

Powder Technology 140 (2004) 40-48

POWDER TECHNOLOGY

www.elsevier.com/locate/powtec

Non-agglomerated dry silica nanoparticles

Roger Mueller^a, Hendrik K. Kammler^a, Sotiris E. Pratsinis^{a,*}, Andri Vital^b, Gregory Beaucage^c, Peter Burtscher^d

^aParticle Technology Laboratory, Department of Mechanical and Process Engineering,

ETH Zurich, Sonneggstrasse 3, ML F25, CH-8092 Zurich, Switzerland

^bSwiss Federal Laboratories for Materials Testing and Research (EMPA),

Laboratory for High-Performance Ceramics, CH-8600 Dübendorf, Switzerland

^cDepartment of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

^dIvoclar Vivadent AG, FL-9494 Schaan, Liechtenstein

Received 1 March 2003; accepted 1 January 2004

Abstract

Silica nanoparticles for polymer nanocomposites are made by oxidation of hexamethyldisiloxane (HMDSO) in methane/oxygen diffusion flames. The flame temperature is measured by in-situ Fourier transform infrared (FTIR) spectroscopy while the degree of agglomeration of the product powder is quantitatively determined by ultra small angle X-ray scattering (USAXS) and is confirmed by transmission electron microscopy (TEM). Precisely controlled, non-agglomerated silica particles having an average primary particle diameter of 18-85 nm, as determined by N₂ adsorption and TEM, are made at low silica production rates of 9 g/h or at low O₂ flow rates at silica production rates of 17 g/h. The differences in morphology result from the completion of gas-to-particle conversion and from the onset of steep cooling in the flames that determines the duration of full coalescence. Nanocomposites with dimethylacrylate polymers are made using non-agglomerated silica particles and compared to the ones made with commercially available silicas.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Nanocomposites; Degree of agglomeration; Flame aerosol reactor

1. Introduction

The degree of agglomeration is an important quality index in a number of applications. For example, agglomerated nanostructured particles are needed in manufacture of fillers, catalysts, lightguide preforms and for filamentary nickel. In contrast, non-agglomerated nanoparticles $(d_p < 200 \text{ nm})$ are needed in ceramics, composites and electronics [1]. Typically non-agglomerated particles are made by wet chemistry. These processes tend to be costly and may give powder of limited consistency during largescale manufacture as they involve many process steps [2]. Furthermore, these particles may contain impurities (e.g. surfactants) requiring further post-processing [3].

Flame technology is attractive for manufacture of solid and rather narrowly distributed particles as it is used to make carbon black, fumed silica, pigmentary titania and other oxide particles on an industrial scale [4]. As these particles form and grow, they evolve through various morphologies including perfectly spherical particles as has been theoretically outlined [5] and experimentally demonstrated by thermophoretic sampling of titania and alumina particles in counterflow diffusion flame reactors [6,7]. The end product of flame reactors, however, tends to be agglomerated particles requiring grinding, limiting thus, their applications [1]. Nevertheless, rather large (80–300 nm) non-agglomerated titania particles have been produced in single diffusion flames at atmospheric pressure [8,9] as was shown by microscopy and confirmed quantitatively by small angle Xray scattering (SAXS) [10]. In contrast, silica particles made at the same conditions were agglomerated as the flame temperatures were not high enough for the fumed silica to fully coalesce [9]. Zhu and Pratsinis [11] also made weakly agglomerated silica particles of around 200 nm in a single diffusion flame using O2 as oxidant as shown by transmission electron microscopy (TEM) images but here quantitative SAXS measurements were not performed to measure the

^{*} Corresponding author. Tel.: +41-1-632-31-80; fax: +41-1-632-15-95. *E-mail address:* pratsinis@ptl.mavt.ethz.ch (S.E. Pratsinis).

degree of agglomeration. Similarly, Glumac et al. [12] reported synthesis of non-agglomerated fumed silica, titania and alumina in low pressure flame reactors but few microscopic or quantitative measurements were made. Arabi-Katbi et al. [13] showed the evolution of particle morphology from fine agglomerates to spherical ones and eventually to agglomerated product particles using thermophoretic sampling in premixed flames. Very recently, Wegner et al. [14] capitalized on this result to freeze particle growth using a burner-quenching nozzle, collecting, thus, particles before reaching the region of final agglomeration.

