Thermally expandable acrylic based core-shell microspheres

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Introduction

Thermally expandable microspheres (TEMs) are already commercially available and have a wide field of application. Some areas demand uniquely designed TEMs with defined properties such as initial size or expansion quality [1,2]. This work is focused on the variation of reaction parameters and their resulting influence on the synthesized TEMs.

Experimental

All syntheses were carried out as free radical oil in water suspension polymerizations via a known polymerization route [3]. The synthesis has four main steps.

- Step 1: preparing the water phase consisting of H_2O, emulsifier (sodium 2-ethylhexyl sulfate - Na-EH-SO_4) and dispersing agent ($Mg(OH)_2$).
- Step 2: preparing the oil phase consisting of monomers (acrylonitrile - ACN, methyl methacrylate - MMA, butyl acrylate – BA, styrene - ST), crosslinker (dipropylene glycol diacrylate – DPGDA) initiator (dilauroyl peroxide - DLPO) and blowing agent (isooctane - IO).
- Step 3: mixing and homogenizing with an IKA Ultra-Turrax™ T25 at 15 000 RPM for 180 s.
- Step 4: polymerization under Ar in a 50 ml glass reactor for 20 ± 1 h.

The parameters of the different experiments can be seen in Table 1 and Table 2.

Table 1: Monomers and their ratios used in the conducted experiments.

No.	ACN / %	MMA / %	ST / %	BA / %	DPGDA / %
1	50	50	-	-	-
2	80	-	20	-	-
3	20	-	80	-	-
4	50	-	50	-	-
5	79	19	-	-	2
6	79	-	19	-	2
7	80	20	-	-	-
8	79	-	19	-	2
9	79	19	-	-	2
10	79	-	-	19	2

Table 2: Water phase composition, blowing agent content and initiator concentration. Percentage added - in relation to the sum of the masses of the monomers.

No.	$Mg(OH)_2$ / %	Na-EH-SO_4 / %	H_2O / parts	IO / %	DLPO / %
1	7	0,10	5/6	30	2,0
2	10	0,50	5/6	25	2,5
3	10	0,50	5/6	30	2,5
4	10	0,50	5/6	30	2,5
5	7	0,10	5/6	30	2,5
6	7	0,10	5/6	30	2,5
7	7	0,10	5/6	30	2,5
8	5	0,05	6/7	30	2,5
9	7	0,10	5/6	30	2,5
10	7	0,10	5/6	30	2,5

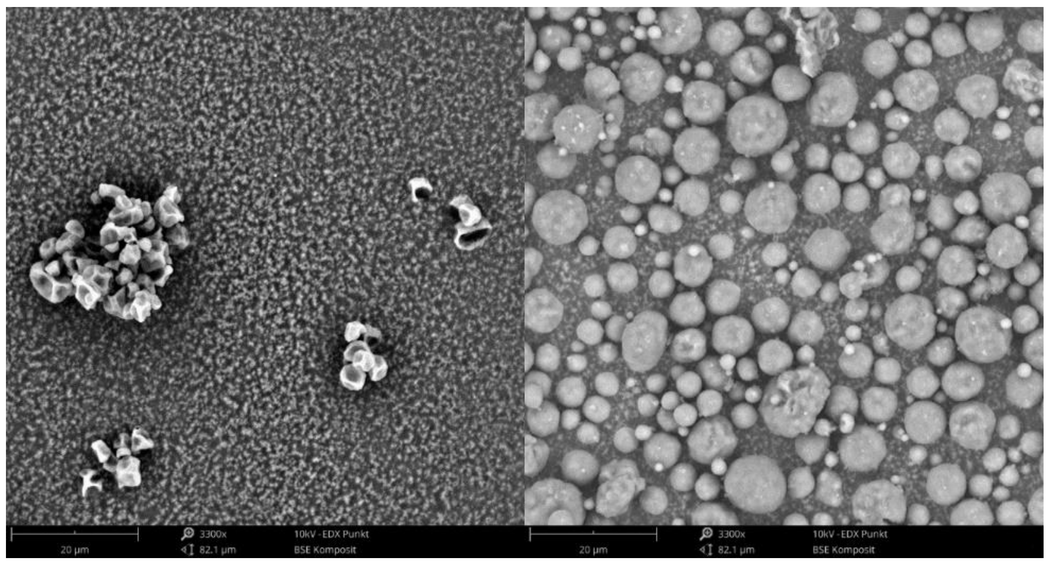

Figure 3: SEM picture of TEMs with blowing agent (No. 7, left) and without blowing agent (right).

