Microencapsulation of butyl stearate with melamine-formaldehyde resin: Effect of decreasing the pH value on the composition and thermal stability of microcapsules

B. Alič, U. Šebenik, M. Krajnc*

University of Ljubljana, Faculty of Chemistry and Chemical Technology, Aškerčeva cesta 5, SI-1001 Ljubljana, Slovenia

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Abstract. The object of this study was to investigate how different decreasing of pH regimes during microencapsulation process with melamine-formaldehyde (MF) resin affects the composition, morphology and thermal stability of microcapsules containing a phase-change material (PCM). Technical butyl stearate was used as PCM. Microencapsulation was carried out at 70°C. For all experiments the starting pH value was 6.0. After one hour of microencapsulation at the starting pH value, the pH value was lowered to final pH value (5.5; 5.0; 4.5) in a stepwise or linear way. The properties of microcapsules were monitored during and after the microencapsulation process. The results showed that pH value decreasing regime was critical for the morphology and stability of microcapsules. During microencapsulations with a stepwise decrease of pH value we observed faster increase of the amount of MF resin in the microencapsulation product compared to the microencapsulations with a linear pH value decrease. However, faster deposition in the case of microencapsulations with stepwise decrease of pH value did not result in thicker MF shells. The shell thickness increased much faster when the pH value was decreased in a linear way or in several smaller steps. It was shown that for the best thermal stability of microcapsules, the pH value during microencapsulation had to be lowered in a linear way or in smaller steps to 5.0 or lower.

Keywords: thermal properties, microencapsulation, melamine-formaldehyde resin, phase-change materials

1. Introduction

Microcapsules are tiny particles with diameters in the range between 1 and 1000 μm that consist of a core material and a covering shell. Through a selection of the core and shell material, it is possible to obtain microcapsules with a variety of functions. This is why microcapsules can be defined as containers, which can release, protect and/or mask various kinds of active core materials [1]. Microencapsulation is mainly used for the separation of core material from the environment, but it can also be used for controlled release of core material in the environment. Microencapsulation has specially attracted a large interest in the field of phase change materials (PCMs) as they are capable of storing and

releasing energy during solid-liquid phase transition. The applications of PCMs in thermal energy storage have been well known and used in many fields [2–11]. For shell material of PCM microcapsules melamine-formaldehyde resin is often used mainly because of its good mechanical [12–14] and thermal stability [9, 14–16]. Melamine-formaldehyde (MF) microcapsules can be prepared by the *in situ* polymerization process by polycondensation, where the melamine-formaldehyde prepolymer is initially soluble in the continuous water phase, while the hydrophobic core material is contained in dispersed droplets. As the polymerization reaction starts in aqueous solution, the formed oligomers start to collapse on the surface of the core droplets.

*Corresponding author, e-mail: matjaz.krajnc@fkkt.uni-lj.si

On the surface, the polymerization continues and crosslinking occurs, which results in a solid MF shell formation [17–21]. The shell formation is particularly linked to the pH value [15, 17, 18, 20], temperature [15, 20, 22], type and the amount of emulsifier used [18, 22–27] and to melamine to formaldehyde molar ratio [20], which all significantly determine thermal stability and shell morphology of microcapsules. For a successful formation of a homogenous and compact MF shell the usage of anionic emulsifiers is necessary. In the case of cationic emulsifiers, charge repulsion between cationic emulsifier and MF resin negatively influences the shell formation in microcapsules. On the other hand, the efficiency of nonionic emulsifiers is medium [26]. Faster MF shell formation is achieved at lower pH values. However, the usage of low pH values results in microcapsules with raspberry-like surface or even in lower microencapsulation efficiency, while at relatively high pH values a smooth MF shell is formed [20].