Here, synthesis of non-agglomerated silica particles is investigated in a standard diffusion flame reactor that can be readily scaled-up [15,16]. Diffusion flame reactors are quite attractive for their flexibility to produce particles with a broad spectrum of sizes and morphologies depending on reactant conditions [1]. Fumed silica is selected here, as it is one of the most challenging materials when it comes to synthesis of non-agglomerated nanoparticles. Non-agglomerated silica with a primary particle diameter smaller than 100 nm is of great interest in dental nanocomposites for replacing up to 60-70% of the conventional polymeric resins in dental fillings. Here, flame-made silica particles of controlled agglomeration state are characterized by TEM, N₂ adsorption, ultra small angle X-ray scattering (USAXS) and thermogravimetric analysis (TGA). Furthermore, axial flame temperatures and fuel conversion are measured in SiO₂ particle-laden diffusion flames with Fourier transform infrared (FTIR) emission/transmission (E/T) spectroscopy.

2. Experimental

2.1. Apparatus and temperature measurements

Fig. 1 shows the experimental set-up. A stainless steel burner consisting of three concentric tubes is used. The inner diameter of the center (first) tube is 4.8 mm, while the subsequent first and second annuli have inner-outer diameters of 5.6-6.4 and 7.3-9 mm, respectively. The hexamethyldisiloxane (HMDSO)-laden carrier N₂ gas and the CH₄ (PanGas, CH, \geq 99.5%) streams are delivered through the center tube while O_2 (PanGas, CH, $\geq 99.999\%$) is delivered through the second annulus. Nitrogen is delivered between them through the first annulus to slightly lift the flame from the burner mouth preventing, thus, particle deposition [15]. The silica precursor (HMDSO; Fluka Chemie, 99%) is delivered by bubbling clean dry N2 (PanGas, CH, \geq 99.999%) through a fritted cylinder, placed in a 1 l flask (Schott) filled up to 3/4 with HMDSO. The flask is stored in a thermostated bath (Huber Kältemaschinenbau) to assure stable HMDSO temperature and delivery. The carrier gas stream (N_2) is fully saturated with HMDSO [17] as confirmed by weighing the flask before and after long-term experiments. The tubing between the flask and the burner is heated with heating tape, at least 20 K higher than the



Fig. 1. Experimental set-up for the synthesis of fumed silica nanoparticles by oxidation of hexamethyldisiloxane (HMDSO) in a methane–oxygen diffusion flame.

HMDSO flask temperature to prevent HMDSO condensation or small droplet entrainment into the burner [15]. The gases are metered by calibrated rotameters (Vögtlin Instruments). In all experiments the carrier gas and the fuel flow rate ranged from 0.7 to 2.9 l/min, the O₂ flow rate from 1.3 to 24 l/min, while the N₂ in the first annulus was 0.5 l/min (at 25 °C and 1.013 bar). The corresponding Reynolds numbers based on the overall burner diameter Re = uD/v are in the range of 700 to 5100, where *u* and *v* are the velocity at the burner exit and the kinematic viscosity of the reactant stream, respectively. Flame flickering is minimized by enclosing the burner with a 250 mm long chimney (plexiglas, i.d. = 140 mm).

Small samples (~ 1 g) of product particles are collected with the aid of a vacuum pump (Vacuubrand RE 8) on a glass fiber filter (Whatmann GF/A) 150 mm in diameter located in a stainless steel holder on top of the chimney. Larger samples (500 g) of product powder are collected at 95% yield with four 60 cm long, 12 cm diameter PTFE (polytetrafluoroethylene, Teflon) coated Nomex baghouse filters in a stainless steel filter house by an air suction ventilator (Meidinger, 1.5 kW, 50 Hz) controlled by a frequency transducer. The particles are removed every 120 s from each one of the baghouse filters by air pressure shocks using 5 bar absolute pressure. Powders collected in the baghouse filters over a long period (30 h) were identical (same specific surface area and morphology) to the ones collected on glass fiber filters over short periods (several minutes) when made at same conditions.

The flame temperature and fuel (CH₄, HMDSO) conversion are measured by FTIR spectroscopy (Fig. 1) operating a Bomem MB155S at 8 cm⁻¹ spectral resolution co-adding typically 256 scans for the transmission and emission (radi-

ance) spectra [18]. Two pairs of identical paraboloidal mirrors guide the IR beam through the flame and a 0.2 cm iris at the first focal point defines the beam diameter in the flame center (second focal point). Transmission and emission (radiance) spectra are collected with wide-band deuterated-triglycine-sulfate (DTGS) detectors. The evaluation of the flame temperature is described in detail by Kammler et al. [19]. From the integral (line-of-sight) transmission measurements through the centerline of the flame the conversion of the fuel is obtained at different heights above the burner (HAB) by comparing the unburned fuel absorption spectra of fuel at each HAB in the region of 3200–2800 and 1450–750 cm⁻¹. The flame height is determined visually as the distance from the burner mouth to the end of the luminous flame zone.

