SYNTHESIS OF THERMALLY EXPANDABLE ACRYLIC BASED MATERIALS WITH CONFINED IMPINGING JET REACTORS

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Introduction

It is known that micro jet reactors with two opposing jets can be used for the production of polymers and nanoparticles through their unique mixing capabilities [1,2]. For the purpose of enhancing 3D-PolyJet printing inks (DIMAP project) this work is focused on the synthesis and characterization of acrylic based thermally expandable microspheres (TEMs) which are in our case polymeric core shell particles with the capability to expand upon energy input (Figure 1). These TEMs are synthesized via a known free radical suspension polymerisation route [3]. The necessary reaction suspension was created by facilitating micro reactors based on the confined impinging jet reactor (CIJR) system where the opposing nozzles have a diameter of 200 µm. The reactor setup can be seen in Figure 2a and 2b. The resulting TEMs were compared with microspheres where the reaction medium was prepared with a T 25 digital ULTRA-TURRAX® homogenizer.

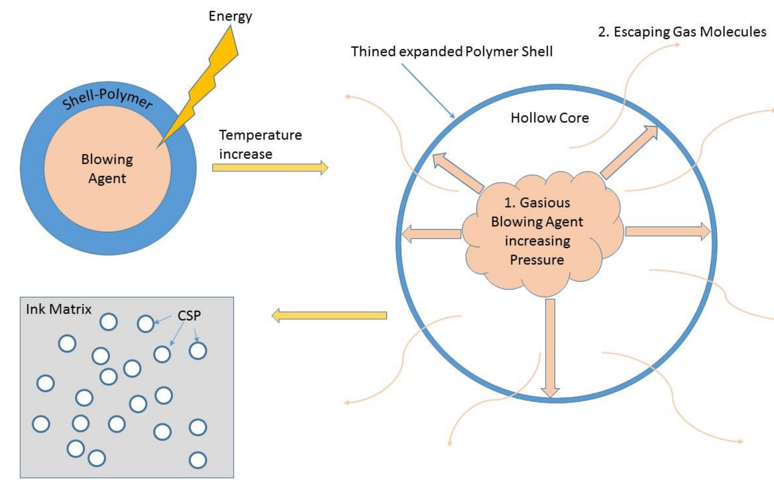

Figure 1: Principle of TEMs in 3D-ink system

Table 1: 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%

Figure 2a: Setup of the CIJR system

Figure 2b: Close up of the CIJR system

Experimental

For comparing the synthesized TEMs, important parameters were kept constant for most experiments (Table 1), whilst others were varied (Table 2). The products were characterized via scanning electron microscopy (SEM) (Figure 3 & 4) and thermogravimetric analysis (TGA) (Figure 5). The expanding process was monitored via optical microscopy. Particles during expansion can be seen in Figure 6 & 7.

