

Original Article

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Characterisation of melamine formaldehyde microspheres synthesised with prolonged microencapsulated reaction time

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Abstract: The aim of the research was to identify the influence of different microencapsulated reaction time on the morphology, size, infrared spectral, thermal and micromechanical properties of melamine formaldehyde microspheres, synthesised with modified *in situ* polymerisation. Microspheres are microencapsulated particles with a blurred boundary of the core and shell due to their same composition. The synthesis of microspheres was paused after 1, 3, 9 and 15 h, and stopped after 23 h. The scanning electron microscopy and granulometric analysis were used to study the morphology and size of microspheres. Regardless of the reaction time, the produced microspheres were spherical in shape and with a rough surface. The average size of microspheres was almost identical (0.709–0.790 μm), while the volume size distribution curve of the particles became narrower with prolonged reaction time. The curing mechanism of melamine formaldehyde resin was studied using the Fourier-transform infrared spectroscopy and thermal analysis, and nano-indentation identification. The results revealed a slightly more cross-linked structure: with minimal (neglected) increased thermal weight loss (only up to 0.5%) and minor increased Young's modulus (up to 2.3%). Using a nano-indenter, the hardness of synthesised particles improved by up to 14.8% after 23 h reaction time.

1 Introduction

Microcapsules usually consist of the core material and a shell. They are produced in a microencapsulation process, where droplets or tiny particles of the core material are surrounded by a coating shell or are embedded in a homogeneous or heterogeneous matrix. Various techniques have been developed for the fabrication of different types and sizes of capsules, the most common being emulsification, spray-drying, coaxial electrospray system, freeze-drying, coacervation, *in situ* polymerisation, extrusion, fluidised-bed-coating and supercritical fluid technology [1]. *In situ* polymerisation is a chemical encapsulation technique, in which the formation of the microcapsule shell takes place in a phase, i.e. water or oil phase, in which the core material is dispersed, and in the presence of a modifier, without which the formation of microcapsules would not be possible, since it acts as an emulsifier for the core material and as a catalyst for the formation of the microcapsule shell. This technique is also used for the preparation of microcapsules with a melamine formaldehyde (MF) shell and various core materials. It is carried out in two phases: The first phase involves the formation of an emulsion between two immiscible substances (usually water and water-insoluble organic material), while the second phase is the polycondensation reaction (curing) of the shell material (amino groups in the case of MF) on the surface of the emulsified particles, resulting in the formation of microencapsulated particles with a constituted core and shell.

The parameters that influence microcapsule parameters during the encapsulation process and the properties of produced microcapsules have been studied by different authors and are briefly presented in the continuation.

The microencapsulation process is influenced by different parameters as suggested by various authors [2, 3]. The mechanical parameters that affect the formation of

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capsules are apparatus configuration, stirring time and rate, mass ratio of the core and shell material. The chemical parameters which affect the polymer curing phase of the shell around the core are interfacial tension, viscosity, density and chemical composition of both phases, type and amount of surfactants, pH at encapsulation, feeding weight ratio of core/shell pre-polymer, temperature, synthesis reaction time etc. The above parameters affect not only the process, but also the final properties of microcapsules, e.g. size and size distribution of particles, morphology of particles (granularity or smoothness of the shell), thickness of the particle shell, the curing mechanism of the shell material, and thermal and mechanical properties of the particles. The curing phase of the shell material influences mainly the thickness, chemical structure, curing and permeability of the shell, the morphology, and the mechanical and thermal properties of the particles.

One of the parameters that influence the properties of microcapsules is also reaction time. In the study by Hu et al. [2] which deals with the mechanical properties of MF microcapsules for a self-healing material prepared with an MF shell and dicyclopentadiene (DCPD) in core, the influence of 3- and 5-h synthesis on the morphology, size, shell thickness and mechanical strength of microcapsules was studied. The authors concluded that a prolonged synthesis does not affect the size of microcapsules but increases the thickness of the MF shell and consequently the mechanical strength of microcapsules. The similar conclusion was found also by Yuan et al. [4]. His study of the characterisation of microencapsulated ethylenediamine with epoxy resin for self-healing composites was based on reaction time with 12, 18 and 24 h. With the longest reaction time, the curing degree of the wall materials and the mechanical strength of the shell are greatly improved. Salaün et al. [5] studied the influence of different parameters (i.e. phase volume ratio, types of surfactants and content, stirring rate and time, pH, reaction time, feeding weight ratio of core/shell pre-polymer) on the encapsulation process in which MF microcapsules contained *n*-hexadecane. The conclusion from the research was that the average size of microcapsules decreases, and their size distribution becomes narrow when the stirring rate and duration of the stirring are increased. They also concluded that the curing of the shell material stops after 240 min. Another interesting research of the influenced size of paraffin/melamine-urea-formaldehyde (shell) microcapsules was made by Han et al. [3], where they studied the influence of 1.5, 2 and 2.5 h reaction time. With longer reaction times, the average particle diameter was increased due to the decreased core (paraffin) content, since part of the melamine-urea-formaldehyde polymer in the reaction system was continuously