In our previous work, the research was focused on the investigation of MF microcapsules with decane core, which were prepared at different temperatures and different pH values [28]. The degree of curing of the MF resin at different process parameters was studied as well. It was found that at higher temperatures and lower pH values the time necessary for stable microcapsules formation is shorter. Thicker shells were obtained in microencapsulations carried out at lower pH values and higher temperatures. At lower pH values the degree of MF resin crosslinking was higher.

In the present work, microencapsulation of butyl stearate with melamine-formaldehyde resin was carried out at 70°C at different pH value decreasing regimes. As PCM butyl stearate was chosen because its phase change temperature is around 20°C, where melting and crystallization occur, and because it has a relatively high heat storage capacity. Therefore, it can be used as an effective thermo regulating material at ambient temperature. For example, microencapsulated butyl stearate can be used as an additive in indoor or outdoor coatings or it may be built in insulating materials, such as foams. The main objective of this study was to investigate the effects of decreasing the pH value regime and final pH value on the composition of microcapsules, their thermal stability and morphology. To study the microencap-

sulation process, properties of microcapsules were investigated during and after the microencapsulation. For this purpose differential scanning calorimetry, scanning electron microscopy and thermogravimetric analysis were used.

2. Experimental

2.1. Materials

We used etherified melamine-formaldehyde (MF) resin (70 wt%, Melapret NF70/M, Melamin, Kočevje, Slovenia), butyl stearate (technical, 40–60%, rest butyl palmitate, Sigma-Aldrich, Steinheim, Germany), sodium dodecyl sulfate (SDS, 98.5%, Sigma-Aldrich, Steinheim, Germany), formic acid (99.8%, Kemika, Zagreb, Croatia) and deionized water.

2.2. Preparation of microcapsules

Emulsion preparation: 25 g of technical butyl stearate, 2.5 g of SDS (used as emulsifier), 15 g of MF resin and 457.5 g of deionized water were mixed for 30 minutes using Ultraturax Dispermat (VMA-Getzmann, Reichshof, Germany) at the rate of 1000 rpm and temperature of 30°C.

Microencapsulation: The emulsion was poured into a glass five neck reactor, equipped with a reflux condenser, a mechanical stirrer, a digital thermometer, a high pressure liquid chromatography (HPLC) pump K-120 (Knauer, Berlin, Germany) and a glass electrode for pH measurements. The reactor content was stirred at the rate of 500 rpm. The pH value of emulsion was adjusted to 6.0 by adding 1 wt% formic acid solution at the rate of 1 mL/min using HPLC pump and then heated to 70°C. During microencapsulation processes the temperature was kept constant at 70°C, while the pH value was regulated according to the regimes shown in Figure 1. Every 30 minutes samples were taken from the reactor to analyze the composition and properties of microcapsules. Before analyses the samples were filtered through paper filter discs (Sartorius 388) and washed with warm deionized water. The wet cake containing microcapsules was dried at room temperature to constant weight and dry powders of microcapsules were used for characterization. In the text of this report, the samples are labeled as MC(*x–y/step/t*) and MC(*x–y/linear/t*) for microencapsulation with stepwise or linear decrease regime of pH values, respectively. MC stands for microcapsules, *x–y* for

Figure 1. pH value regimes during microencapsulation processes

starting and final pH value of microencapsulation and t for sampling time.

2.3. Characterization of microcapsules

The morphology of microcapsules was observed by scanning electron microscopy using a FE-SEM ULTRA Plus (Carl Zeiss, Oberkochen, Germany) instrument. Before SEM analysis the samples were partly mechanically cut with a razor blade. The cutting lasted for several minutes until the analyzed sample contained enough damaged microcapsules for their shell thickness determination. Treated samples (containing damaged and whole microcapsules) were sparsely sprinkled onto a carbon tape attached to metal stubs, dried in vacuum at 100°C for 48 hours and then gold coated at 20 mA for 1.5 min (SCD 030 gold coater, Balzers Union model FL-9496, Liechtenstein). The samples were then

imaged using an accelerating voltage of 1 kV. For the purpose of determining shell thickness at least four SEM images of the same sample were taken. The shell thickness was measured using SmartSEM software. The average shell thickness value was calculated out of at least ten shell thickness values obtained for an individual sample.

