Pollen-like particles can be prepared by exposure of polymer microparticles to an electron beam

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Abstract
Plant pollen shows a wide variety of surface structures that develop during pollen sporogenesis. Some of the structures are similar to wrinkle structures that are formed when a layered material with different Young’s moduli is compressed. Here we report on the formation of wrinkled surface structures in polymer particles that is caused by electron beam irradiation of poly(methyl methacrylate) microparticles.

Objective
In this paper, we describe the formation of wrinkles on PMMA microbeads after coating with a thin metal layer and irradiation with a 12 kV electron beam in a scanning electron microscope. The beads were imaged in situ and we could show that a characteristic wrinkle structure appeared after a few minutes that got more pronounced over time.

Introduction
Wrinkles occur in layered systems in which the components have different Young’s moduli and can swell or can be compressed. Wrinkled polymer microparticles, for example, can be prepared in situ during polymerisation. Polyimide microparticles were prepared by electrospray of a precursor solution, and the evaporation of the solvent during imidisation lead to wrinkles [1]. Using another approach, Polydimethylsiloxane (PDMS) particles show dimple and wrinkles after ozone treatment and swelling with ethanol. The ozone treatment forms a hard silicon oxide layer and the difference in Young’s modulus then leads to wrinkles after swelling [2] [3]. Instead of ozone, a wet chemical oxidation can also be used [4]. Simple swelling and de-swelling of a polymer particle fixed on a substrate also caused a buckling and the formation of surface dimples [5]. Inorganic core-shell microparticles can show dimple structures by thermal treatment, for example, particles with an Ag-core and SiO2-shell [6]. A general theory to describe labyrinth and hexagonal patterns on spherical particles has been published outlining the generality of the processes [3]. Poly(methyl methacrylate) (PMMA) is a known electron beam resist [7] in which a main chain scission of PMMA molecules by ionising radiation occurs via a stable radical species [8]. Thus, a PMMA bead should decompose and shrink upon electron beam irradiation. We have reported on the fabrication of polymer microparticles by a rapid evaporation of an oil-in-water emulsion [9] [10]. With this method, both particles from a single polymer as well as from polymer blends can be produced.
PolLEN-LIKE PARTICLES CAN BE PREPARED BY EXPOSURE OF POLYMER MICROPARTICLES TO AN ELECTRON BEAM

a

b
Pollen-like particles can be prepared by exposure of polymer microparticles to an electron beam.

**Figure Legend**

a: Temporal development of the wrinkle structure during the irradiation with 12 keV electrons. The scale bar is 5 µm.
b: Dependence of the wrinkle structure upon the metal layer thickness. The metal layer thickness was not directly determined, but the thickness is directly proportional to the sputtering time. Thus a threefold longer sputtering time gives a three times thicker metal layer. The irradiation time with 12 keV electrons in the electron microscope was 10 minutes for all samples. Cut-out quadrants show the difference of wrinkle ‘sharpness’. The scale bar is 5 µm.
c: Left: Wrinkle patterns for core-shell and Janus particles. The scale bar is 5 µm. Right: Fluorescence microscope images of particles before metal coating that reveal the polymer phase separation for both types of particles. Polystyrene fluoresces red, PMMA green. The scale bar is 20 µm.

**Results & Discussion**

Figure a shows the temporal development of the wrinkle structure on a PMMA particle that had been metal-sputtered for 100 seconds. The acceleration voltage of the e-beam was 12 kV and we estimate the penetration depth to be about 1 µm for an organic polymer that only contains elements with a low atom number - in our case, hydrogen, carbon, and oxygen [11]. First wrinkles appear nearly immediately when the irradiation started. The wrinkles are most pronounced on the top of the particle, because there is the highest flux of electrons per surface unit area of polymer. The sloped sides of the particles develop wrinkles at longer irradiation times. Once a wrinkle is formed, it does not change in position or in width, but it becomes deeper with ongoing irradiation. Wrinkles depend on the difference in Young’s modulus of the bulk material and the hard skin layer [5]. Thus, the thickness of the metal layer should have an effect. In order to observe this, we coated the polymer particles at the same ion sputtering conditions for different times. Figure b shows the results of four samples in which the coating time was between 50 and 300 seconds. The absolute thickness of the metal layer was not directly observed, but it should be around 5nm for 50s, and 25nm for 300s sputtering, according to the operation manual. Figure 2 shows that there is a slight dependence of the wrinkle width and periodicity upon sputtering time. The longer the time, the smaller and more ‘crispy’ (i.e. with sharper edges and deeper grooves) the pattern becomes, but the
effect is not very pronounced, and the wrinkle structure does not depend critically on the thickness of the skin layer.

In order to elucidate the effect of the thickness of the soft polymer layer, we produced core-shell particles for which polystyrene-core/PMMA-shell particles had been synthesised by rapid emulsion evaporation as already reported in the literature [9]. Polystyrene is inert towards electron beam irradiation and does not decompose. Thus, polystyrene particles do not show wrinkle structures. Figure c shows that a thin PMMA layer on top of a polystyrene core leads to a shorter wavelength of the wrinkle structure. On the other hand, Janus-type particles show a surface structure in which the PMMA hemisphere shows the usual, large wrinkle wavelength and the polystyrene hemisphere is wrinkle-free.

In this paper, we could show that electron beam decomposition of PMMA containing polymer microparticles that had been coated with a thin metal layer can be used to prepare wrinkled particle surfaces. Even though wrinkled particles have been prepared by other methods described in the introduction, an interesting aspect of our e-beam irradiation is the particle irradiation of particles. Thus, in contrast to other methods, even the wrinkling of a selected area on a single particle should be possible in principle. This will lead to a tailor-made hierarchical surface structure in which micron-size particles are covered with a nanometer-sized surface structure. Applications may range from biocompatible surfaces to superhydrophobic coatings.

**Additional Information**

**Methods and Supplementary Material**
Please see https://sciencematters.io/articles/201603000009.

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**Ethics Statement**
Not applicable.

**Citations**