adsorbed by melamine-urea-formaldehyde wall. Also the encapsulation efficiency of paraffin increased with the increase in reaction time and scored the peak at 2 h of reaction time. But above 2 h, the efficiency started to decrease. Cheong et al. [6] concluded that according to the thickness of the MF microcapsule shell, the maximum polymerisation time of the MF resin is two to 3 h. Fei et al. [7] and Bartkowiak [8] came to very similar conclusions. In the research by Hwang et al. [9], microcapsules composed of the MF shell with fragrant oil as the core were analysed. One of their conclusions was that according to the particle size distribution, the optimum stirring time is 20 min for the preparation of MF microcapsules. Kage et al. [10] reported a 15-min synthesis time after which the curing of the MF resin is stopped. Although an additional amount of the core material was added after 15 min, a satisfactory encapsulation of the nucleus no longer occurred. In the research by Long et al. [11], the MF microcapsules containing an oil-based industrial precursor were produced in four and 24-h synthesis. The conclusion of this research was that after 4 h, the extent of curing is still increasing while the shell thickness is not. Increasing the shell thickness and curing density of the shell material is also the cause for increased rupture force and nominal rupture stress of particles as stated by Hu et al. [2]. In addition, they concluded that smaller microcapsules are stronger than larger ones as the nominal rupture stress decreases with diameter. In the study by Ollier et al. [12], the effect of pH and type of emulsifier on the quality, size and surface morphology of microcapsules prepared from poly(melamine formaldehyde) (PMF) as the shell material and diglycidyl ether of bisphenol F resin as the liquid core substance was studied. They concluded that an increase in reaction time (from one to 2 h by lowering pH and slightly increasing temperature) greatly improves the thermal stability of capsules due to the higher degree of curing of the PMF resin. Consequently, the shell becomes stronger. The interesting conclusion of the research was that the surface roughness of the shell of capsules slightly increases with reaction time. The same conclusions were noticed in some other studies as well [2, 5, 11].

All the above studies describe the influence of reaction time on the characterised properties of core-shell microcapsules, while the influence of prolonged synthesis reaction time on the characterisation of (MF) microspheres has not yet been investigated. Thus, the aim of our research was to study microspheres uniformly prepared solely from the MF resin. While microcapsules are heterogeneous particles where the boundary between core and shell is separable due to their different composition [13, 14], the microspheres consist of the same material homogeneously dispersed and enclosed through the core and shell, and thus

the boundary between them is blurred (inseparable) [13, 15]. The reaction time of our microspheres was extended to 23 h, and the particle size and size distribution, surface morphology, and the changes in their spectral infrared and thermal properties were studied and analysed.

2 Materials and methods

2.1 Sample preparation

In the study, microspheres (MS) were prepared by modified *in situ* polymerisation. The microspheres consisted of polymerised melamine formaldehyde resin. The reaction mechanism of microsphere formation is presented in Figure 1.

A partly methylated 3-methylol melamine (Melamin, Slovenia) was used as a prepolymer. A styrene maleic acid (SMA) anhydride copolymer was used as the modifying agent/polycondensation initiator

for the *in situ* polymerisation. The analytical grade sodium hydroxide (Kemika, Slovenia) was used for the termination of the polycondensation reaction and pH neutralisation. To remove the formaldehyde released during the polycondensation, ammonia (Kemika, Slovenia) was added to the suspension of microspheres as a scavenger. A schematic presentation of the developed process is presented in Figure 2.

After the induction of *in situ* polymerisation, samples of microsphere suspensions were taken from the reactor reaction flask after 1, 3, 9, 15 and 23 h (samples marked MS_{1 h}, MS_{3 h}, MS_{9 h}, MS_{15 h} and MS_{23 h}).

2.2 Methods

The surface morphology of microspheres was observed with a scanning electron microscope JSM-6060LV (Jeol, Japan). For observation, the samples were covered with an ultrathin coating of gold (with high vacuum evaporation). When observing the microspheres in suspension, a drop of suspension was applied on the specimen stub and allowed to air-dry.

