SYNTHESIS AND APPLICATION OF THERMALLY EXPANDABLE CORE-SHELL MICROSPHERES

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Introduction

For the purpose of enhancing 3D-PolyJet printing inks (DIMAP project) this work is focused on the synthesis and characterization of polymeric microspheres as well as their implementation into ink matrices to create 3D printable foams. Polymeric microspheres with a core – shell structure have a wide variety of applications, such as in the food industry or in the medical field as drug delivery systems [1-3]. Thermally expandable microspheres (TEMs) are in our case polymeric core – shell particles with the capability to expand upon energy input. Development of a suitable foaming and curing procedure is an important part of the printing process, as it defines the structure and stability of the printed foam. The curing procedure consists of 3 steps (Figure 1): short low-power UV-irradiation to increase the ink viscosity, foaming of embedded TEMs and short high-power UV-irradiation to fully cure the matrix in order to stabilize the formed foam structure. Figure 2 shows the curing degree of a possible matrix material for the light weight polymeric ink during UV-polymerization.

Experimental

The known polymerization route [4], 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 3 & Figure 4) and thermogravimetric analysis (TGA) (Figure 5 & 6). The expanding process was monitored through optical microscopy. Particles during expansion can be seen in Figure 7. The unexpanded particles suspended are depicted in Figure 8. After applying the appropriate curing procedure, the resulting foam can be seen in Figure 9.