2.2. Characterization

The powder specific surface area, SSA, is determined from N₂ adsorption and the average BET-primary particle diameter, d_p , is calculated by $d_p = 6/(\rho_p SSA)$, where ρ_p is the density of SiO₂, 2.2 g/cm³ [16]. Error bars always show two times the standard deviation of multiple experiments.

The USAXS measurements are performed at the UNI-CAT facility of the Advanced Photon Source, Argonne National Laboratories, USA. The USAXS camera uses a Bonse-Hart (BH) geometry instrument on the ID-33 beamline [20]. The incident beam is of the order of 1 mm^2 at the sample and samples are measured under ambient pressure. Data are corrected for background and desmeared prior to analysis using the UNI-CAT software "Indra" version 2, that uses the unified SAXS model [21]. Desmaring corrects for gemoetric effects of the light scattering as follows: With the BH camera the X-ray beam is collimated (made narrow and straight) by reflections on crystals. Because of this, the effective beam profile on the sample is a line rather than a point. The collected intensity at a fixed detector angle (analyzer angle in a BH camera) reflects the sum of intensities scattered along a close to infinitely thin line profile normal to the detection arc in this step scan camera.

For different points on the line the scattering angle is different. The data are corrected for this geometric effect (desmeared) through various mathematical routines, which are well documented in the literature. Desmearing results in data that are identical to pinhole SAXS data as has been demonstrated through comparison with a number of pinhole cameras [22,23]. The mass fractal dimension, $D_{\rm f}$, is obtained from the USAXS data by the negative slope of logarithmic intensity, *I*, versus logarithmic scattering vector, *q*, in a power-law regime [10].

Samples for TEM are prepared by dipping the carbon coated TEM grids (PLANO, W. Plannet) into the collected powder without further treatment. The TEM analysis is performed on a Hitachi H 600 electron microscope operated at 100 kV, using magnifications between 10 and 30 k. The composition of the collected powders is determined by thermogravimetric analysis (TGA) [16,24]. Only perfectly white powders, indicating carbon free silica, were analyzed here. The visual indication of carbon free powders is cross-checked by TGA coupled with a mass spectrometer [16,24].

For preparation of the nanocomposites, the surface of the product silica powder (filler) is treated with *y*-methacryloxypropyltrimethoxy silane to establish a good bonding between the filler and the monomer matrix. This matrix is prepared by mixing bisphenol-A-glycidyldimethacrylate (Bis-GMA), triethylenglycol dimethacrylate (TEGDMA), and decandiol dimethacrylate (D₃MA) at a ratio of 2:1.5:1 and dissolving 0.3% camphorquinone (CQ) and 0.6% *N*,*N*cyanoethylmethylanilin (CEMA). The fillers are added to the monomer mixture by stirring under vacuum to make composites consisting of 18.3 wt.% monomer, 22.7 wt.% filler, 50.2 wt.% prepolymer, and 8.8 wt.% ytterbiumfluoride.

3. Results

Fig. 2 shows pictures of particle-laden diffusion flames at O_2 flow rates of (a) 2.5, (b) 4.7, (c) 8.5, (d) 13.3 and (e) 24 l/min at 1.4 l/min CH₄ and 2.9 l/min HMDSO-laden N₂ flow corresponding to silica production of 17 g/h. Increasing the



Fig. 2. Diffusion flames producing 17 g/h of silica using 1.4 l/min CH₄, 2.9 l/min HMDSO-laden N₂ flow and O₂ flow rates of (a) 2.5, (b) 4.7, (c) 8.5, (d) 13.3 and (e) 24 l/min.

 O_2 flow rate above 2.5 l/min stabilizes and shortens the flame up to 65% at 24 l/min O_2 flow rate. Early in the flame a bluish-white part can be seen (Fig. 2) indicating the formation of silica particles as the Si–CH₃ bonds of HMDSO split first. This part becomes more and more transparent with increasing O_2 flow rate as the silica aerosol in the flame is diluted with the added O_2 gas. At low O_2 flow rates, the upper part of the flame is yellow indicating that combustion of the hydrocarbon components of HMDSO is taking place along with soot formation and oxidation. Increasing the O_2 flow rate, the yellow part of the flame is reduced and completely vanishes at 24 l/min O_2 flow rate as enough O_2 is provided for rapid soot combustion.