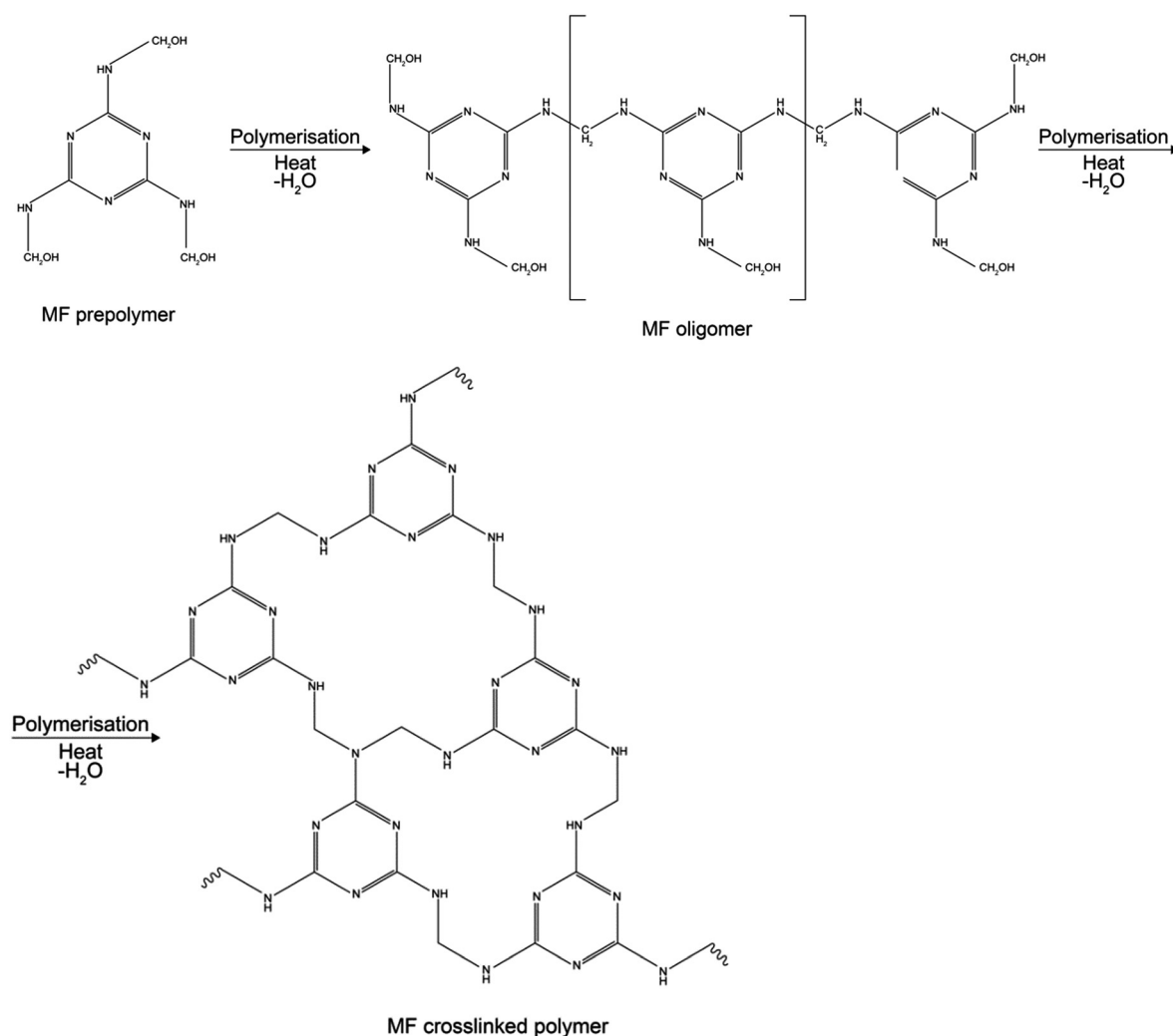


Figure 1: Reaction mechanism of microsphere formation.

The size and volume size distribution of the samples were determined with a granulometric analysis. In our research, a particle size analyser was used, i.e. Microtrac FRA 9200 (Leeds & Northrup, USA), to analyse the size distribution of microspheres in the suspension. The analyser uses the laser diffraction technique. The measuring time for wet particles was 20 s.

The Fourier-transform infrared spectroscopy (FT-IR) was used to identify the chemical differences between samples $MS_{1\text{ h}}$ and $MS_{23\text{ h}}$. Spectral acquisition was performed with a Spectrum GX (Perkin Elmer, Great Britain). The spectral resolution was 4 cm^{-1} within the frequency $600\text{--}4000\text{ cm}^{-1}$.

The thermal properties of samples $MS_{1\text{ h}}$ and $MS_{23\text{ h}}$ were determined with a STA (simultaneous thermal analysis) 449 Jupiter (Netzsch, Germany). The samples in aluminium crucibles were heated at the rate of 10 °C/min from 25 to 600 °C in an argon atmosphere.

The micromechanical properties of $MS_{1\text{ h}}$ and $MS_{23\text{ h}}$ were determined with a Nano Indenter G200 (Agilent Technologies, USA), using the continuous stiffness measurement method (CSM). For the analysis, a drop of suspension of each sample was put on the glass plate and dried in the air. A cone tip was used to measure the hardness and Young's modulus. The allowable drift rate was 0.40 nm/s , depth limit 150 nm , harmonic displacement target 1.0 nm , minimum/maximum depth was on average $140/150\text{ nm}$, strain rate target 0.01 s^{-1} and the surface approach velocity was 10 nm/s .

3 Results and discussion

3.1 Morphology of microspheres

The surface morphology of microspheres in the suspension produced in 1 and 23 h reaction times is shown in Figure 3.

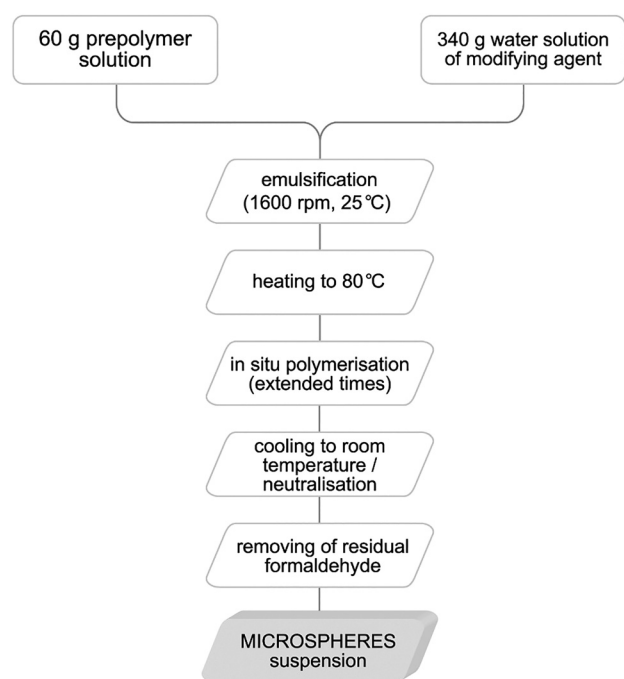


Figure 2: Schematic presentation of *in situ* microsphere formation.