Differential scanning calorimetry (DSC) was used to define mass percentage of shell material in microcapsules. The measurements were performed on a Mettler Toledo DSC1 instrument with intra-cooler using STAR software. In and Zn standards were used for the temperature calibration and for the determination of the instrument time constant. Standard 40 μ L alumina pans and air atmosphere were used. Sample mass was about 10 mg. The following temperature program was used: An isothermal segment at 50°C for 5 minutes was followed by a cooling segment from 50 to –50°C with a cooling rate of –5°C/min. Then a heating segment from –50 to 50°C with a heating rate of 5°C/min was performed. This temperature interval was chosen because the phase change temperature of butyl stearate is around 20°C. Each sample was analyzed three times and the average weight percentage of core material was calculated from melting enthalpies of bulk and encapsulated core material. Termograms of butyl stearate and samples isolated at 180 minutes are presented in Figure 2. To confirm the core to shell weight ratio obtained by DSC analysis a gravimetric analysis was performed by Soxhlet extraction of core material in acetone for 72 hours. Duration of one extraction cycle was 4 minutes. After extraction, sample residues were dried at room temperature for

Figure 2. Thermograms for butyl stearate and microcapsules obtained at the end of microencapsulation: (a) butyl stearate crystallization peaks and (b) butyl stearate melting peaks

12 hours and additional 15 hours in vacuum at 50°C. The dried sample residues were weighed and the weight percentage of shell material in microcapsules was calculated. To confirm complete Soxhlet extraction of core material, DSC analysis of sample residue was also performed.

Thermogravimetric analysis (TGA) of microcapsules was performed using a Mettler Toledo TGA/DSC1 instrument with STAR software. All the experiments were conducted in a nitrogen atmosphere with a flow rate of 50 mL/min at a heating rate of 10°C/min from 50 to 500°C. Standard 80 μL Al_2O_3 crucibles were used. For all measurements the baseline was subtracted. Sample mass was about 10 mg.

3. Results and discussion

3.1. Microcapsule composition and morphology

Variations of weight percentage of MF resin in samples during microencapsulations carried out at different process parameters are presented in Figure 3.

Figure 3. Weight percentage of MF resin in samples during microencapsulation processes determined by DSC analysis

Until 60 minutes of microencapsulation processes, which was carried out at pH value 6.0 for all experiments, the weight percentage of MF resin in samples was constant and within the range of 7–10%. Discrepancies between individual microencapsulation samples can be attributed to incomplete stability of microcapsule shells [28]. At the point when the pH value started decreasing, the weight percentage of MF resin in samples started to increase, depending on the regime by which pH value was decreased and on the final pH value. The increase of the amount of MF resin was faster in the case of stepwise pH value decrease, than in the case of linear pH value decrease. As expected, the fastest increase of the amount of MF resin was observed in microencapsulation MC(6.0–4.5/step), i.e. when we used a stepwise pH value decrease to the lowest pH value. This is explained by faster MF resin polymerization [29, 30], curing reactions [31] and consecutive deposition [20] of MF resin on microcapsules surface at lower pH values. In MC(6.0–4.5/step) synthesis the final weight percentage of MF resin was reached already at 90 minutes (30 minutes after lowering the pH value from 6.0 to 4.5). The lowest increase of MF resin amount was achieved in synthesis MC(6.0–5.5/linear), i.e. at linear pH value decrease to the highest final pH value. To verify the accuracy of DSC results a gravimetric analysis by Soxhlet extraction was performed. DSC and gravimetric measurements results for samples of microencapsulations are shown in Table 1. DSC results were in good agreement with gravimetric results.