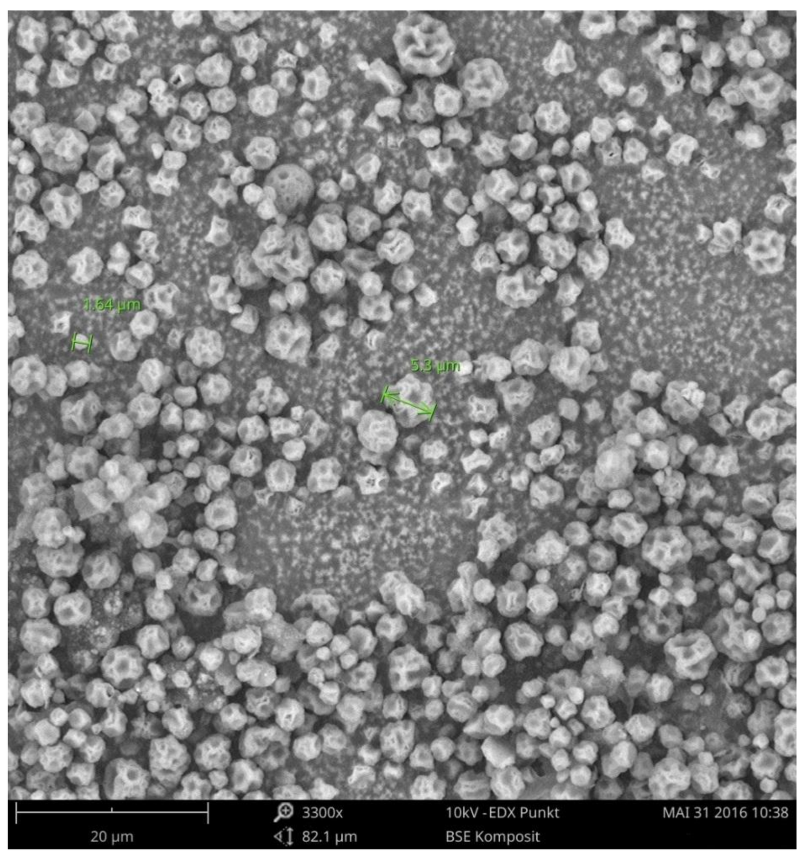

Figure 3: SEM of TEMs No.1

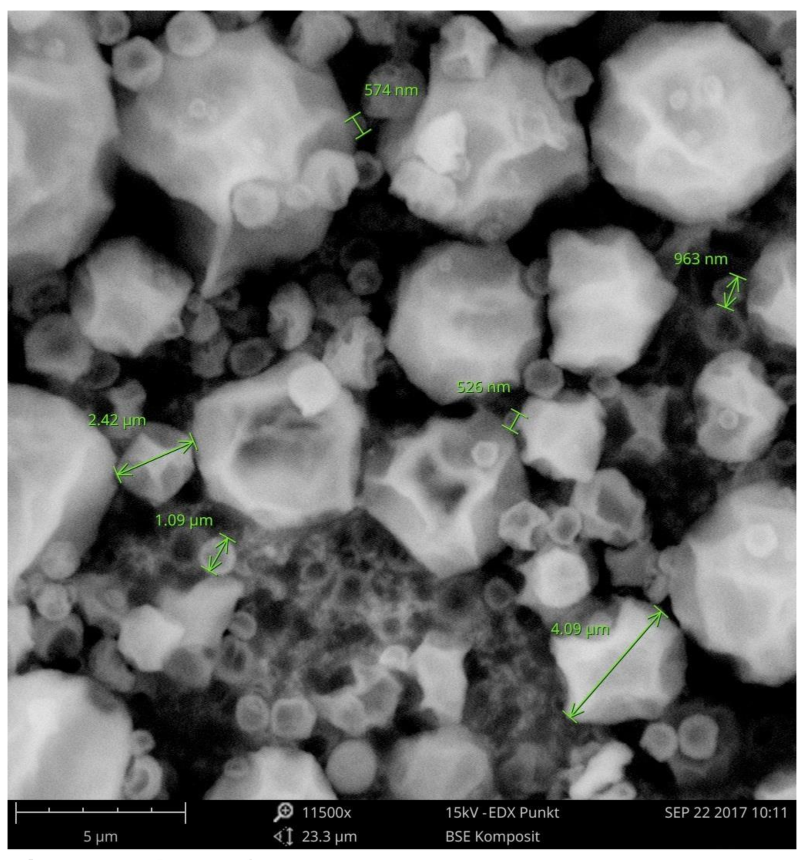

Figure 4: SEM of TEMs No. M4

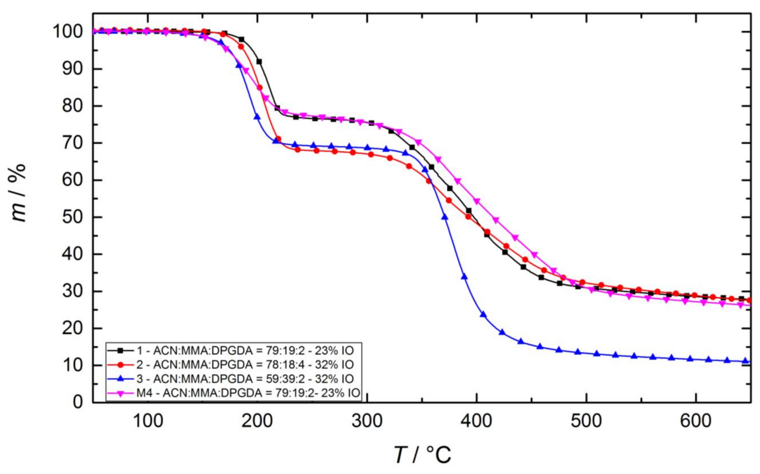

Figure 5 (left): TGA of different TEMs. See Table 2 for details.

Table 2: Varied parameters of different polymerisations. Monomers used: acrylonitrile (ACN) and methyl methacrylate (MMA). Isooctane (IO) serves as blowing agent. T_{exp} denotes the expansion temperature of the TEMs. “M” indicates a CIJR experiment.