The spheres, regardless of the reaction time, are spherical in shape. The surface of microspheres is in both samples visibly rough (granular) and slightly more in the particles capsulated at 1 h, which is contrary to the findings by Ollier et al. and Salaün et al. [5, 12], where the particle surface roughness of microcapsules increases with prolonged reaction time. However, as suggested by Salaün and Ollier [5, 12], the rough surface of MF microcapsules could originate from the formation of MF pre-polymer tiny particles, which tend to deposit onto the core droplet surface before the crosslinking. Another reason might be the drying process, in which the residues of unreacted MF resins, the amorphous modifying agent and the unencapsulated core material present in the suspension are deposited on the surface of microspheres [16]. The mentioned explanation might be used also in the case of MF microspheres.

Between the particles, solid bridges are visible in all samples. This is a consequence of the surface tension and capillary forces among the particles during drying [17].

3.2 Particle size and particle size distribution

The average sizes of microspheres produced in different reaction times are presented in Table 1, while the volume size distribution curves are shown in Figure 3.

From the results in Table 1, it can be seen that the average size of MS in the suspension only slightly differs among samples (minimum size was $0.709\text{ }\mu\text{m}$ and maximum $0.790\text{ }\mu\text{m}$). Similar results were also presented in the study by Hu et al. [2], in which the average size of MF microcapsules did not change significantly with prolonged reaction time. As Figure 4 shows, the shape of the volume size distribution curve of $MS_{1\text{ h}}$ was broader, while when the reaction time was prolonged to 23 h, the curve became narrower due to the lower dispersion of particle sizes. The same phenomenon is also described by Salaün et al. in the case of MF microcapsules [5]. For the reaction time of 1 h, the sizes of MS are in the range from 0.3 to $1.6\text{ }\mu\text{m}$, while after 3, 9, 15 and 23 h, the range changes from 0.4 to $1.2\text{ }\mu\text{m}$.

3.3 Infrared spectroscopic properties (FT-IR)

3.3.1 FT-IR analysis of methylol melamine derivative (3-methylol melamine)

With a FT-IR analysis, the chemical changes occurring at curing the MF resin after 1-h and prolonged 23-h reaction times were studied. The curing mechanism of the MF resin

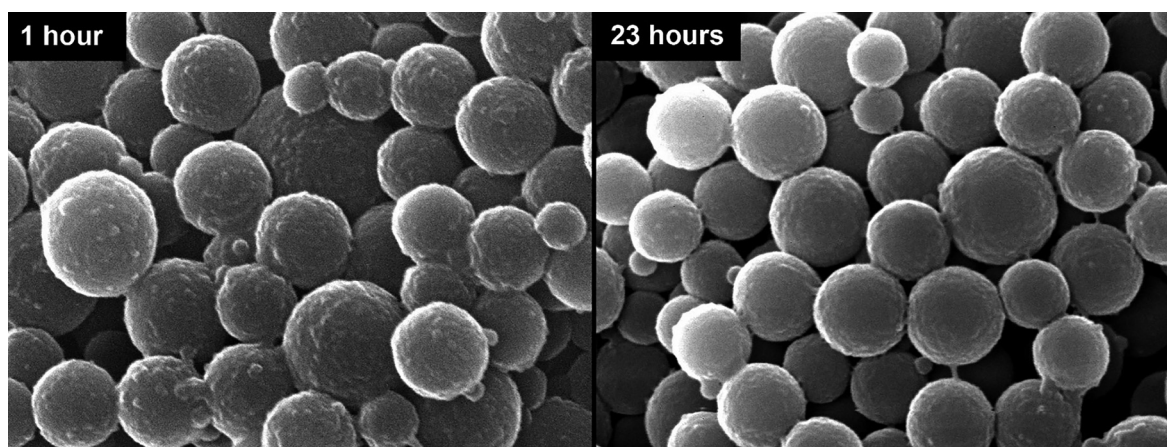


Figure 3: SEM images (magnification: 25.000×) of air-dried suspension of microspheres produced in different reaction times.

Table 1: Average size of samples MS_{1h} , MS_{3h} , MS_{9h} , MS_{15h} and MS_{23h} (SD, standard deviation).

Sample	Average size of particles/SD (μm)	Maximum particle size (μm)
MS_{1h}	0.709/0.215	1.640
MS_{3h}	0.790/0.127	1.160
MS_{9h}	0.760/0.136	1.380
MS_{15h}	0.757/0.117	1.160
MS_{23h}	0.754/0.102	1.160

was monitored through the formation of molecular groups that are characteristic of 3-methylol melamine and MS suspensions. The FT-IR spectra of 3-methylol melamine are shown in Figure 5.

The 3-methylol melamine is the result of the methylation reaction [18] between melamine and formaldehyde.