Shell morphology and thickness of microcapsules were evaluated using SEM images. Selected images of microcapsules, obtained at different process parameters and different process times, are shown in Figures 4 and 5.

Table 1. DSC and gravimetric results for weight percentage of the MF resin in samples of microencapsulation

Microencapsulation	MF resin in samples [wt%]					
	DSC analysis			Gravimetric analysis		
	60 min	120 min	180 min	60 min	120 min	180 min
MC(6.0–5.5/step)	9.1	9.9	19.7	–	–	19.3
MC(6.0–5.0/step)	8.4	29.1	30.1	–	–	29.6
MC(6.0–4.5/step)	7.9	29.5	29.9	8.2	28.6	29.2
MC(6.0–5.5–5.0/step)	7.3	9.6	29.4	–	–	29.1
MC(6.0–5.5/linear)	8.4	8.3	10.1	–	–	10.3
MC(6.0–5.0/linear)	8.4	9.5	28.8	–	–	27.6
MC(6.0–4.5/linear)	9.1	16.4	29.8	10.4	17.1	29.6

Figure 4. SEM image of microcapsules isolated during microencapsulations with stepwise decrease of the pH value: a→b→c for MC(6.0–5.5–5.0/step) at 60, 120 and 180 minutes; a→b→f for MC(6.0–5.5–5.0/step/180 min) at 60, 120 and 180 minutes; a→e→h for MC(6.0–5.0/step) at 60, 120 and 180 minutes and a→d→g for MC(6.0–4.5/step) at 60, 120 and 180 minutes

Since in all microencapsulations the process parameters were the same till 60 minutes, the microcapsules morphology was also the same. As can be seen from SEM images of microcapsules at 60 minutes (Figure 4a and Figure 5a), microcapsules have a smooth shell with only a few pure MF particles attached to them. After the pH value was decreased the pure MF particles started depositing faster on the surface. Deposition of MF particles was particularly rapid in the case of stepwise decrease of the pH value to 5.0 (Figures 4e and 4h) and 4.5 (Fig-

ures 4d and 4g). The MF particles were not deposited evenly all over the surfaces of microcapsules. Moreover, the MF particles were not firmly attached to the surface as several free clusters of MF particles were noticed.

Treatment (cutting, crushing) of microcapsules before actual SEM analysis allowed for the determination of the average shell thickness. An example of shell thickness determination for sample MC(6.0–4.5/linear/180 min) is given in Figure 6.

Figure 5. SEM image of microcapsules isolated during microencapsulations with linear decrease of the pH value: a→b→c for MC(6.0–5.5/linear) at 60, 120 and 180 minutes; a→e→g for MC(6.0–5.0/linear) at 60, 120 and 180 minutes; a→d→f for MC(6.0–4.5/linear) at 60, 120 and 180 minutes

Figure 6. Shell thickness determination for microcapsules MC(6.0–4.5/linear/180 min)

In this figure we can clearly observe the small pure MF particles. For determining the shell thickness only the thickness of the smooth part of the shell without small particles on the surface was measured. Changes in the average shell thicknesses during microencapsulation processes are shown in Figure 7.

Shell thickness of microcapsules after one hour of microencapsulation was almost the same in all experiments because of identical process parameters used during the first 60 minutes. The average shell thickness at 60 minutes was between 290 and

Figure 7. Average shell thickness during microencapsulation processes

300 nm. After that, in all syntheses the average shell thickness increased with microencapsulation time. The increase depended on the pH value and on the manner in which the pH value was lowered. In microencapsulations with stepwise pH value decrease the shell thickness increased slowly and there were no major differences in shell thickness between the experiments. Among these samples the thickest shell was observed in sample MC(6.0–5.5–5.0/step/180 min) for which the pH value decrease was performed in two steps. On the other hand, in microencapsulations with linear pH value decrease significant differences in shell thickness between samples with different final pH value were observed. Namely, the shell thickness increased with decreasing the final pH value. The shells of microcapsules, obtained by linear decrease the pH value, were therefore significantly thicker than those of microcapsules obtained by stepwise pH value decrease.

