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Synthesis of polyorganosiloxane particles

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Summary Hybrid particles have been synthesized from methyltriethoxysilane (MTEOS) by the sol-gel process. The particle size, size distribution, particle surface morphology conductivity and pH of the reaction solution at different reaction times were determined. Compared with tetraethyl orthosilicate (TEOS) and p-(chloromethyl)phenyl-trimethoxysilane (CMPTOS), MTEOS has a slower hydrolysis rate.

Introduction

A number of organosiloxane polymer systems have been prepared but no organosilixane particles were reported. Most of these studies have focused on tetraethyl orthosilicate (TEOS) or tetramethyl orthosilicate (TMOS) systems[1-5] while organic-inorganic hybrid materials research has been directed more to controlling aging, drying, and the dispersion of the polymers in silicon gels at the molecular level. Wei[6] and Novak[7] reported a novel route to decrease the volume shrinkage in organo-silicone hybrid materials by releasing small molecules and combining a simultaneous free radical polymerization. Another route for decreasing the volume shrinkage of these hybrids is to utilize supercritical drying[8]. Recently, Chujo and his coworkers[9] have blended several polymers in the sol-gel process with TEOS to develop new hybrid materials.

A novel approach has been explored in our laboratory to prepare organosilicone particles, using trifunctional silanes as the monomer with one alkyl group covalently bonded to the silicon atom. In this report, MTEOS (methyltriethoxysilane) was used to synthesize several micron size particles under base-catalyzed conditions.

Experimental

Methyl triethoxylilane (4 mL), 90 mL of 5 M alcoholic ammonia solution and 6 mL of water were mixed and added to a one-neck flask which was then sealed. The reaction flask was mounted on a shaker and agitated at room temperature for 24h. The crude product was washed six times with ethanol to remove the remaining water and ammonia. Fine particles were obtained after the ethanol was removed by evaporation.

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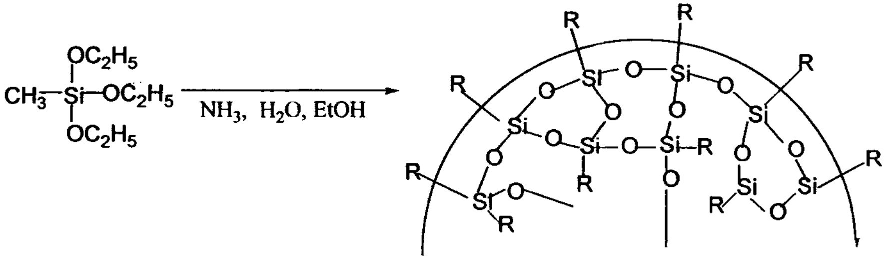
Results and discussion

According to a SEM analysis, the particles were about 3 µm in size with a highly porous surface. Density analysis showed that the MTEOS particles were only 1.31 g/cm^3 which is much lower than 2.5 g/cm^3 for glass beads. The IR spectrum showed no hydrogen bond absorption for H_2O at 3400-3600 cm^{-1}. The TGA demonstrated no weight loss below 180 °C. Neither the TGA nor IR analysis detected any surface water on the particles prepared from MTEOS by the sol-gel process indicating a hydrophobic surface. After calcination at 700 °C for 10 min, allowing the organic portion to pyrolyze, the surface of the particles changed from hydrophobic to hydrophilic. The enhanced hydrophilic character was evident by an observed increase in the particle dispersibility in water and the appearance of adsorbed H_2O on the particle surface by IR.

Generally, the condensation of silanes prefer to maximize the number of Si-O-Si bonds and minimize the number of terminal hydroxyl groups. Based on Iler's "particle grow" mechanism[10], after nucleration, the particles basically grow from the nuclei by internal condensation of the hydroxyl groups within the particles which would leave the methyl groups on the surface.



Although the conductivity and pH of the system changed very little during the reaction, changes in the ammonia and water concentrations affected the particle size. An increase in the ammonia concentration or the r-value (H_2O/Si) produced larger MTEOS derived particles. This is consistent with the results of Stöber[11]. However, these two factors played different roles in the sol-gel process with MTEOS. A high concentration of ammonia (NH_3/Si=30) produced a broad particle size distribution and an increase in the r-value favored the formation of uniform particles.

Reaction time also affected the particle size and particle size distribution due to the slow hydrolysis rate. Small particles (about 1 µm) formed within 30 min. After 3 h, the particle size did not change but the number of particles increased. According to the TGA data, the hydrolysis was complete in about 8 h. This indicated that the MTEOS hydrolyzed more slowly than TEOS[5]. In general, if the hydrolysis rate is higher than the condensation rate, complete hydrolysis will occur; if the hydrolysis rate is equal to or smaller than the condensation rate then the hydrolysis will be followed immediately by condensation. In the second case, some unhydrolyzed alkoxide groups will remain in the particle due to incomplete hydrolysis, thus the MTEOS derived particles may have some residual unhydrolyzed ethoxide groups.

In conclusion, a novel and porous hybrid particle can be obtained from MTEOS by sol-gel process. The particle size and particle size distribution can be controlled by appropriate catalyst and water concentrations and reaction time.

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