During this reaction, maximum six methylol ($-\text{CH}_2\text{-OH}$) groups are formed and are bound to the same melamine molecule (Figure 6). The reaction is carried out at all pH values [19]. The 3-methylol melamine is uncured, which is proven by the peaks at 3328, 2941, 1492, 1363, 1177, 1051, 1000, 870 and 812 cm^{-1} . The peak at 3328 cm^{-1} is characteristic of the vibration of secondary amino groups ($-\text{NH}-\text{CH}_2-$) of 3-methylol melamine [20], the peak at 2941 cm^{-1} is assigned to methylol groups ($-\text{CH}_2\text{-OH}$) [20, 21], while the peaks at 1492 and 1363 cm^{-1} belong to the vibration of methylene bonds (C-H) [9, 20, 22, 23] and indicate the methylol groups in derivative. The peak at 1177 cm^{-1} indicates the marked vibration of the aliphatic ($-\text{C-N-}$) bond between the methylol group and the triazine ring. The peak at 1051 cm^{-1} belongs to the vibration of ether bonds (C-O) in 3-methylol melamine [20]. The peak at 1000 cm^{-1} is characteristic of the uncured structure of 3-methylol melamine and can be assigned to the

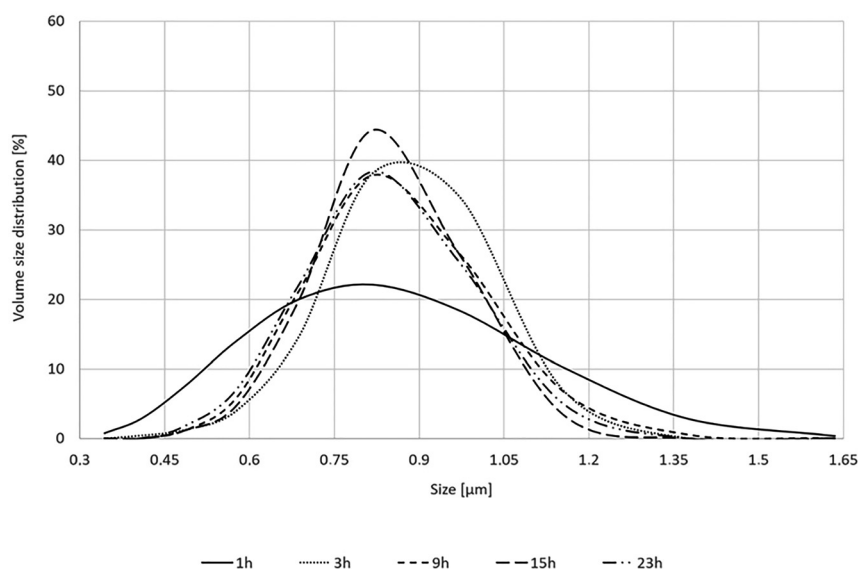


Figure 4: Volume size distribution of microspheres in suspension produced in different reaction times.

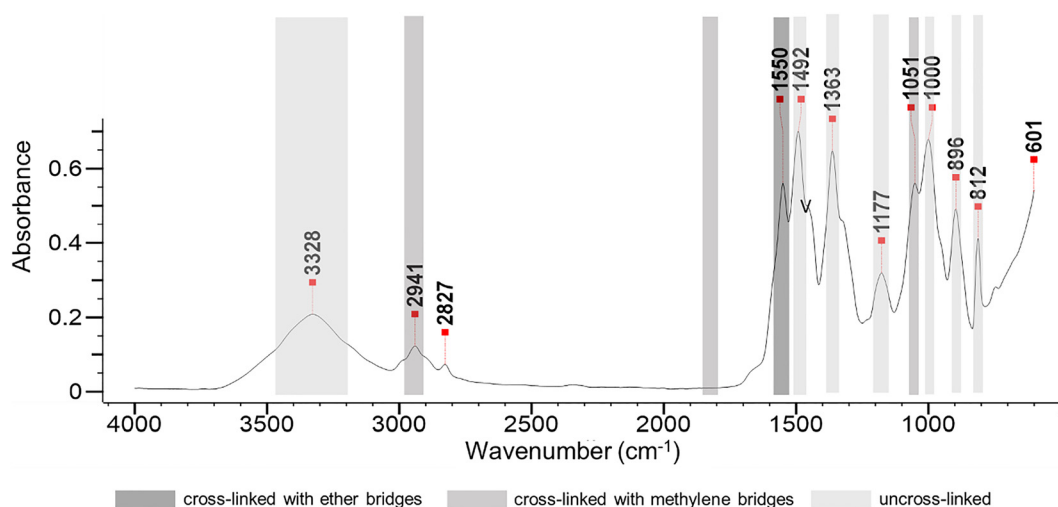


Figure 5: FT-IR spectra of 3-methylol melamine.

vibration of methylene bonds (C–H) [20]. The peaks at 812 and 896 cm^{-1} are assigned to carbon nitrogen bonds ($-\text{C}=\text{N}-$) in 2,4,6-substituted places of the triazine ring vibration [20, 21, 23, 24].

Since the peaks at 2941 and 1550 cm^{-1} [21] are presented in the spectra, this implies that 3-methylol melamine is slightly crosslinked with unstable ether bridges. The peak at 2941 cm^{-1} is assigned to methylol groups and can also indicate the parallel vibration of methylene bonds (C–H) in CH_2 groups of ether bridges ($-\text{CH}_2-\text{O}-\text{CH}_2-$), while the peak at 1051 cm^{-1} is assigned to the vibration of ether bonds (C–O) in the ether bridge vibration of the triazine ring [25]. The existence of the unstable ether bridge can be assigned to the peak at 1550 cm^{-1} , which reflects the vibration of carbon nitrogen bonds ($-\text{C}=\text{N}-$) of the triazine ring [19, 26].