3.2. Thermal stability of microcapsules

TGA was used to investigate thermal stability of microcapsules and its pure components. Thermal characteristics of starting components (butyl stearate and dried MF prepolymer Melapret NF 70/M) and by Soxhlet extraction isolated MF resin of samples MC(6.0–5.0/linear/180 min) and MC(6.0–5.5–5.0/step/180 min) are shown in Figure 8. Butyl stearate evaporated/decomposed completely in one step from 160 to 300°C (Table 2). For dried uncured MF resin Melapret NF 70/M two distinctive steps of weight loss were observed. In two partially cured MF resins (microcapsules' shell material) the weight loss did not occur as distinctively on the account of differences in the chemical structure between partially cured and non-cured MF resin. Thermal stability of MF resins was studied in detail by Manley

Figure 8. TGA curves of butyl stearate, dried MF prepolymer Melapret NF70/M and isolated MF resins of MC(6.0–5.0/linear/180 min) and MC(6.0–4.5/step/180 min)

Table 2. Results TGA analysis of core material, isolated MF resins and microcapsules at 180 minutes

Sample	Shell thickness [nm]	MF resin [wt%]	At 300°C			Residue at 500°C [wt%]
			Total weight loss [wt%]	Weight loss on account of core material [wt%]	Evaporated core material [wt%]	
butyl stearate	–	0	100	100	100	0
isolated MF resins	–	100	15*	0	0	32
MC(6.0–5.5/step/180 min)	307	19.7	20.5	17.5	22	5.2
MC(6.0–5.0/step/180 min)	307	30.2	29.6	25.1	36	8.9
MC(6.0–4.5/step/180 min)	307	29.9	40.0	35.5	51	9.4
MC(6.0–5.5–5.0/step/180 min)	313	29.4	18.6	14.2	20	8.4
MC(6.0–5.5/linear/180 min)	318	10.1	24.3	22.8	25	2.6
MC(6.0–5.0/linear/180 min)	329	28.8	17.5	13.3	19	8.6
MC(6.0–4.5/linear/180 min)	347	29.8	19.0	14.5	21	9.9

*average weight loss of the isolated MF resins

and Higgs [32] and Devallencourt *et al.* [33]. For Melapret NF 70/M the first significant weight loss occurs at the temperature around 160°C, which can be attributed to evaporation of methanol, formaldehyde and water during curing reactions. The next major weight loss step occurs above 350°C, when the methylene bridges start to breakdown. Above 400°C the three-dimensional polymer structure of MF resin continues to decompose slowly. At these temperatures ammonia, formaldehyde and other volatile decomposition products are released. The nonvolatile residue contains –NH– bridges between melamine rings as well as different cyameluric structures [33]. In isolated cured MF resins the decrease of weight starts already below 100°C, presumably as a result of adsorbed water on MF resin. With increasing the temperature (140–260°C), MF resin starts to cure and the weight loss can be ascribed to evaporation of water, formaldehyde and methanol. As these resins were partially cured [28] before TGA analysis, the weight loss due to crosslinking reactions is smaller compared to uncured MF resin Melapret NF 70/M. At temperatures above 280°C weight loss is visible, which can be mainly ascribed to transformation of dimethylene ether bridges to methylene bridges. The weight loss step of isolated MF resin due to decomposition of methylene bridges is not as distinctive as in the case of Melapret NF 70/M and shifts towards higher temperatures (400°C).