No.	ACN / %	MMA / %	IO / %	IO / % incorporated	T_{exp} / °C
1	79	19	23	99	193
2	79	19	32	98	185
3	59	39	32	96	174
M4	79	19	23	46	162

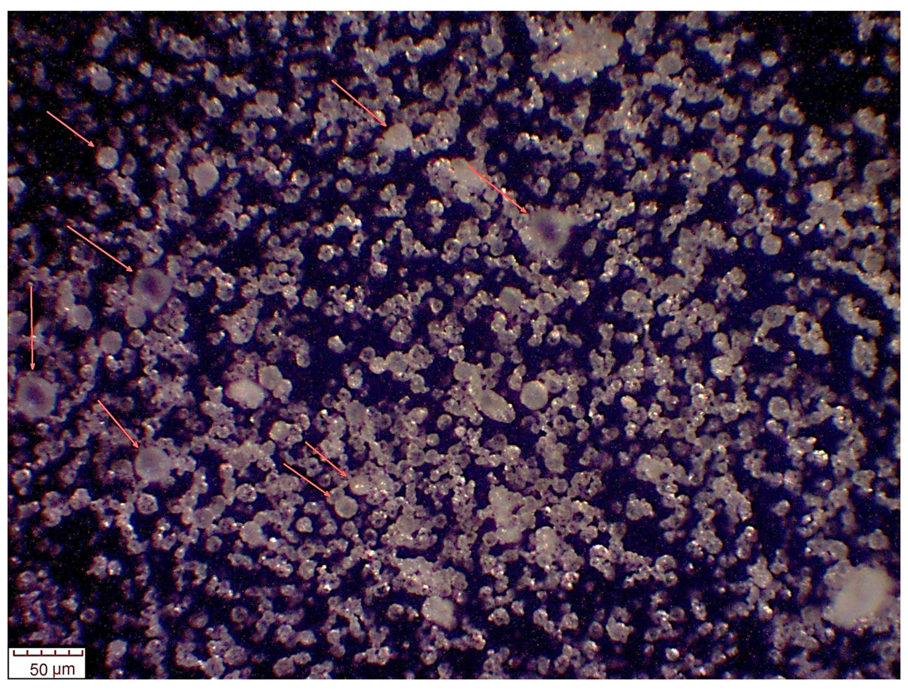

Figure 6: TEMs No.1 during expansion

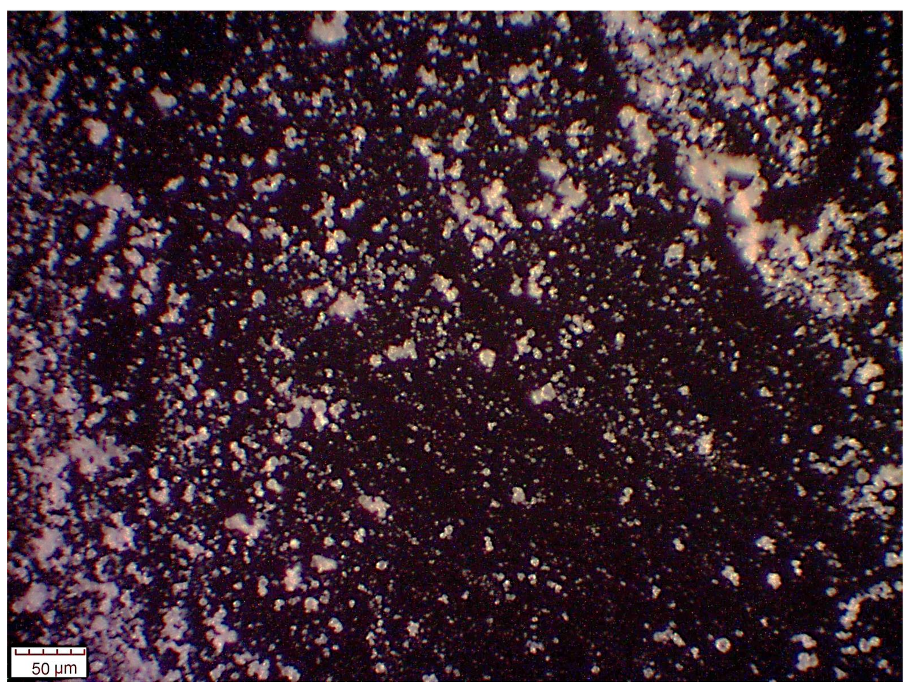

Figure 7: TEMs No. M4 during expansion

Results & Discussion

It is shown that the CIJR System can be facilitated to produce acrylate based TEMs which are considerable smaller than TEMs where the reaction medium is prepared with a rotor-stator type emulsifier. This is confirmed by optical microscopy and SEM. The TEMs are nevertheless comparable in blowing agent content and expansion temperature which is confirmed by TGA.

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