3.3.2 FT-IR analysis of samples $\text{MS}_{1\text{ h}}$ and $\text{MS}_{23\text{ h}}$

As suggested by Merline et al. [20], the curing reaction of MF proceeds in two different steps, i.e. *methylolation step*

(as described above) and *condensation step*. In the condensation step, dimethylene-ether bridges ($>\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}<$) are formed in the crosslinking reaction of 3-methylol melamine; however, by eliminating formaldehyde, the ether-linkages are transformed into stable methylene bridges ($>\text{N}-\text{CH}_2-\text{N}<$). Additionally, Merline et al. [20] suggested another reaction in the final cured product between 3-methylol melamine (formed in methylolation) and melamine which also leads to the formation of stable methylene bridges ($>\text{N}-\text{CH}_2-\text{N}<$) [9, 20, 27, 28].

Although methylene and dimethylene-ether bridges dominate in the crosslinked structure of the MF resin, some methylol groups in the structure are uncured. The percentage of formed bridges mainly depends on pH values. If the pH value is relatively low ($\text{pH} = 7-8$), methylene bridges dominate, while at higher values ($\text{pH} > 9$), ether bridges are formed in a greater extent [20, 28].

According to the FT-IR study of samples $\text{MS}_{1\text{ h}}$ and $\text{MS}_{23\text{ h}}$ (Figure 7), the vibration of free methylene bonds in methylol groups decreased in both samples, which could be proven by

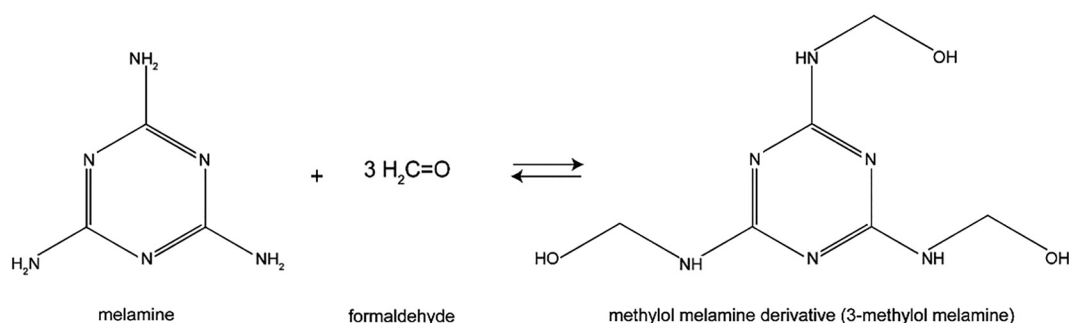


Figure 6: Formation of 3-methylol melamine [20].

the disappeared peaks at 3328, 1051 and 1000 cm^{-1} , and decreased intensity of the peaks 1495 and 1361 cm^{-1} for $\text{MS}_{1\text{h}}$, and the peaks at 1494 in 1358 cm^{-1} for $\text{MS}_{23\text{h}}$. Methylene bonds C–H begin to vibrate within ether groups again, which is proven by the peak at 1014 cm^{-1} for $\text{MS}_{1\text{h}}$ and at 1012 cm^{-1} for $\text{MS}_{23\text{h}}$. This suggests that by curing 3-methylol melamine, dimethylene-ether bridges ($>\text{N}-\text{CH}_2-\text{O}-\text{CH}_2-\text{N}<$) are formed. Nevertheless, the unstable ether bridges transform into more stable methylene bridges ($>\text{H}-\text{CH}_2-\text{N}<$) [19, 22, 26], which was proven in our research as follows:

- peaks of methylene C–H bonds at 2952 and 2953 cm^{-1} for $\text{MS}_{1\text{h}}$ and $\text{MS}_{23\text{h}}$, respectively; since the intensity of the peak at 2952 cm^{-1} is more pronounced in sample $\text{MS}_{1\text{h}}$, it could be concluded that unstable ether bridges are transformed into more stable methylene bridges during the prolonged synthesis;

- peaks at 1554 and 1551 cm^{-1} for $\text{MS}_{1\text{h}}$ and $\text{MS}_{23\text{h}}$, respectively, belong to the vibration of $-\text{C}=\text{N}$ bonds in the triazine ring; in sample $\text{MS}_{1\text{h}}$, this vibration is more intensive compared to sample $\text{MS}_{23\text{h}}$, which points to additional curing of the MF resin in the prolonged synthesis.

The peak at 811 cm^{-1} belongs to the vibration of bonds in the triazine ring, and was in both samples, $\text{MS}_{1\text{h}}$ and $\text{MS}_{23\text{h}}$, less intense since in the cured MF resin, the vibration of the ring is sterically hindered.