TGA curves of butyl stearate and microcapsules isolated at the end of microencapsulations are shown in Figure 9. At temperatures below 140°C the differences between samples are minimal and are due to weight loss caused by the adsorbed water evaporation. The remaining parts of TGA curves have two main weight loss stages. The first stage is in the temperature range between 140–300°C, where weight loss can be attributed mainly to evaporation of butyl stearate. Namely, microcapsules contained 70 wt% or more of core material. Of course, a certain part of weight decrease in this temperature range must also be ascribed to the evaporation of water, methanol and formaldehyde as a consequence of MF resin curing reactions. However, considering the core/shell ratio the thermal degradation of MF resin may be ascribed to a maximum of 4.5 wt% decrease in this temperature range (Figure 8). The second main weight decrease for micro-

Figure 9. TGA curves of butyl stearate and microcapsules isolated at 180 minutes

capsules occurs above 350°C, where MF shell was unable to hold the expanding core material and its decomposition products within microcapsules due to enhanced disintegration of three-dimensional resin structure.

For the purpose of comparing thermal stabilities of microcapsules obtained at different pH lowering regimes we focused on the weight losses at temperature point of 300°C, since 300°C is the temperature where butyl stearate exhibited 100% weight loss. By comparing the results of TGA analysis of samples after 180 minutes of microencapsulation (Table 2) we can observe that samples MC(6.0–4.5/step/180 min), MC(6.0–5.0/step/180 min) and MC(6.0–5.5/linear/180 min) had the highest weight loss in respective order. Other samples have comparable weight losses at 300°C. Distinct weight losses were calculated from the determined core/shell mass ratio (DSC measurements) and TGA results of pure butyl stearate and isolated MF resins. Weight percentage of evaporated core material was obtained by dividing weight loss on the account of core material at 300°C by weight percentage of core material in microcapsules before TGA analysis. Based on the results, presented in Table 2 it may be concluded, that in microcapsules MC(6.0–5.0/linear/180 min) only 19% of the core material evaporated till 300°C. On the other hand, in microcapsules MC(6.0–5.0/step/180 min), a 36 wt% loss of the core material was observed. The lower thermal stability of sample MC(6.0–5.0/step/180 min) may be explained by its thinner shell thickness since both samples contained around 30 wt% of shell

material. Shell thickness of sample MC(6.0–5.5–5.0/step/180 min) was between samples MC(6.0–5.0/linear/180 min) and MC(6.0–5.0/step/180 min). Therefore it may be concluded that if the end pH value is fixed, thermal stability of microcapsules increases with increasing the shell thickness, which is strongly dependent on the pH value lowering regime.

By comparing the results of the microcapsules obtained by lowering the pH value to different end values in one step, we can observe that a large pH value drop had a negative effect on thermal stability. In this case the shell thickness could not be the reason for the differences we noticed, since the shell thickness for all the samples (MC(6.0–4.5/step/180 min), MC(6.0–5.0/step/180 min) and MC(6.0–5.5/step/180 min), presented in Table 2, was the same. The reason may be due to the crosslink density of the MF shell, which is, together with shell thickness, the most important factor for good thermal stability of microcapsules. In the case of a large step decrease of the pH value, the curing of MF resin was strongly accelerated. Consequently, this leads to the formation of a thin outer layer of higher cured MF shell. On the other hand, the inner part of microcapsules shell (which was not in contact with the continuous phase with lowered pH value) remained less cured. Moreover, despite the fact that curing was faster, the crosslinking and resin density were lower at lower pH values. Namely, at high curing rate the crosslinking bonds are formed quickly and the molecules do not have sufficient time to orient themselves in positions to form the maximal

number of crosslinks. A lower crosslink density results in a brittle and permeable MF shell.