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%

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

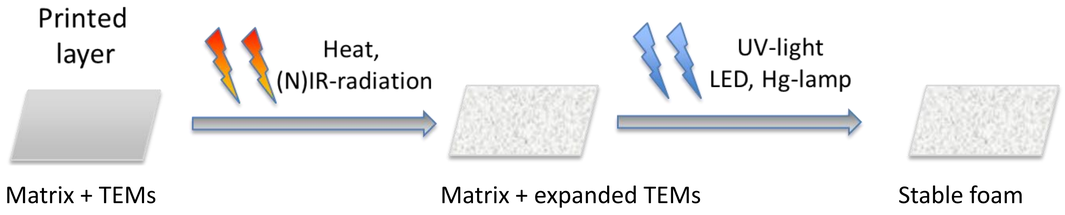

Figure 1: Principle of foaming and curing procedure

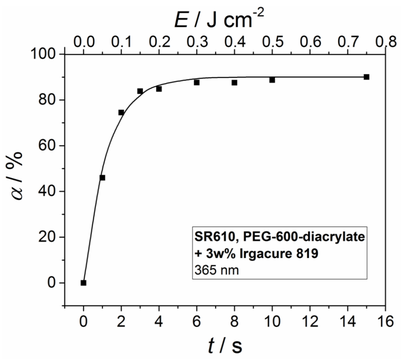

Figure 2: Curing degree of ink matrix material

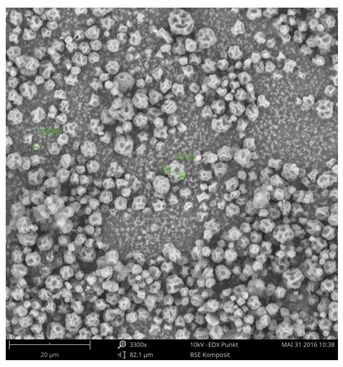

Figure 3: SEM of TEMs No.1

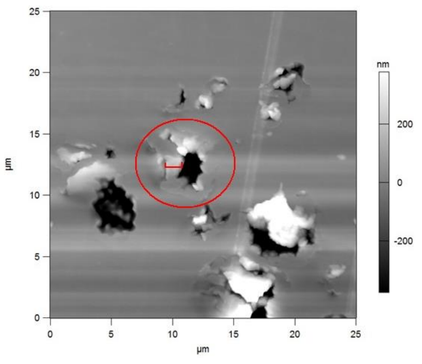

Figure 4: AFM of TEMs No. 1

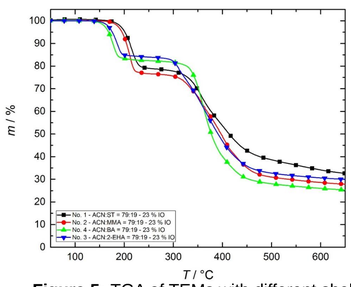

Figure 5: TGA of TEMs with different shell monomers

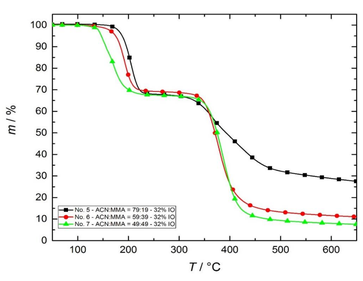

Figure 6: TGA of TEMs: ACN and MMA as shell monomers

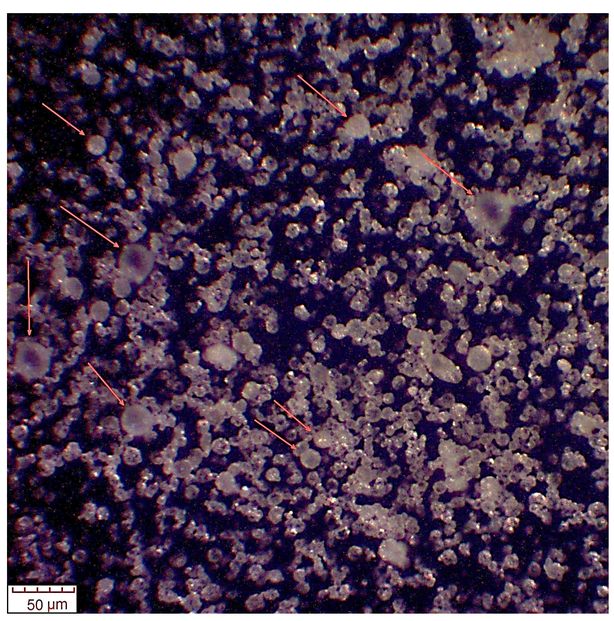

Figure 7: TEMs during expansion

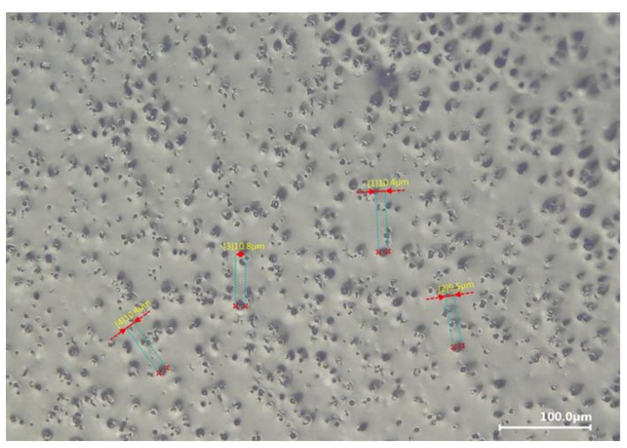

Figure 8: UV 3D inkjet ink with 10 w% TEMs after UV-exposure

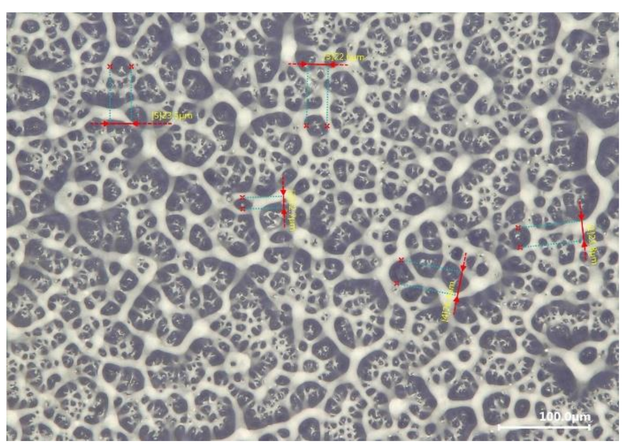

Figure 9: UV 3D inkjet ink with 10 w% TEMs after both NIR- and UV-exposure with visible foam structure

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. Expansion of the TEMs could be monitored via optical microscopy. The TEMs were successfully incorporated into an ink matrix and foaming was achieved.

Acknowledgement

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