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FILLER/ POLYCARBOSILANE SYSTEMS AS CMC MATRIX PRECURSORS

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ABSTRACT

Pyrolytic conversion of polymeric precursors to ceramics is accompanied by loss of volatiles and large volume changes. Infiltration of a low viscosity polymer into a fiber preform will fill small spaces within fiber tows by capillary forces, but create large matrix cracks within large, intertow areas. One approach to minimizing shrinkage and reducing the number of required infiltration cycles is to use particlulate fillers. In this study, Starfire allylhydridopolycarbosilane (AHPCS) was blended with a silicon carbide powder, with and without dispersant, using shear mixing. The polymer and polymer/particle interactions were characterized using nuclear magnetic resonance, differential scanning calorimetry, thermogravimetric analysis and rheometry. Polymer/particulate slurries and suspensions were used to infiltrate a rigidized preform of an eight ply five harness satin CG Nicalon fiber having a dual layer BN/SiC interface coating, and the resulting composites characterized by optical and scanning electron microscopy.

INTRODUCTION

Fabrication of ceramic matrix composites (CMC) by pyrolytic conversion of preceramic polymers typically is accompanied by large volume shrinkages which depend on the char yield of the starting polymer, as well as bond redistribution and densification which take place at higher temperatures. In a ply layup material, such shrinkages often are accompanied by transverse cracking. In the situation in which matrix is infiltrated into a rigidized preform, the preform itself does not shrink during pyrolysis, and, if the interface is sufficiently weak, the matrix breaks into blocks, or islands, around which subsequent precursor can be reinfiltrated. Frequently 6-15 cycles can be required for optimal densification.

One approach to minimizing the number of reimpregnation cycles required, and hence reduce material cost, is to use active or inert fillers[1-3] which can either be blended with the precursor polymer, or slurry infiltrated into the preform first, followed by reimpregnation with the matrix precursor. If a suspension having the appropriate rheological properties for infiltration into a given preform architecture can be obtained to produce a relatively uniform distribution of filler, the number of matrix infiltrations and formation of closed porosity both can be minimized. Key parameters to achieving this are filler volume fraction, particle shape and size distribution, particle/polymer interactions, the ability of the suspension to wet the preform, and infiltration techniques optimized for the preform architecture.

Allylhydridopolycarbosilane (AHPCS)[4-7], having an allyl content of 7.5% (Starfire Systems, Watervliet, NY), was selected as the polymer precursor for this study, as it converts to a near stoichiometric SiC at relatively low temperatures. Starck UF 10 α SiC was used as the filler, and a glycol copolymer (Dow EP 530 evaluated as a dispersant. An eight ply five harness satin Nicalon fiber coated with a dual BN and SiC interface coating (Dupont Lanxide Composites, Inc., Newark, Delaware) was chosen as the preform architecture. Two composite panels, using a "standard" 5% allyl AHPCS and repeated (10) infiltration and pyrolysis cycles and autoclave or free standing cure, were fabricated to characterize the current baseline microstructure and materials properties. The polymer precursor was characterized by ^{1}H and ^{29}Si nuclear magnetic resonance spectroscopy (NMR), gel permeation chromatography (GPC), simultaneous thermogravimetric analysis (TG) and differential scanning calorimetry (DSC), and rheometry. Composites were characterized by optical and field emission scanning electron microscopy.

RESULTS AND DISCUSSION

AHPCS is a polycarbosilane having the nominal structure shown in Figure 1, as confirmed by ^{1}H and ^{29}Si NMR.[6,7] The allyl content can be tailored, and batches with 5% and 7.5% as formulated allyl content (based on the number of Si atoms) were characterized. The higher allyl content materials were found to be of lower viscosity among several batches, and the viscosity remained more consistent with refrigerator storage over a period of months; therefore the 7.5% allyl polymer was chosen for filler studies. Residual tetrahydrofuran (THF) was present in all the materials received, as well as a small amount of residual hexane in some batches. Ratios of $SiH:SiH_2:SiH_3$ of 1.0:1.45:0.45 were observed in the 7.5% material, with