3.4 Thermal properties (STA)

According to the studies by Hu et al. [2] and Salaün et al. [5] performed with MF microcapsules, and our FT-IR results,

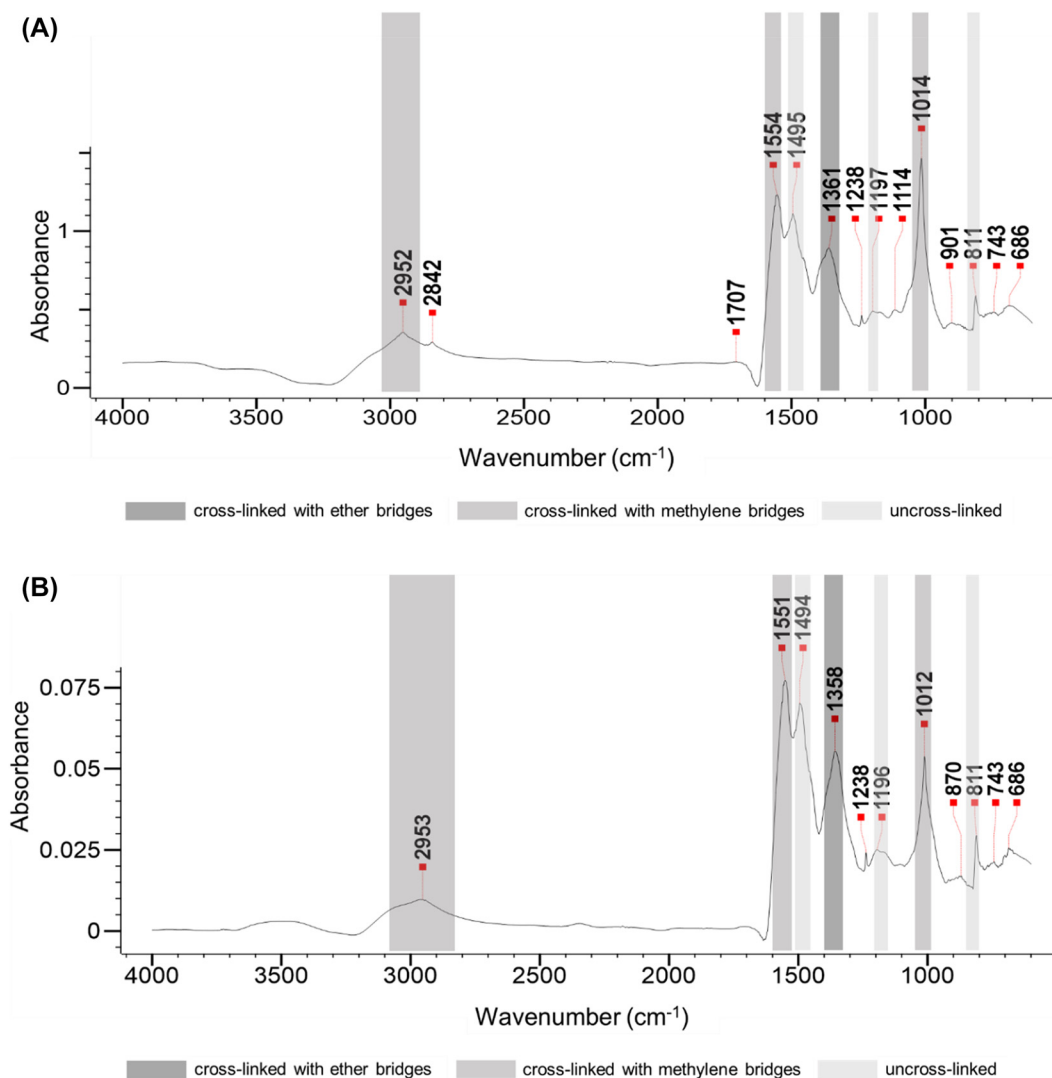


Figure 7: Fourier-transform infrared spectroscopy (FT-IR) spectra of microspheres in suspension produced in (A) 1 h ($\text{MS}_{1\text{h}}$) and (B) 23 h ($\text{MS}_{23\text{h}}$) synthesis.

the prolonged reaction time increases the share of the cured MF resin, which could affect the thermal analysis. Samples MS_{1h} and MS_{23h} were thus analysed with STA. The results are shown in Figure 8.

As it can be seen from the diagram in Figure 8, the differential scanning calorimetry (DSC) and thermogravimetric (TG) curves of samples MS_{1h} and MS_{23h} have a slightly different run. The first interval, which ranges from 30 to 88 °C in both curves of samples MS_{1h} and MS_{23h} , corresponds to the evaporation of water [20, 26]. The weight loss in both samples was 4%.

After the first endotherm peak, both curves increased, reaching exothermic peaks at 122 and 138 °C for sample MS_{1h} and MS_{23h} , respectively. The increase indicates the beginning of the resin curing. After that, the curve of sample MS_{1h} decreased to the next minimum at 189 °C; however, during that heating, the exothermic peak at 159 °C was detected. According to the research by Merline et al. [20], the interval from 100 to about 180 °C is associated with curing reactions, i.e. self-condensation of methylol groups, which leads to the formation of ether bridges (140–160 °C), and another condensation reaction between methylol groups ($-CH_2-OH$) and melamine (melamine is formed with a reverse reaction (decomposition) of 3-methylol melamine in the temperature range from 140–160 °C, leading to the formation of methylene bridges at the temperature >160 °C. The curve after the endotherm peak at 189 °C increased to 351 °C. Merline et al. [20] suggested that ether bridges are in this temperature range transformed into methylene bridges by the elimination of formaldehyde. The course of the DSC curve of sample MS_{23h} in the temperature range 88–342 °C is slightly different than at sample MS_{1h} . After reaching the exothermic peak at 138 °C, the DSC curve was slightly

decreasing until the temperature was 191 °C. In contrast to sample MS_{1h} , no additional peaks in the interval around 160 °C were noticed. After that, the curve slowly increased to 342 °C.

