

Photochemical Alteration of the Stability of Polymer Nano-Agglomerates

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ABSTRACT

In this work the mechanical stability of nanoscale polystyrene (PS) agglomerates was examined by experimental determination of the fragmentation energy by impact fragmentation. The potential of Aerosol-Photochemistry was investigated to alter agglomerate stability. Spherical particles of PS were generated by nebulization of a PS-CCl₄ solution. The surface modification of the particles was performed in a continuous vacuum ultraviolet (VUV) reactor before agglomeration of the primary particles was allowed. The radical chemical reactions induced by VUV radiation that occurred on the particle surface were dependent on the carrier gas composition and dose of irradiation. Thus, the interparticle forces could be enhanced by increasing the number of carboxyl groups (hydrogen bridge linkage, condensation reaction) on the particle surface and weakened by introducing chlorine groups (repulsive interaction).

Keywords: interparticle forces, bond energy, polymer nanoparticles

1 INTRODUCTION

Polymer nanoparticles and polymer coatings on nanostructures are gaining more and more attention in areas of application where special properties of materials need to be protected against an aggressive environment to retain their activity or where timed release is desired. For optical and electronic applications quantum dots have very attractive properties which in some cases (e.g. Si) require protective coating against oxidation. In pharmaceutical applications nanoparticle formulations allow the delivery of oleophilic substances into aqueous systems. The high reactivity of nanoparticles may however necessitate a coating to prevent local poisoning effects due to the rapid dissolution kinetics.

A general problem in the handling of nanoparticle products is their tendency to form agglomerates with properties differing from the ones of the primary particles. On one hand, the high surface energies of nanoparticles favor the reduction of overall surface area by maximization of the number of contacts as well as chemical bond formation and sintering. On the other hand, the small dimensions of the particles make deagglomeration using shear fields or inertia-based methods like sonication

inefficient. In other cases of application however, strong interparticle contacts are desired. The aim of this work was thus to gain control over the strength of interparticle bonds in polymer nanoagglomerates as a decisive product parameter. As a model system, polystyrene (PS) particles were chosen. The interparticle bonds are due to van der Waals interactions and hydrogen bridge linkage as well as chemical bonds. Chemical bonds can be formed by the condensation reaction between two carboxyl groups. The stability of a particle-particle bond can also be weakened by the introduction of surface groups like chlorine or fluorine, which strongly repulse each other when brought in close proximity. The alteration of the interparticle bond strength was achieved by photochemically induced reactions, changing the chemistry of the particle surface.

2 EXPERIMENTAL

The PS particles were generated by nebulization of a PS-CCl₄ solution and subsequent evaporation of the solvent (see fig. 1). This procedure yielded non-agglomerated spherical PS particles with relatively narrow size distributions and a median particle size of 95 nm. In direct line the particle surface was manipulated by Vacuum Ultraviolet (VUV) radiation in a continuous aerosol photoreactor. The chemical reactions (Oxidation or Oxichlorination) which occurred on the particle surface were dependant on the carrier gas composition as well as irradiation parameters, and were thereby tunable. In the presence of oxygen in the carrier gas the surface of the PS nanoparticles was attacked by oxygen radicals, increasing the concentration of carboxyl- and carbonyl groups. At very low oxygen concentrations the chlorine radicals from the photochemically dissociated solvent CCl₄ dominated the surface reaction and lead to an increase of chlorine groups. The changes in surface chemistry associated with the photoreaction were determined offline by FTIR for carbonyl and carboxyl, yielding only qualitative information, and by XPS for the concentration of chlorine groups. Fig. 2 shows the concentrations of the three surface groups of interest. In air, a strong increase of the carbonyl and carboxyl groups with rising intensity of irradiation was observed. In nitrogen an increase in the chlorine concentration was found in the same range of irradiation intensities.

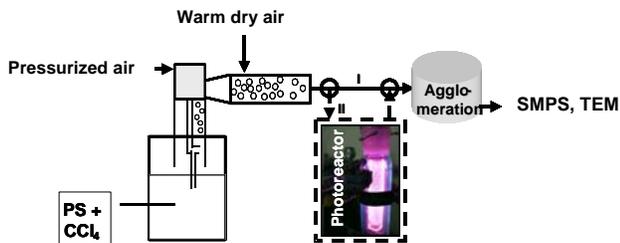


Fig. 1: Experimental setup for particle generation and alteration of the particle surface by aerosol photochemistry

The particles were agglomerated subsequent to photochemical functionalization in the aerosol state. Using a method based on inertial deposition the mechanical stability of the thus generated agglomerates was examined (Seipenbusch et al. 2002 and 2006). The particles were deposited with various impact velocities, directly onto TEM-grids. Offline image analysis of the fractured particles allowed the determination of the fracturing efficiency, which could then be correlated to the kinetic energies upon impaction. Fig. 3 shows the fragmentation efficiency for particles with varied surface chemistry. The strength of PS nanoparticle agglomerates could be lowered, as indicated by a shift to the left, or increased, shifting the curve to the right, by photochemical means inline with the synthesis step. The increase of carboxyl and carbonyl groups lead to a maximum increase in the fragmentation energy by an order of magnitude, though the dose of irradiation also allows the realization of intermediate bond energies. However, the introduction of chlorine efficiently decreases the agglomerate strength and allows adjustment in the other direction of the energy scale.

The aerosol photochemistry technique is in line with particle generation and thus shows very good potential for application in integrated processes for nanoparticle synthesis.

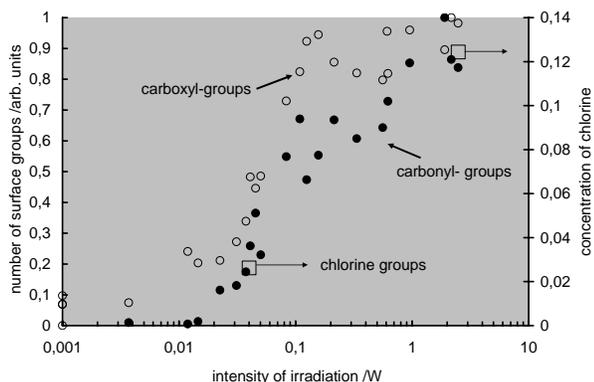


Fig. 2: concentration of chlorine in PS particles at varied intensity of irradiation in the aerosol photoreactor and relative concentrations of carboxyl and carbonyl groups determined using XPS and FTIR respectively.

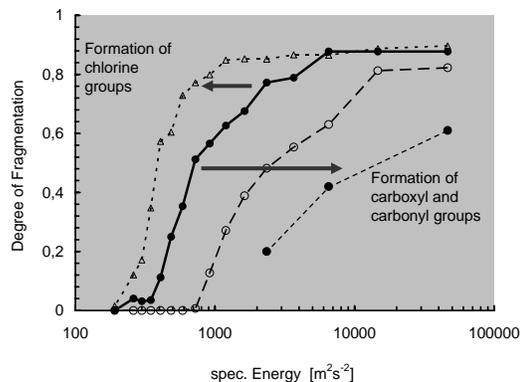


Fig. 3: Degree of Fragmentation of PS nanoparticles as a function of the mass specific fragmentation energy. Alteration of surface chemistry allows to shift the curve up and down the energy scale.

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