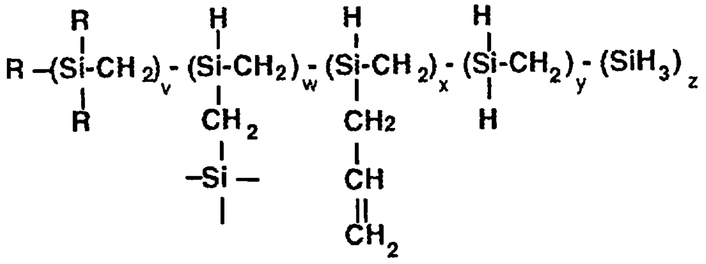

Figure 1. AHPCS structure

R_4Si groups being negligible; the 5% allyl polymer, in contrast, exhibited some R_4Si content on storage, consistent with its observed higher viscosity. Nominal molecular weight of the 7.5% AHPCS was determined as M_n of 10,000, M_w of 15,500 by elution in toluene, using a refractive index detector. (Elution in THF produced extremely high and varying values of M_w which were inconsistent with observed viscosities, leading to the conclusion that the material was polymerizing on the column, likely the result of peroxide presence in the unpreserved THF, even when using freshly distilled solvent.)

Simultaneous DSC/TG characterization (Figure 2) showed a char yield at 1200°C of approximately 77% (argon atmosphere). A characteristic exothermic peak is seen at 230°C, with an enthalpy of 117 J/g, corresponding to further polymerization; the peak position and exotherm were well reproduced from batch to batch and run to run. (The exotherm at 1050°C is likely the result of silicate formation with the alumina crucible; the same behavior was observed for runs in a zirconia crucible, and diminishes as the crucible is reused.) "Popping" of material from the crucible, with accompanying weight loss, was frequently observed at

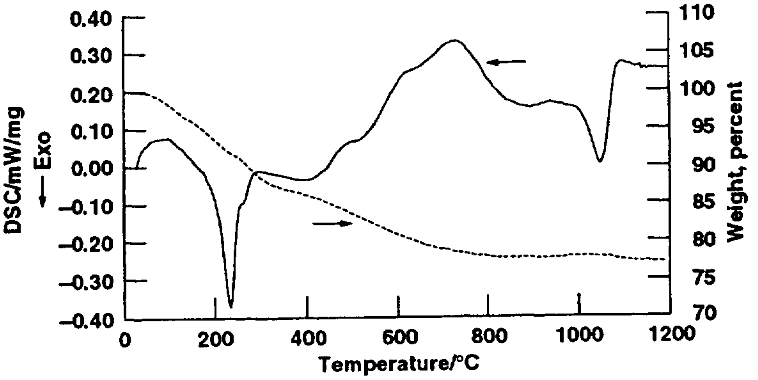

Figure 2. DSC/TG trace of 7.5% AHPCS

250-260°C, due to buildup of evolved gases. On the basis of the DSC/TG results, heating cycles for composite fabrication were established with holds near the onset of the polymerization region.

Viscosity of the neat polymer, and the polymer with addition of 0.06-0.5 vol. % of a glycol copolymer (Dow EP 530, 2000 molecular weight, 100 cps viscosity) were determined using a rheometer with rotating spindle and cylinder over shear rates of 10 to 100 sec^{-1}. Addition of the glycol produced only slight increase in shear viscosity of the polymer, and shear thinning behavior was observed for the polymer alone and over all glycol concentrations (Figure 3). Polymer/filler mixtures using 25 vol. % α SiC powder (Starck UF 10, 90% <1.8 μm, BET 9-11 m^2/g surface area) were prepared by controlled shear rate mixing at a rate of 3 x 10^3 min^{-1}. The influence of dispersant on the polymer/ filler system is shown in Figure 4. At 0.5% glycol, the AHPCS/ filler system viscosity increased from nominally 20 cps (system with no glycol), to > 1700 cps. For system without dispersant, as well as with glycol additions of 0.25-0.5% EP 530 (0.5% is offscale for this plot), the system was shear thinning; at 0.125% glycol the curve is almost flat, and at 0.06% EP 530 the suspension viscosity is at a minimum value of 170 cps, which is lower than that for AHPCS/filler alone, and a slightly shear thickening behavior is seen. The large influence of glycol addition on viscosity is indicative of strong glycol/particle interaction, and with glycol addition, particles

