SUSPENSION POLYMERIZATION OF THERMALLY EXPANDABLE MICROSPHERES

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Introduction

Thermally expandable microspheres (TEMs) are in our case polymeric core shell particles (CSP) with the capability to expand upon energy input (Figure 1). For the purpose of enhancing 3D-PolyJet printing inks (DIMAP project) this work is focused on the synthesis and characterization of TEMs.

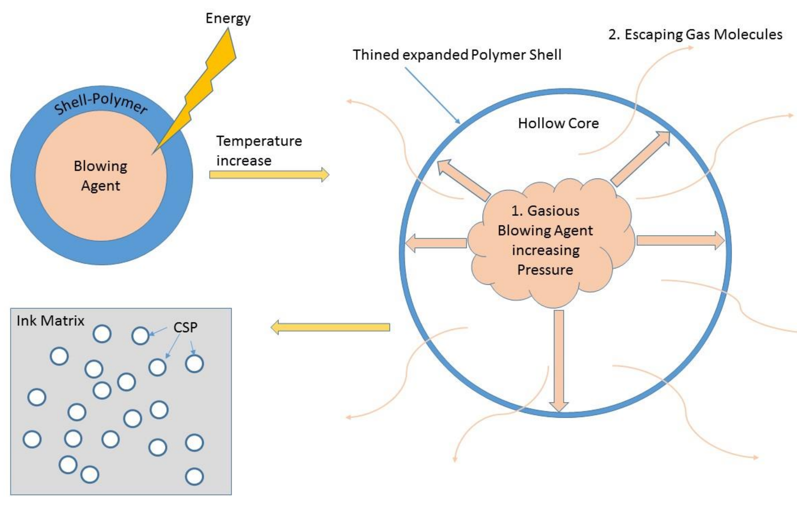

Figure 1: Principle of TEMs in 3D-ink system

Table 1: Invariant parameters of the suspension polymerisations

Parameter	Value
Crosslinker	Dipropylene glycol diacrylate / 2%
Inorganic suspension aid	$Mg(OH)_2$ / 5%
Emulsifier	Sodium 2-ethylhexyl sulfate / 0,05%
Reaction time	18 h
Reaction temperature	70 °C
Initiator	Dilauroyl peroxide / 2,5%

Experimental

The known polymerization route [1], an oil in water free radical polymerization, was adjusted to the specific task of DIMAP: to create small and uniform, low temperature expanding microspheres. Important parameters that were kept constant for all experiments are listed in Table 1, whereas parameter variations are shown in Table 2. The products were characterized via scanning electron microscopy (SEM), atomic force microscopy (AFM) (Figure 2 & Figure 3) and thermogravimetric analysis (TGA) (Figure 4 & 5). The expanding process was monitored via optical microscopy. Particles during expansion can be seen in Figure 6.

Table 2: Varied parameters of different suspension polymerisations. Monomers used: acrylonitrile (ACN), methyl methacrylate (MMA), styrene (ST), butyl acrylate (BA) and 2-ethylhexyl acrylate (2-EHA). Isooctane (IO) serves as blowing agent. T_{exp} denotes the expansion temperature of the TEMs

No.	ACN / %	MMA / %	ST / %	BA / %	2-EHA / %	IO / %	IO / % incorporated	T_{exp} / °C
1	79		19			23	93	197
2	79	19				23	99	193
3	79				19	23	75	167
4	79			19		23	80	160
5	79	19				32	98	185
6	59	39				32	96	174
7	49	49				32	98	141