Representative TEM-pictures of powders made in the flames shown in Fig. 2 are presented in Fig. 3 as well as commercially available OX-50 powder (Degussa). Rather big spherical particles with diameters of about 100 nm are made in flames at low oxidant flow rates (Fig. 3a,b). The contours of these particles with limited necking (Fig. 3b) are clearly shown in Fig. 3a, b and c, indicating only a low degree of agglomeration. Large single, as well as small agglomerated silica particles are observed when made at very low O₂ flow rates (Fig. 3a), while few small agglomerated ones are observed at slightly higher O₂ flow rate (Fig. 3b). At the highest O_2 flow rates (13.3 and 24 l/min), only agglomerates of small primary particles are made (Fig. 3d,e). The morphology of the OX-50 powder (Fig. 3f) is similar to the powder made at 13.3 $l/min O_2$ flow rate (Fig. 3d) even though also domains with rather non-agglomerated particle can be observed for this powder [25].



Fig. 3. Transmission electron micrographs of silica nanoparticles at production rates of 17 g/h with 1.4 l/min CH₄ and 2.9 l/min HMDSO-laden N₂ flow rates and (a) 2.5, (b) 4.7, (c) 8.5, (d) 13.3, and (e) 24 l/min O₂ flow rates and (f) commercially available OX-50 powder (Degussa).



Fig. 4. Transmission electron micrographs of silica nanoparticles at production rates of 9 g/h with 0.7 l/min CH_4 and 1.4 l/min HMDSO-laden N_2 flow rates and (a) 1.3, (b) 4.7, (c) 11.4, and (d) 24 l/min O_2 flow rates.

Fig. 4 shows representative TEM-pictures of powders made at production rate of 9 g/h using 0.7 l/min CH₄ and 1.4 l/min N₂ flow rates for 1.3, 4.7, 11.4, and 24 l/min HMDSO-laden O₂ flow rate. Rather big spherical particles with diameters of about 100 nm are made in the flames with low O₂ flow rates (Fig. 4a,b) similar to the silica produced at 17 g/h (Fig. 3). Only a low degree of agglomeration is observed in those powders. At O₂ flow rates of 11.4 and 24 l/min, the primary particle size decreases but still perfectly spherical large particles along with small ones are observed at such O₂ flow rates (Fig. 4c,d).

Fig. 5 shows the BET-primary particle diameter of the product powder as a function of O₂ flow rate at silica production rates of 17 g/h (diamonds) and 9 g/h (circles). For the 17 g/h production rate, the particle diameter of the product powder first increases from 44 to 78 nm with increasing O₂ flow rate from 2.5 to 4.7 l/min and then decreases steadily down to 23 nm when increasing the O₂ flow rate to 24 l/min. When the production rate was reduced to 9 g/h by keeping constant the HMDSO temperature but reducing the CH₄ and N₂ carrier gas flow rates to 0.7 and 1.4 l/min, respectively, a similar trend is observed regarding the effect of O₂ flow rate on BET-primary particle diameter. Here, the particle diameter increases from 71 to 85 nm with increasing O₂ flow rate from 1.3 to 2.5 l/min and then decreases continuously down to 18 nm when increasing the O_2 flow rate to 24 l/min.

The average mass fractal dimensions, $D_{\rm fr}$ measured with USAXS for the Degussa Aerosil 200 and 380 are 2.2 ± 0.2 and 2.1 ± 0.1 , respectively, which are typical for flame made aerosols. The $D_{\rm f}$ for OX-50 measured by USAXS was lower ($D_{\rm f}$ = 1.6 ± 0.1), which could be explained by the presence of more linear agglomerates with higher aspect ratios and less branched structures compared to the Aerosil powders. The mass fractal dimension of the agglomerated powders made here is 1.6 and 1.9 when made with 13.3 l/min and 24 l/min O₂ flow, respectively, at silica production of 17 g/h which is consistent with the TEM images (Fig.



Fig. 5. BET-primary particle diameter as a function of O_2 flow rate at powder production rates of 17 g/h (diamonds) and 9 g/h (circles).

3d,e). The $D_{\rm f}$ for OX-50 is identical to that for the powder made here at 13.3 l/min O₂ flow rate which are consistent also with TEM (Fig. 3d,f). All other silica powders produced here (17 and 9 g/h) are found to be non-agglomerated by USAXS. All powders produced in this study as well as the commercial ones had smooth primary particle surfaces as indicated by the USAXS scattering exponent of -4[26,27] at high *q*.

