Particle Functionalisation for Dispersion of inorganic 'Dust' within Low Density Polymeric Targets

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Introduction

Low density materials are often desired for high power laser targets because the length of laser-matter interaction can be increased without increasing the mass of material relative to solid targets.

Dispersion of nano and micro particulate within the 'foams' provides routes to generating x-rays which are often desired for high power laser experiments, as well as simulating astrophysical phenomena[1].

Dispersion of the particles can prove to be difficult due to aggregation caused by unfavoured interactions between the chemical phases. Methods of improving particle dispersion in the low density phase have clear benefits for the quality of laser targets available to users. This paper reports on experiments carried out on the use of silanization to improve particle dispersion in foams.

Silanization

Silanization is the process by which alkoxysilane molecules are attached to surfaces via the formation of a covalent linkage between the silane and surface hydroxyl groups.

The mechanism proceeds through activation of the hydroxyl group (typically with an acid or base) which in turn reacts with the silane via a condensation reaction. This leaves a Si-O link between surface and silane.

The silanes are often attached to a functional moiety which allows for chemical modification of the surface[2,3]. This can be used to alter dispersibility in liquid media and interaction with other components.
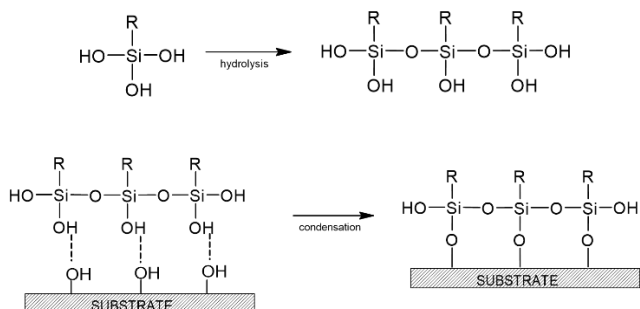

Figure 1: Schematic of the silanization process

This report describes the application of hydrophobic silanes to hydrophilic silicon dioxide nanoparticles to improve dispersion in an organic solvent.

The coated nanoparticles are then incorporated into the low density foam process to produce highly dispersed nano-SiO_2 doped CH foams.

Choice of silanization agent

Two silanization agents were used for this experiment: trimethoxymethylsiolane (TMMS) and triethoxyoctylsilane (TEOS).

TMMS has the benefit of a faster reaction rate and, being a smaller molecule, will have less effect on the overall diameter of the nanoparticles. TEOS has a long 8 atom hydrocarbon chain providing better coating of the particle surface and should improve dispersion, relative to TMMS.

Characterisation

The mass of coating on the particles was characterized by thermogravimetric analysis (TGA) during which the organic portion was burned off in a nitrogen atmosphere leaving the more thermally stables SiO_2 and thereby providing the desired ratio of coating to particle.

ATR FTIR was used for surface analysis of functional groups showing a notable presence of hydroxyl groups.

Micro-computed tomography (CT) was used to assess the distribution of the particles in the foams which was required because the foams are opaque and require internal characterisation to determine distribution.

Materials and methods

SiO_2 nanoparticles (US-nano) were dispersed in water at a 10% w/v loading. This was stirred at 300 rpm for 10 minutes at 60°C. To this NaOH (Sigma Aldrich) was added dropwise at a concentration of 5% relative to SiO_2 to hydroxylate the surfaces.

Silanes were hydrolysed by mixing in deionized water at a 10% concentration. This solution was then added dropwise to the SiO_2 dispersion; the reaction was allowed to run for 3 to 16 hours.

The product was worked up by 3 washes with deionized water followed by evaporative drying.

Foams were made by the established supercritical drying procedure. A solution of trimethylolpropane triacrylate (TMPTA) and Brij 40 solvent are made to the desired TMPTA density (w/v) with a 5% loading of benzil. This is cured by UV to form a gel which is then solvent exchanged with methanol. The exchanged gels are processed by CO_2 exchanging until no methanol remains. The CO_2 is then heated, under pressure, to

supercritical conditions. This is then slowly vented off leaving a low density foam with the same dimensions as the original gel.