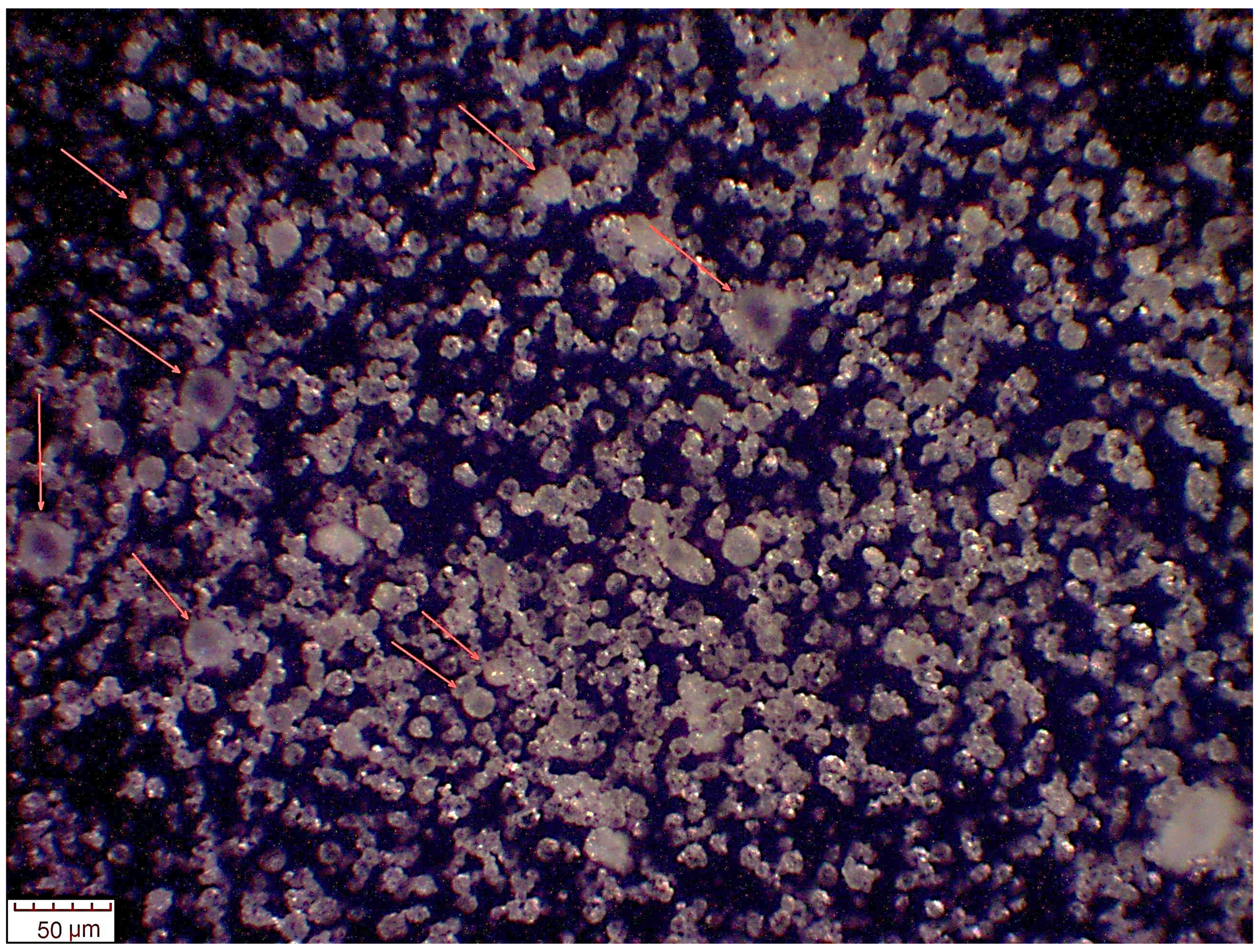

Figure 6: TEMs during expansion

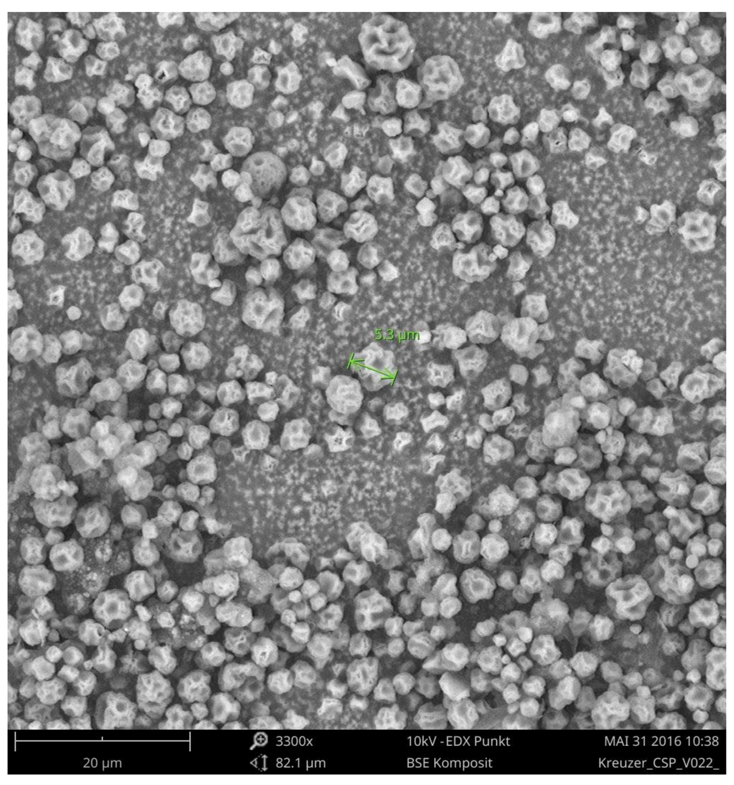

Figure 2: SEM of TEMs No.1

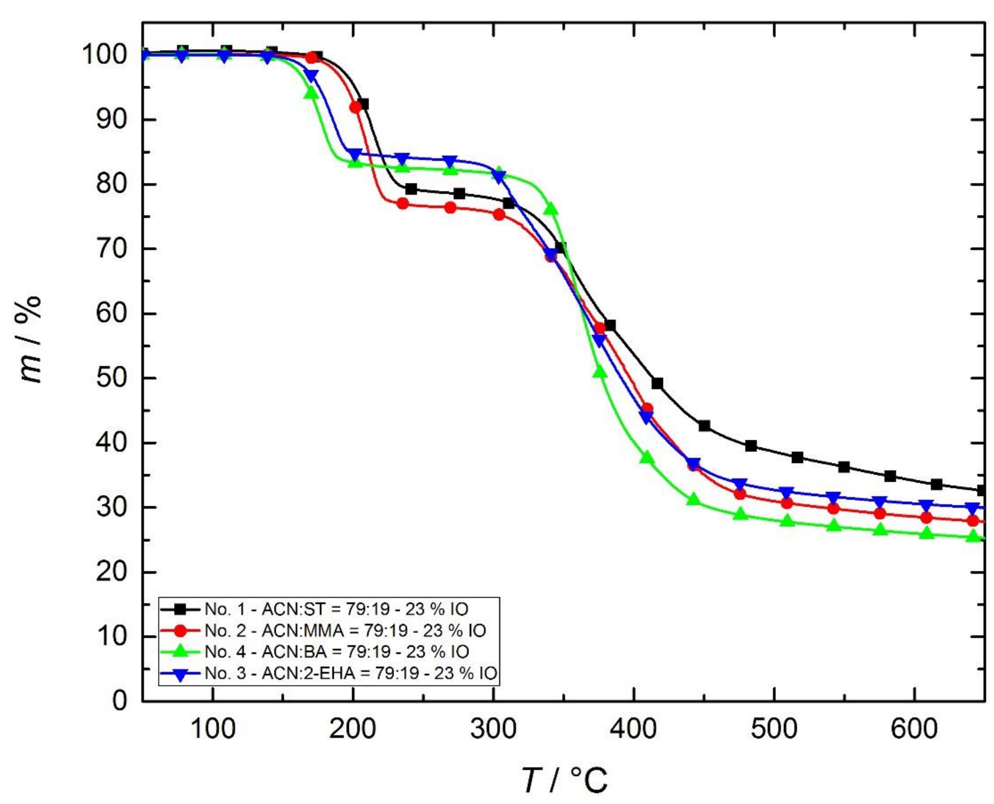

Figure 4: TGA of TEMs with different shell monomers

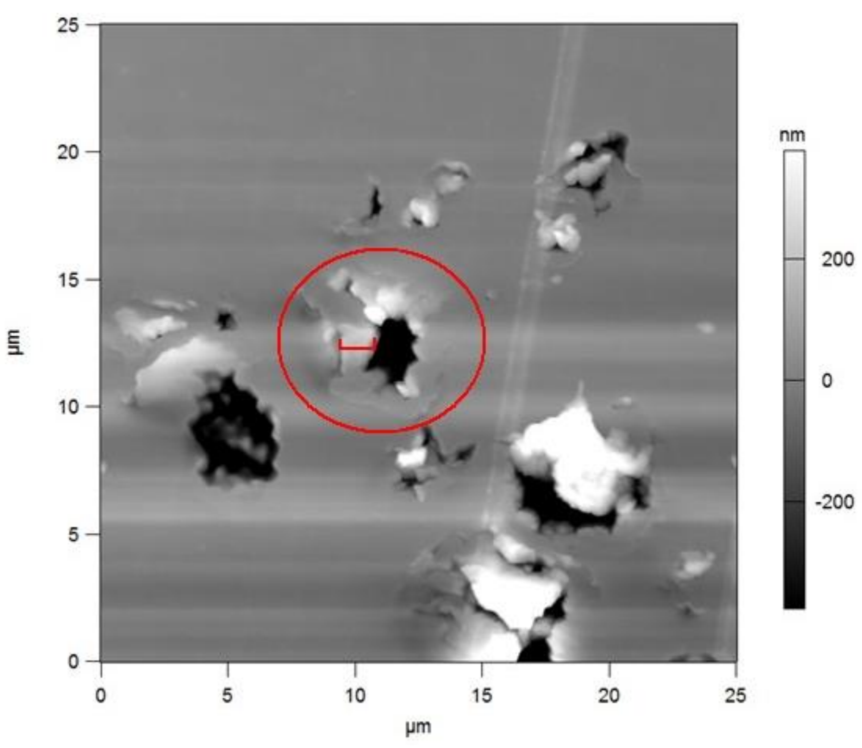

Figure 3: AFM of TEMs No. 1

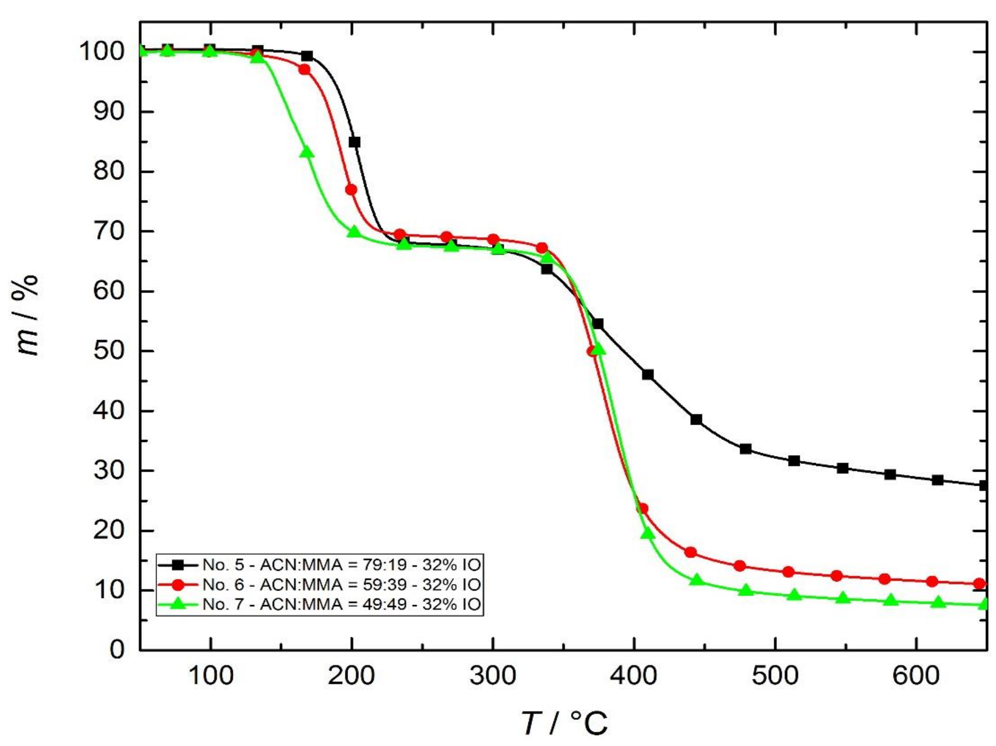

Figure 5: TGA of TEMs: ACN and MMA as shell monomers

Results & Discussion

By varying the monomer type and concentration as well as the blowing agent concentration, different types of TEMs could by synthesized. The monomer mixture and incorporated blowing agent influence the expanding temperature as can be seen in Table 2. The size of the TEMs is as low as the systems homogenizer mean droplet size. To produce even smaller TEMs a different reactor and homogenizer setup seems to be necessary.

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References

[1] Lundqvist J., Expandable thermoplastic microspheres and the process for the production and use of thereof, US5155138 A, (**1992**)