Fig. 6a shows the absorbance spectra of the unburned CH₄ (3200-2800 and 1400-1250 cm⁻¹) and HMDSO $(2965, 1260, 1073, \text{ and } 850 \text{ cm}^{-1})$ as well as those of the combustion products H₂O (1800-1200, and 800-600 cm^{-1}), CO₂ (around 2350 cm^{-1}), and SiO₂ (around 1000 cm⁻¹) and unburned fuel (CH₄ and HMDSO) at various HAB of the flame shown in Fig. 2a. Clearly, it can be seen that with increasing HAB the intensity of the absorption bands of the fuel is decreasing indicating that the combustion of fuel is not completed up to 90 mm HAB. Furthermore, with increasing HAB the CO₂ peak is increasing, as a result of the progress of combustion. Fig. 6b shows the conversion of fuel (CH₄ and HMDSO) along the burner axis (centerline) of the flames shown in Fig. 2. At 90 mm HAB the fuel is almost completely converted for the 2.5 l/min O₂ flow rate (diamonds) while complete conversion is achieved at 90, 70, 60, and 50 mm HAB using 4.7 (circles), 8.5 (squares), 13.3 (stars) and 22.7 l/min (triangles) O2 flow rates, respectively.

Fig. 7a shows line-of-sight temperature profiles of diffusion flames (Fig. 2) along the burner axis (centerline) for O_2 flow rates of 2.5 l/min (diamonds), 4.7 l/min (circles), 8.5 l/min (squares), 13.3 l/min (stars) and 22.7 l/min (triangles) at silica production rate of 17 g/h. With increasing HAB, the flame temperature increases and reaches a maximum (around 2250 K) at about 10 mm HAB for all O_2 flow rates. The flame temperature of the 2.5 and 4.7 l/min O_2

flames decreases slightly to around 2000 K after this maximum. Then, the flame temperature is almost constant between 50 and 170 mm HAB while it is slightly higher for the 4.7 l/min than the 2.5 l/min O_2 flame. At higher locations (HAB>175 mm) the temperature decreases continuously for the 2.5 and 4.7 l/min O_2 flames. The flame temperature of the 8.5 l/min and 13.3 l/min O_2 flames decreases much faster to around 1900 and 2000 K, respectively, at 30 mm HAB. Then, the flame temperature is



Fig. 6. (a) FTIR absorption spectra of the unburned gases at the burner exit as well as that of the flame (2.5 l/min O_2 , Fig. 2a) at various HABs. The spectra are shifted by 0.1 for better visual observation. (b) Conversion of fuel (CH₄ and HMDSO) of diffusion flame producing 17 g/h of silica along the burner axis (centerline) as a function of the height above burner (HAB) for O_2 flow rates of 2.5 l/min (diamonds), 4.7 l/min (circles), 8.5 l/min (squares), 13.3 l/min (stars) and 22.7 l/min (triangles) as determined by integral FTIR transmission measurements through the flame center.



Fig. 7. Average flame temperature along the burner axis (centerline) of diffusion flames as a function of height above burner (HAB) for various O_2 flow rates for flames producing (a) 17 and (b) 9 g/h of silica.

constant up to 100 and 60 mm HAB for the 8.5 and 13.3 l/ min O_2 flames, respectively, and then starts decreasing continuously similarly to the 2.5 and 4.7 l/min O_2 flames. The flame temperature of the 22.7 l/min O_2 flame is constant up to 50 mm HAB at the maximum temperature and then decreases sharply. Fig. 7b shows line-of-sight temperature profiles of 9 g/h silica producing diffusion flames along the burner axis (centerline) for O_2 flow rates of 1.3 l/min (diamonds), 4.7 l/min (circles), 11.4 l/min (squares) and 22.7 l/min (triangles). Similarly to the profiles shown in Fig. 7a the flame temperature increases and reaches a maximum at about 10 mm HAB for all O_2 flow rates. The flame temperature of the 1.3 and 4.7 l/min O_2 flames is constant at this maximum flame temperature between 10–80 and 10–50 mm HAB, respectively, while at higher locations the temperature decreases continuously for both flames. The flame temperature of the 11.4 and 22.7 l/min O_2 flames decreases continuously right after the maximum flame temperature is reached (Fig. 7b).