Results & Discussion

When the polymerizations were carried out below 65 °C or an initiator content below 2,5 %, no blowing agent was incorporated or no polymerization took place at all. The obtained polymers of the successful experiments were characterized by the means of TGA and SEM. TGA reveals that when styrene was used as monomer incorporation of IO could only be achieved with lower Na-EH-SO_4 and $Mg(OH)_2$ content and with DPGDA. In contrast MMA and BA were reacting more readily (Figure 1 & Figure 2). SEM reveals a deformation of the synthesized TEMs when compared to the equivalent reaction without blowing agent (Figure 3). A possible explanation for this phenomenon is the volume contraction of the IO due to temperature changes. The onset temperatures of the IO loss and the onset decomposition temperatures of the polymers were comparable when similar reaction parameters were used (Table 3).

Table 3: Reaction temperatures and TGA results.

No.	T_R / °C	IO / %	T IO loss / °C	T decomp. / °C
1	63	-	-	-
2	68	-	-	289 / 404
3	68	-	-	404
4	70	-	-	290 / 411
5	70	19	181	328
6	70	7	170	289 / 406
7	73	23	205	339
8	70	21	197	329
9	73	27	160	356
10	70	18	151	341

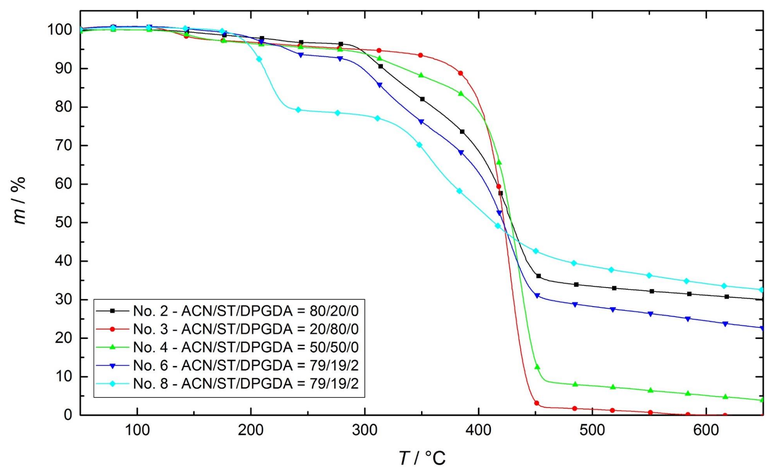

Figure 1: TGA analysis of TEMs with styrene as copolymer.

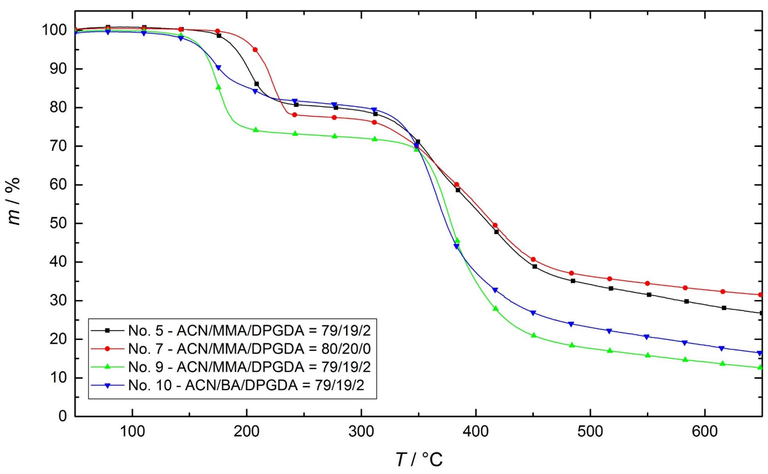

Figure 2: TGA analysis of TEMs with MMA and BA as copolymers.

Acknowledgement

This project has received funding from the European Union's Horizon 2020 program for research and innovation under Grant Agreement No. 685937.
The author gratefully thanks all involved project partners for the good cooperation and their helpful input.

A special thanks to DI Dr. Sebastian Leitner from Wood K plus for the SEM measurements.

DIMAP is funded under EU H2020-NMP-PILOTS-2015, GA 685937

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