To determine the changes in thermal stability of microcapsules during microencapsulation, and to prove that large pH value decrease in stepwise procedure has indeed a negative influence on thermal stability of microcapsules, microcapsules were also investigated for MC(6.0–5.0/step), MC(6.0–5.5–5.0/step) and MC(6.0–5.0/linear) at 60 and 120 minutes. Detailed results of TGA analysis of the core material, isolated MF shell material and microcapsules isolated at 60, 120 and 180 minutes of microencapsulations MC(6.0–5.0/step), MC(6.0–5.5–5.0/step) and MC(6.0–5.0/linear) are presented in Table 3. Due to identical reaction parameters till 60 minutes of microencapsulations, TGA curves for MC(6.0–5.0/step/60 min), MC(6.0–5.5–5.0/step/60 min) and MC(6.0–5.0/linear/60 min) are similar, as it was expected from the results of SEM analysis, i.e. microcapsules isolated at 60 minutes had identical morphology and comparable shell thicknesses. Minor differences between TGA with the microcapsules isolated at 60 minutes could be attributed to the fragile shells of microcapsules (possible rupture of microcapsules). Since different regimes of the pH value decrease were employed, there was also a greater differentiation in thermal stability of the microcapsules. While thermal stability of MC(6.0–5.0/linear) and MC(6.0–5.5–5.0/step) microcapsules increased with decreasing the pH value, the stability of microcapsules MC(6.0–5.0/step) decreased. In MC(6.0–5.0/step) the weight loss of the core material decreased from starting 28% at 60 minutes

Table 3. Results of TGA analysis of core material, isolated MF resins and microcapsules isolated at 60, 120 and 180 minutes of microencapsulations MC(6.0–5.0/step), MC(6.0–5.5–5.0/step) and MC(6.0–5.0/linear)

Sample	Shell thickness [nm]	MF resin [wt%]	At 300°C			Residue at 500°C [wt%]
			Total weight loss [wt%]	Weight loss on account of core material [wt%]	Evaporated core material [wt%]	
butyl stearate	–	0	100	100	100	0
isolated MF resins	–	100	15*	0	0	32
MC(6.0–5.0/step/60 min)	290	8.4	26.9	25.6	28	1.7
MC(6.0–5.0/step/120 min)	301	29.1	41.1	36.7	52	7.9
MC(6.0–5.0/step/180 min)	307	30.2	29.6	25.1	36	8.9
MC(6.0–5.5–5.0/step/60 min)	290	7.3	25.1	24.0	26	1.7
MC(6.0–5.5–5.0/step/120 min)	299	9.6	22.1	20.7	23	1.7
MC(6.0–5.5–5.0/step/180 min)	313	29.4	18.6	14.2	20	8.4
MC(6.0–5.0/linear/60 min)	298	8.4	23.8	22.5	25	2.0
MC(6.0–5.0/linear/120 min)	323	9.5	20.8	19.4	21	2.1
MC(6.0–5.0/linear/180 min)	329	28.8	17.5	13.2	19	8.6

*average weight loss of the isolated MF resins

to 52% at 120 minutes of microencapsulation. As microencapsulation continued, thermal stability of microcapsules MC(6.0–5.0/step) increased again. Weight loss due to core material evaporation was 36% in MC(6.0–5.0/step/180 min). Initial decrease of thermal stability could be explained by the formation of thin highly cured and less crosslinked outer layer of the microcapsules shell, while the inner layer was still incompletely cured. The shell, being rigid and thin, has lower mechanical stability, and consequently it is less able to retain core material. With microencapsulation time the inner layer of microcapsule shell slowly cures and the thermal stability of microcapsules increases.

4. Conclusions

In this paper we investigated the influence of different pH regimes during preparation of PCM microcapsules by *in situ* polymerization with melamine-formaldehyde resin on the composition of microcapsules, their morphology and stability. While on the one hand the decrease to a low pH value in one step resulted in a rapid increase of the weight percentage of MF resin in samples, thermal stability and morphology of microcapsules were unsatisfactory on the other. To attain better thermal stability it is necessary to ensure slow curing reaction and deposition of the MF resin on the microcapsule surface, which can be achieved by decreasing the pH value during microencapsulation in several smaller steps or in a linear way. With linear decrease of the pH value, microcapsules with thicker and better cured MF shells were obtained.

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