A plateau of constant high temperature occurs at about 2000 K (Fig. 7a) and 2150 K (Fig. 7b) for the 17 and 9 g/h silica producing flames, respectively. The carrier and fuel gas flow rates are reduced by a factor of 2 when producing 9 g/h of silica. This leads to higher relative velocities between fuel-precursor carrier gas (tube 1) and oxygen streams (tube 3). Thus mixing is intensified so accelerating fuel combustion and leading therefore to higher, constant flame temper-



Fig. 8. Residence time of silica particles at the high temperature plateau of diffusion flames producing (a) 17 g/h and (b) 9 g/h of silica as a function of the BET-primary particle diameter. The corresponding coalescence lines of 2000 K (a) and 2150 K (b) are shown also.

ature compared to the flames synthesizing 17 g/h of silica (Fig. 7). For all flame configurations radial temperature profiles at constant HAB exhibit the typical M-shape [28] as long as the fuel-precursor conversion is not completed (Fig. 6b). Thereafter, a parabolic temperature profile develops further downstream. The maximum radial temperature is measured at the flame front between the $CH_4/HMDSO$ and O_2 streams.

Fig. 8 shows the residence times of particles made in (a) 17 g/h and (b) 9 g/h silica producing diffusion flames as a function of the BET-primary particle diameter (Fig. 5). The corresponding coalescence lines based on the BET-primary particle diameter and the sintering time of silica [29] for 2000 K (Fig. 8a) and 2150 K (Fig. 8b) are shown as well. The temperature of the coalescence line corresponds to that of the high temperature plateau (Fig. 7) for the 17 and 9 g/h silica producing flame which is 2000 and 2150 K, respectively. The particle residence time is calculated from the overall gas flow rate, the burner area (inner diameter of tube 3) at the above flame temperatures and the HAB where the flame temperature decreases sharply for each oxygen flow rate (Fig. 7). Clearly, it can be seen that the high



Fig. 9. Non-agglomerated silica in a dimethylacrylate matrix (50:50 by weight) of (a) commercially available SiO₂ (OX-50 from Degussa) and (b) silica powder made here in the diffusion flame with 4.7 l/min O₂ flow rate at production rate of 17 g/h.

temperature particle residence times are larger than the corresponding coalescence times for oxygen flow rates of 2.5, 4.7 and 8.5 l/min for the 17 g/h silica producing flame (Fig. 8a), thus, non-agglomerated particles are formed, consistent with TEM (Fig. 3a-c) and USAXS measurements. In contrast, when the residence time of the particles is shorter than the corresponding coalescence time, as for particles made at oxygen flow rates of 13.3 and 22.7 l/min (Fig. 8a), the particles are agglomerated, consistent with TEM (Fig. 3d,e) and USAXS also. The high temperature residence times for particles made at 9 g/h silica production rate are larger than the corresponding coalescence times for all oxygen flow rates (Fig. 8b), indicating non-agglomerated particles which is consistent with TEM (Fig. 4) and USAXS as well.

Fig. 9 shows TEM-pictures of nanocomposites using as filler (a) commercially available silica powder (OX-50, Degussa) and (b) non-agglomerated powder made here with 4.7 l/min O_2 flow rate (17 g/h production rate). The particles made here seem to be more uniform (smaller aspect ratio) and better dispersed in the polymer matrix compared to the commercial ones. Furthermore, the elastic modulus of nano-composites using the fumed silica particles made here is 14% larger than that made with OX-50.

4. Discussion

The residence time of the particles at high temperatures strongly affects the size and morphology of the product powder [1]. The formation of non-agglomerated particles is favored when the particle residence time at high temperature is long enough to complete particle coalescence or sintering upon collision (Fig. 8). Here, the O_2 flow rate is used to control the particle size and morphology. Non-agglomerated powders are made at low O₂ flow rates up to 8.5 l/min at a production rate of 17 g/h (Fig. 3a-c) where the particles remain longer at high temperatures (Fig. 7a) than the corresponding coalescence times (Fig. 8a). In the powders shown in Fig. 3a-c, the large particles are non-agglomerated and coexist with small quantities of agglomerates with significantly smaller primary particle sizes. Computational fluid dynamic (CFD) simulations by Johannessen et al. [30] showed the formation of larger particles close to the centerline as well as the formation of smaller ones far off from the flame axis, explaining the observed distribution of sizes (Fig. 3a-c). The particles formed near the flame axis completely coalesce before their growth is stopped when the sintering time is less than or equal to the collision time. As the axial flame temperature is similar and only slightly higher between 50 and 170 mm HAB (Fig. 7a) for the 2.5 and 4.7 l/min O₂ flame, the primary particle diameter increases (Fig. 5) when increasing the O₂ flow rate from 2.5 to 4.7 l/min even though the particle residence time at high temperature is decreased. The flame is slightly unstable when using only 2.5 l/min O₂ flow rate (Fig. 2a) since the

burner exit velocity of the center tube is larger than that of the second annulus. This leads to the formation of large spherical and small agglomerated particles (Fig. 3a) and thus to a smaller average particle diameter compared to particles made with 4.7 or 8.5 l/min O_2 (Fig. 5). The latter flames are more stable leading to the formation of more uniform non-agglomerated particles (Fig. 3b,c) than those made with 2.5 l/min O_2 (Fig. 3a). It is worth noting that for O_2 flow rates less or equal to 8.5 l/min the precursor has been consumed (Fig. 6b) before the onset of steep cooling (Fig. 7a) that will greatly increase the sintering time and will essentially stop coalescence.

