Sintering of polymer particle - Experiments and modelling of temperature- and time-dependent contacts

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Introduction

High quality performance of modern sintered technical products like e.g. polymeric filter media requires a fundamental understanding of sintering for short and long times-scales. Classical sinter models based on two-spheres like proposed by Frenkel [1] or Pokluda et al. [2] neglected the contribution of surface forces and the resultant contact deformation in the early stage of sintering. Experimental results are required to improve existing sinter models and the theoretical understanding of granular matter under varying temperature- and time-conditions, which is a determining factor in materials processing.

In the present work, temperature-, time- and size-dependent sintering kinetics of polystyrene (PS) particles at the single particle and bulk level were analysed by utilizing colloid probe technique, 3D tomography (FIB/SEM), nanoindentation and confocal microscopy. The first method is used for particle surface force measurements during the first seconds of sintering (< 10 s) whereas the last ones give access to the sinter kinetic of larger timescales as well as the bulk-flow behaviour of thin (< 30 particle diameters) layers of sintered particles. A significant effect of multiple contact partners on the sintering rate was shown in simulation [3]. Our experimental results will be correlated with Discrete Element Method (DEM) simulations to calibrate temperature- and time- dependent sintering model parameters.

Materials and Methods

PS spheres featuring nominal particle radii of 0.5 µm, 1 µm, 1.5 µm and 4 µm were synthesis by dispersion polymerization as reported in [4] and stored in aqueous solution. AFM colloidal probes were prepared by attaching 4 µm PS spheres (Loctite 9497, 2 components, Epoxy) to Mikromasch NSC11 tip-less cantilevers. Particle surface force measurements during the first seconds of sintering (< 10 s) at various temperatures (60-110 °C) were carried out on EnviroScope AFM (Veeco) equipped with a sample heater. PS multilayer thin films were

realized by placing 10 µl of a dispersion (1:1, PS particle: Ethanol) on an oxygen-plasma hydrophilized glass substrate for each particle radius. After complete evaporation, the samples were heated up to temperatures above the glass transition temperature of PS for different periods of time and each particle radius. The samples were analysed by utilizing 3D tomography (FIB/SEM), nanoindentation and insitu nanoindentation with confocal microscopy. In the first method, a focused ion beam (FIB) supplied by FEI (Helios 600) was used to mill 20 nm thick slices in a 12x8x6 µm block, slice by slice inside the sintered PS particle layers. SEM images for each slice were collected and used for 3D reconstructions by using Amira 3.1.1 (Visage Imaging, San Diego, USA) to determine the neck radius X. Nanoindentation measurements were performed with a standard-force MFP NanoIndenter (Asylum Research, Santa Barbara, CA) equipped with a spherical ruby indenter (d = 127 µm). Indentations were performed in load-controlled mode. The applied load varies between 4 and 1 mN with loading rates between 200 µN/s to 800 µN/s. The reduced elastic modulus (Ered) for each sintered PS film was obtained from the unloading portion of the load-displacement curve using the Oliver & Pharr method with a spherical area function. Additionally, the nanoindenter was placed on the sample stage of a home-build confocal microscope, which has the capability to measure in-situ the real-time topography deformation within the sintered particle layers during nanoindentation testing. The spherical tip was pressed displacement controlled with a rate of 3 nm/s inside the sintered sample while the structure was imaged simultaneously.

Results and Discussion

To study the contribution of surface forces and the resultant contact deformation in the early stage of sintering, adhesion force measurements were carried out with a colloidal probe sphere radius of 4 µm on flat Si (100) surface. The results are shown in Figure 1.

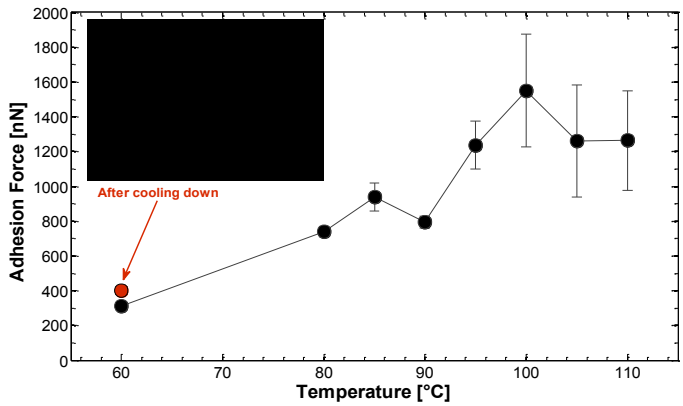

Fig. 1: Adhesion force between PS colloid probe and Si surface with increasing temperature. SEM image (upper left) show the contact deformation.

A significant increase in adhesion force with higher temperature is observed. The adhesion force is three times higher closed to the glass transition temperature (T_g) of PS (~ 100 °C) compared to the measured value at room temperate. With higher temperatures above 100 °C the adhesion force stayed constant. A higher adhesion force is measured after cooling down. Such behaviour can be attributed to contact deformation and therefore higher contact area, which is shown in the SEM image of Figure 1. A representative plot of the time dependent increase of the sintering neck diameter at 110 °C is shown in Figure 2. The experimental results obtained with 3D reconstruction show a higher rate of growth in the early stages (< 0.5) of sintering compared to the prediction of the classical sinter models like Frenkel [1] and the modified Frenkel model [2], which hints to an additional contribution of surface forces to the sinter process.

