbF_6^- counterion will also cure the epoxy resin to a high degree of conversion whereas the Br^- form will not. Quantitative determination of extent of cure, mechanism for each cure stage, and overall surface concentration effects is being investigated.

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