The formation of non-agglomerated powders is limited, however, when the residence time at high temperature is shorter than the characteristic time for gas-to-particle conversion (complete conversion of fuel as measured by FTIR; Fig. 6b) or the characteristic time for coalescence. This occurs when the O_2 flow is further increased (13.3 and 22.7 l/min) enhancing flame turbulence and reactant mixing, accelerating combustion (Fig. 6b) that shortens the flame height (Fig. 2). This shortens the particle residence time at high temperature and increases flame cooling with increasing HAB (Fig. 7a) that leads to the formation of hard agglomerates consisting of small primary particles (Fig. 3d,e). Here, the precursor is consumed at about 60 mm and 50 mm HAB for the flames made with 13.3 l/min and 22.7 l/min O_2 flows (Fig. 6b), respectively, thus, close to the onset of the steep cooling (Fig. 7a). It is quite likely that new particles are forming as the characteristic time for sintering rapidly increases, freezing their growth upon collision as shown in Fig. 3d and e.

The TEM observations are corroborated by USAXS measurements, where the powders made at 17 g/h are non-agglomerated up to an O₂ flow rate of 8.5 l/min, while at higher O₂ flow rates (13.3–24 l/min) the product powders are agglomerated as determined by USAXS [27]. This is consistent with Hyeon-Lee et al. [10] who found only agglomerated silica particles made in diffusion flames with SiCl₄ as precursor in a similar burner configuration [9] but at lower flame temperatures.

All powders made at 9 g/h (circles in Fig. 5) are nonagglomerated as measured by USAXS and consistent with the TEM (Fig. 4). Even at high O_2 flow rates spherical nonagglomerated particles are observed (Fig. 4c,d) as also in this case the particle residence time at high temperature is longer than the corresponding coalescence time (Fig. 8b). At these conditions of low HMDSO and CH₄ concentration compared to 17 g/h SiO₂ production, enough oxidant is always supplied to complete gas-to-particle conversion before the onset of steep cooling, as observed also experimentally similarly to Figs. 6b and 7b. For stable flames $(O_2 \ge 4.7 \text{ l/min})$ the particles made at 9 g/h are smaller by about 30% than the ones made at 17 g/h (Fig. 5) consistent with a $(17/9)^{2/5}$ dependence on the mass balance of a coagulation-coalescence dominated growth in the free molecular regime [31].

5. Conclusions

A systematic investigation of flame synthesis of silica nanoparticles for polymer nanocomposites was carried out in a diffusion flame aerosol reactor. Non-agglomerated spherical silica particles of $d_p = 44-78$ nm were made by variation of the O2 flow rate using 2.5-8.5 l/min O2 at powder production rates of 17 g/h. By reducing the particle concentration, non-agglomerated tailor-made silica particles were synthesized at all O₂ flow rates with diameters ranging from 18 to 85 nm. The degree of agglomeration was quantitatively determined by USAXS and was consistent with TEM observations. Non-agglomerated particles were formed when gas-to-particle conversion was completed or the residence time at high temperature (as defined by the onset of steep cooling) was larger than the characteristic time for sintering or coalescence. In application, these particles were well dispersed in a polymer matrix resulting in nanocomposites with increased elastic modulus.

Acknowledgements

We acknowledge the financial support from the Kommission für Technologie und Innovation (KTI Project No. 4954.1) and Swiss National Science Foundation (Nos. 2100-055469.98 and 2100-063632.00/1). We thank Dr. M. Müller (ETH Zurich) for help with TEM. The use of the UNI-CAT beamline was possible through the gracious support of UNI-CAT. The UNI-CAT facility at the Advanced Photon Source (APS) is supported by the Univ. of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. DOE, the State of Illinois-IBHE-HECA, and the NSF), the Oak Ridge National Laboratory (U.S. DOE under contract with UT-Battelle LLC), the National Institute of Standards and Technology (U.S. Department of Commerce) and UOP LLC. The APS is supported by the U.S. DOE, Basic Energy Sciences, Office of Science under contract No. W-31-109-ENG-38. G. Beaucage was supported by the National Science Foundation under grants CTS-9986656 and CTS-0070214.