To incorporate particles they are introduced during the solution phase.

Results

Initial results showed a noticeable increase in surface OH groups on the SiO_2 after the surface activation. Both basic and acidic routes were explored, with NaOH showing the best performance.

FTIR analysis was used to assess the reduction of OH groups on the surface and subsequent replacement with aliphatic moieties. TMMS had finished reacting after 4.5 hours with no detectable increases after that. TEOS took 12 hours to reach maximum conversion.

The FTIR in Figure 2 shows a typical result of silanization with a prominent OH stretching peak around 3300 cm^{-1} which was then less visible after silane treatment.

TEOS performed better at particle surface coverage although requiring a longer reaction. This was expected due to the much longer aliphatic chains.
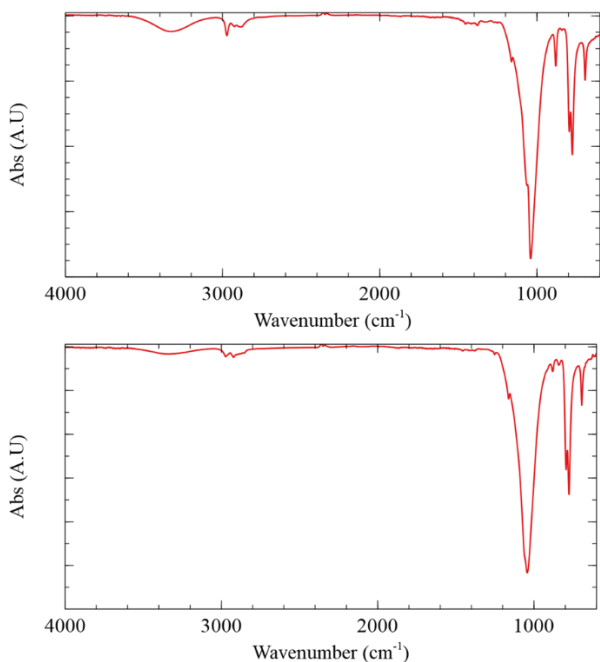
Figure 2: FTIR spectra of silica powders before (top) and after coating (bottom)

The functionalised powders were initially tested in the Brij 40 organic solvent with stirring and probe sonication. Dispersion was found to be comparable to that found with the untreated powders in water. However, the dispersion stability was significantly reduced; dispersions were stable for 2-4 hours for the modified samples compared to weeks (or more) for raw silica. The outcome for this was that it was necessary to use the powders as soon as possible after reaction.

Upon application in the foam synthesis process the powders maintained dispersion. This process was helped by the fact that particles are spatially fixed after the UV curing process so it is only necessary to ensure dispersion for up to 30 minutes.

The supercritical drying process was not affected by the presence of powders. CT analysis of the powders post processing showed good dispersion of particles much improved relative to the untreated powders. No improvement was seen with the TEOS

coated particles, thus TMMS was used going forward due its simpler reaction.

Figure 3 - An example of the changes of dispersion stability before (left) and after (right) silanization treatment of the particles [in Brij 40, after 3h]

Further work

Future work for this project will involve testing surface functionalization for other commonly used dust particles. Some of this will entail oxidation of metals followed by silanization; other work intends to look at thiolation. The latter is especially useful for gold powders because the Au-S bond is readily formed and there already exists a variety of molecules with the thiol group containing a number of moieties with which to effect changes in surface chemistry.

A final avenue of research is to introduce alkene functionality to particle surfaces via the same surface techniques already discussed. The advantage of this will be to chemically incorporate the particles into the foam which is produced through a vinyl group free radical addition polymerization.

Conclusions

Surface functionalization of silica particles was achieved through established silanization techniques to generate changes in particle surface chemistry notably changing from a hydrophilic to hydrophobic surface. This allowed for a highly dispersed incorporation of the nanoparticles into a low density foam, which can been used for 'dusty target' experiments.

References

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