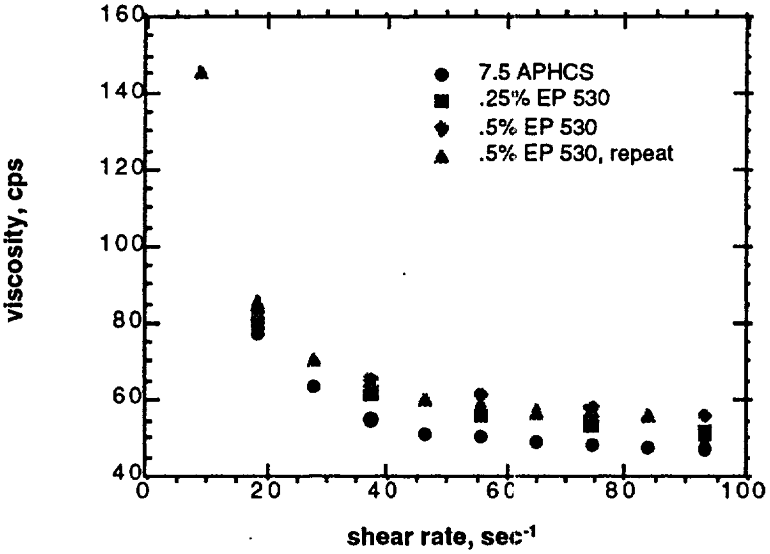

Figure 3. Viscosity of AHPCS with EP 530 addition

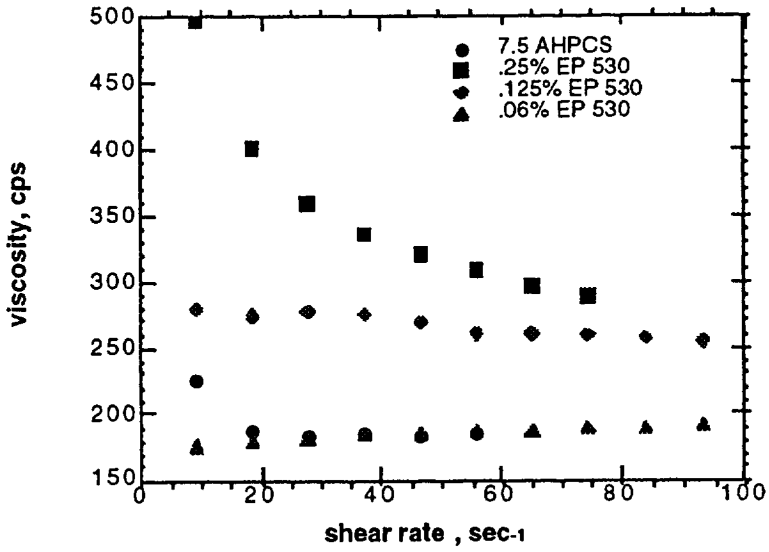

Figure 4. Viscosity of AHPCS/ 25 v/o UF10 SiC with polyglycol addition

have remained in suspension for several weeks. Because of its minimum viscosity and flat response with shear rate, the 0.06% polyglycol system was the one chosen for composite fabrication.