References

- [1] S.E. Pratsinis, Prog. Energy Combust. Sci. 24 (1998) 197-219.
- [2] S.E. Pratsinis, S.V.R. Mastrangelo, Chem. Eng. Prog. 85 (1989) 62–66.
- [3] Y.J. Chen, N.G. Glumac, G. Skandan, B.H. Kear, ACS Symp. Ser. 681 (1998) 158–169.
- [4] G.D. Ulrich, Chem. Eng. News 62 (1984) 22–29.
- [5] J.L. Katz, P.F. Miquel, Nanostruct. Mater. 4 (1994) 551-557.
- [6] C.H. Hung, P.F. Miquel, J.L. Katz, J. Mater. Res. 7 (1992) 1870–1875.
 [7] Y.C. Xing, U.O. Koylu, D.E. Rosner, Combust. Flame 107 (1996)
- 85–102.
- [8] S.E. Pratsinis, W.H. Zhu, S. Vemury, Powder Technol. 86 (1996) 87–93.

- [9] W.H. Zhu, S.E. Pratsinis, ACS Symp. Ser. 622 (1996) 64-78.
- [10] J. Hyeon-Lee, G. Beaucage, S.E. Pratsinis, S. Vemury, Langmuir 14 (1998) 5751–5756.
- [11] W.H. Zhu, S.E. Pratsinis, AIChE J. 43 (1997) 2657-2664.
- [12] N.G. Glumac, Y.J. Chen, G. Skandan, B. Kear, Mater. Lett. 34 (1998) 148–153.
- [13] O.I. Arabi-Katbi, S.E. Pratsinis, P.W. Morrison Jr., C.M. Megaridis, Combust. Flame 124 (2001) 560–572.
- [14] K. Wegner, W.J. Stark, S.E. Pratsinis, Mater. Lett. 55 (2002) 318-321.
- [15] H.K. Kammler, S.E. Pratsinis, J. Nanopart. Res. 1 (1999) 467-477.
- [16] H.K. Kammler, R. Mueller, O. Senn, S.E. Pratsinis, AIChE J. 47 (2001) 1533–1543.
- [17] T. Boublik, V. Fried, E. Hala, The Vapor Pressures of Pure Substances, Elsevier, Amsterdam, 1984.
- [18] P.W. Morrison, R. Raghavan, A.J. Timpone, C.P. Artelt, S.E. Pratsinis, Chem. Mater. 9 (1997) 2702–2708.
- [19] H.K. Kammler, S.E. Pratsinis, P.W. Morrison Jr., B. Hemmerling, Combust. Flame 128 (2002) 369–381.
- [20] G.G. Long, A.J. Allen, J. Ilavsky, P.R. Jemian, P. Zschack, The ultrasmall-angle X-ray scattering instrument on UNICAT at the APS,

SRI99, "Eleventh U.S. National Synchrotron Radiation Instrumentation Conference", AIP Conference Proceeding CP521, American Institute of Physics, New York, 1999, pp. 183–187.

- [21] G. Beaucage, J. Appl. Crystallogr. 28 (1995) 717-728.
- [22] P.R. Jemian, A.J. Allen, J. Appl. Crystallogr. 27 (1994) 693-702.
- [23] A.J. Allen, P.R. Jemian, D.R. Black, H.E. Burdette, R.D. Spal, S. Krueger, G.G. Long, Nucl. Instrum. Methods Phys. Res., Sect. A, Accel. Spectrom. Detect. Assoc. Equip. 347 (1994) 487–490.
- [24] R. Mueller, H.K. Kammler, K. Wegner, S.E. Pratsinis, Langmuir 19 (2003) 160–165.
- [25] G. Michael, H. Ferch, Degussa Tech. Bull. Pigments 11 (2001) 24.
- [26] D.W. Schaefer, A.J. Hurd, Aerosol Sci. Technol. 12 (1990) 876-890.
- [27] H.K. Kammler, G. Beaucage, R. Mueller, S.E. Pratsinis, Langmuir 20 (2004) 1915–1921.
- [28] R.J. Santoro, J.H. Miller, Langmuir 3 (1987) 244-254.
- [29] W.D. Kingery, H.K. Bowen, D.R. Uhlmann, Introduction to Ceramics, Wiley, New York, 1976.
- [30] T. Johannessen, S.E. Pratsinis, H. Livbjerg, Powder Technol. 118 (2001) 242–250.
- [31] W. Koch, S.K. Friedlander, Part. Part. Syst. Charact. 8 (1991) 86-89.