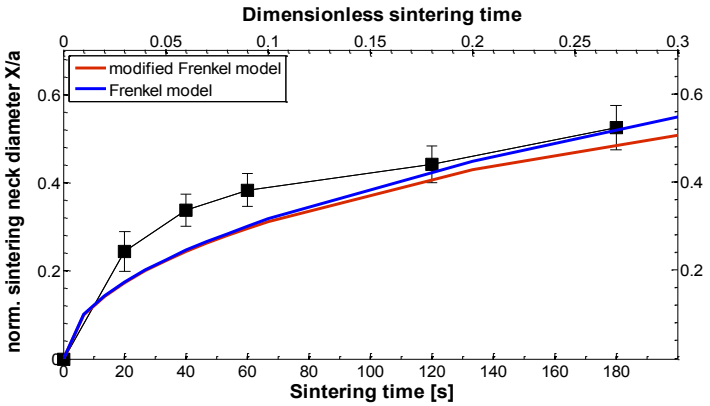

Fig. 2: Sinter kinetic of PS particle (4 µm) at temperature of 110°C compared with Frenkel model (blue line) and modified Frenkel model (red line).

Figure 3 shows the mechanical properties of sintered PS multilayers with particle radius of 1.5 µm at different temperatures and times. The reduced elastic modulus increases with sintering temperature closed to T_g of PS because of the densification of powder compacts at elevated temperatures. While no time dependent sintering process is observed for PS layer sintered below Tg (< 100°C), above Tg an increase of Ered with time is measurable.

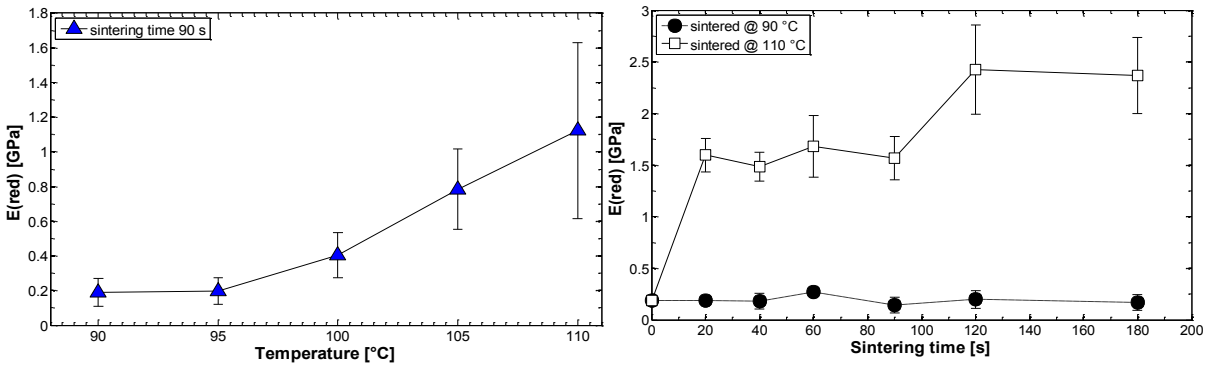

Fig. 3: Mechanical properties of sintered PS multilayers with particle radius of 1.5 µm.

The mechanical properties of porous materials have been theoretically predicted by a number of models, which could be expressed as function of porosity. According to these models, the reduced elastic modulus is increased with the densification of the porous solids, which is in agreement with our results. Additional to this, in-situ real-time topography deformation within the sintered particle layers during nanoindentation was studied with the help of confocal microscopy. A representative image series of such an indentation is shown in Figure 4. Further studies concerning the particle tracking and the correlation with DEM simulation is subject to work in progress.

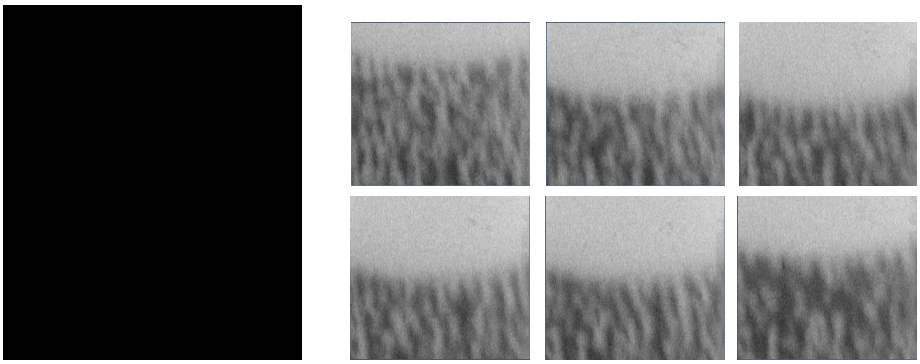

Fig. 4: In-situ nanoindentation and confocal microscopy setup (left) and real-time confocal microscopy image series (right) during nanoindentation of a not sintered PS film.

Conclusion

This study on particle sintering enables us to shed some light on the sinter kinetic of PS particles at the single particle and bulk level and moreover improve existing sinter models by including the contribution of surface forces.

Acknowledgements

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