"Baseline" system composites were fabricated by Starfire Systems with their "standard" 5% AHPCS infiltrated into 2D preforms of 40 vol. % ceramic grade Nicalon fiber, a dual layer 11 vol. % BN interface coating and 28 vol. % SiC overcoating, and nominally 20 vol. % porosity, utilizing 10 infiltration cycles with either an autoclave or ambient pressure cure, followed by pyrolyis. Microstructure of autoclaved composites showed blocks of matrix material with varying gray levels, most probably indicative of the differing number of processing cycles and levels of densification each had experienced (Figure 5). The panel which underwent ambient pressure cure exhibited more matrix voids than the one which was autoclaved.

Composite coupons were fabricated to evaluate matrix infiltration with the filled system, with and without dispersant, after a single impregantion and pyrolysis cycle, based on the rationale that the matrix structure produced on the first cycle determines the matrix architecture and channels available to subsequent impregnation cycles. The preforms were infiltrated under vacuum with the polymer/filler slurry (no dispersant) or suspension (with EP 530 addition); no solvents were used. The panels were cured in argon at ambient pressure, followed by ambient pressure pyrolysis in argon to 1200°C.

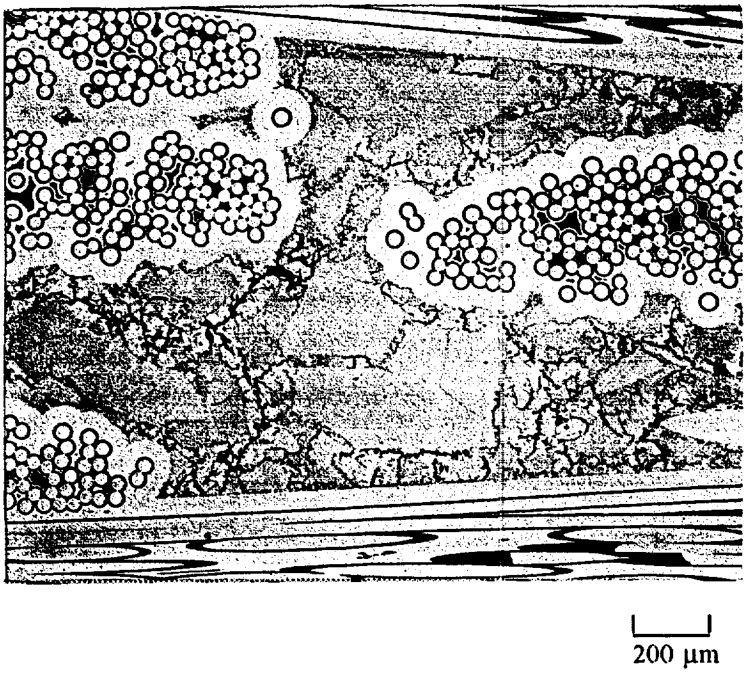

Figure 5. Autoclave processed composite, 10 infiltration cycles using 5% AHPCS

Optical micrographs of polished sections of composite coupons infiltrated without use of the glycol dispersant showed infiltration of the slurry into many small channels as well as wetting around the perimeter of large pore spaces, and filling of the "corners" of larger spaces. (Accessibility of entire space to surface infiltration was confirmed by reinfiltration of the composite with epoxy containing a fluorescent dye in preparation for polishing.) SEM characterization (not shown here) revealed that, within the larger preform spaces, islands of the polymer-derived particulate matrix exhibited a gradation of particulate concentration, indicative of separation of polymer and powder during the composite processing. With addition of 0.06 % glycol (Figure 6), there is infiltration of many small spaces, improved infiltration of some large cavities, and, in the larger spaces, powder separation has been averted. More recent pressure infiltration of the polymer/particulate/dispersant suspension shows an increase of 60% in weight gain in the first cycle compared with vacuum infiltration.

SUMMARY

An allylhydriopolycarbosilane (AHPCS) having a formulated allyl content of 7.5%, when combined with 25 vol. % UF10 α SiC powder, has been established

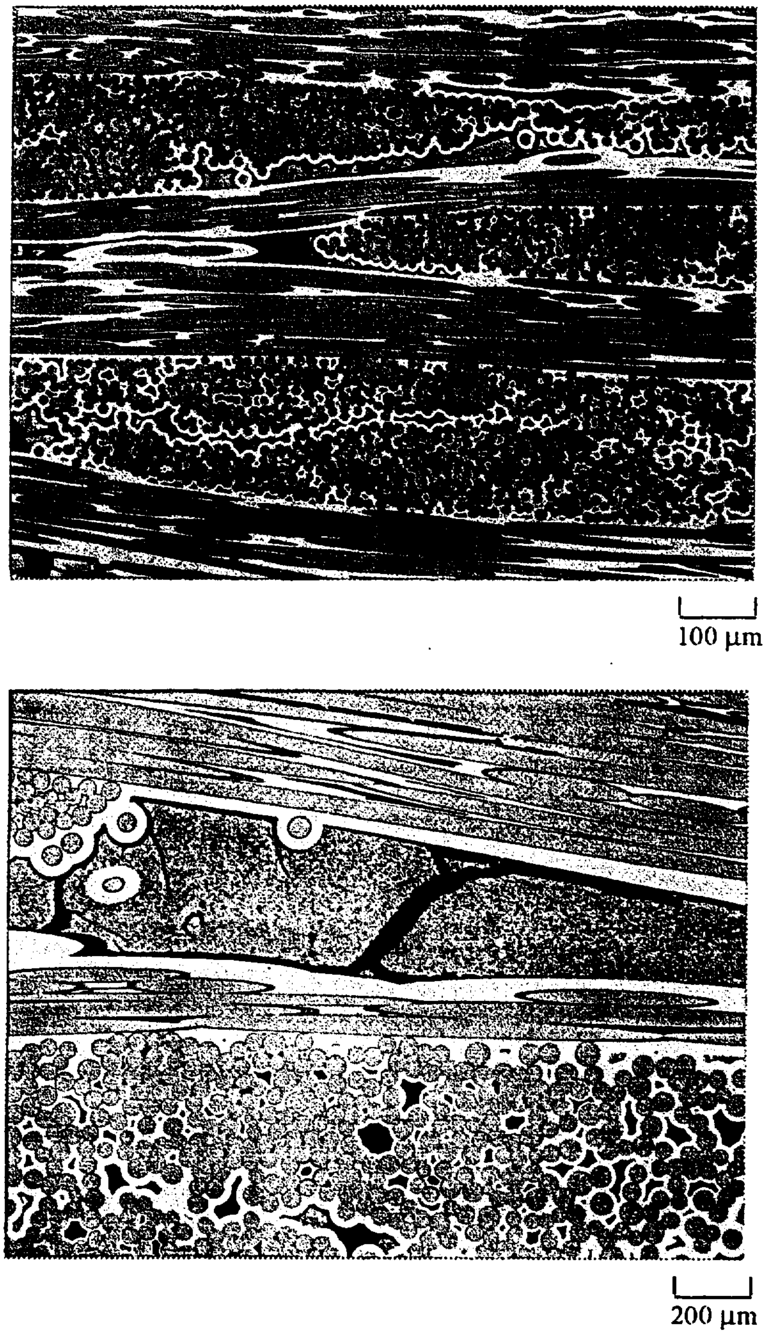

Figure 6. Optical micrographs of composite with 7.5 AHPCS/25 vol. % UF 10 SiC/ 0.06 vol. % EP 530 matrix, prepared by vacuum infiltration and free standing cure and pyrolysis.

to have viscosity and rheological behavior appropriate for infiltration of a 2D Nicalon/BN/SiC preform with approximately 20 vol. % porosity. A suspension of the polymer and filler can be stabilized by addition of 0.06 vol. % EP 530 polyglycol. Infiltration of smaller channels, and wetting and partial infiltration of larger pore spaces, can be attained by vacuum infiltration. Pressure substantially increases infiltration. Optimization of filler concentration, with simultaneous optimization of glycol addition, number of infiltration pyrolysis cycles, pressure, and consistent infiltration technique remain to be established.

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