According to the literature [2, 5, 22], the MF resin structure becomes more cured with prolonged reaction time. After 1 h reaction time, 3-methylol melamine did not react to a full extent in the process of curing; thus, further crosslinking through the described reactions, and the release of methanol and formaldehyde were noticed and detected through the FT-IR analysis. In the case of 23-h reaction time, sample MS_{23h} was mainly cured, which is reflected in the DSC curve without noticeable peaks.

In the temperature range 351–402 and 342–398 °C for samples MS_{1h} and MS_{23h} , respectively, the highest weight loss was detected. This interval is attributed to the breakdown of methylene bridges. At the temperature >402 °C for sample MS_{1h} and >398 °C for sample MS_{23h} , the thermal degradation of the triazine ring proceeded, while the MF resin, in line with the findings by Merline et al. [20], progressively deaminated to form HCN (hydrogen cyanide).

The total weight loss in the temperature range 30–600 °C was 70.0% (sample MS_{1h}) and 70.5% sample MS_{23h}), respectively. The difference is very small, yet consistent with the data reported in the literature [12], namely that a denser, more crosslinked structure of MS produced with prolonged reaction time increases thermal stability.

3.5 Micromechanical properties

Micromechanical properties were determined for samples MS_{1h} and MS_{23h} . The results of measuring the Young's modulus and hardness are shown in Table 2.

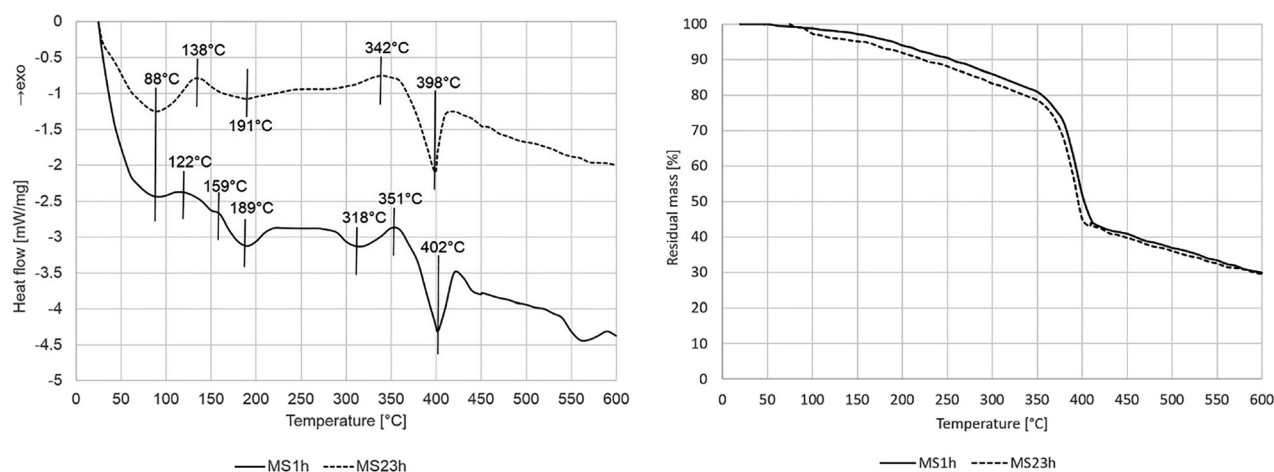


Figure 8: Differential scanning calorimetry (DSC) and thermogravimetric (TG) curves of samples MS_{1h} and MS_{23h} .

Table 2: Young's modulus and hardness of samples MS_{1h} and MS_{23h} (SD, standard deviation).

Sample	Young's modulus/SD (GPa)	Hardness/SD (GPa)
MS _{1h}	4.2/1.1	0.27/0.10
MS _{23h}	4.3/0.4	0.31/0.08

According to the results, the hardness value for MS_{1h} is slightly lower, and can be attributed to its lower curing density and stiffness (as already proven by the FT-IR and STA analysis). Sample MS_{23h} has a slightly higher Young's modulus, possibly due to the higher extent of more stable methylene bonds and curing density, which is the reason why the microspheres are more resistant to elastic deformation. Nevertheless, standard deviation should be mentioned as well, since it is increasingly high in the case of sample MS_{1h}. Despite the fact that over 50 measurements were made for each sample, the scattering of the results was relatively substantial. The results should hence be taken with reserve.

4 Conclusions

In our study, MF microspheres were successfully synthesised and analysed with prolonged microencapsulated reaction time.

The results showed a noticeable impact of prolonged reaction time on the curing mechanism of the MF resin, density of microspheres together with their mechanical and thermal stability, but an insignificant impact on the surface morphology and average size of the microspheres in suspension. Nevertheless, the influence on the volume size distribution of microspheres is more significant.

The spectroscopic FT-IR analysis of methylol melamine derivative and formed MF microparticles with 1 and 23 h reaction time revealed the transformation of unstable ether bridges into more stable methylene bridges of the MF resin as a continues process, identified also at 23-h reaction time.

The thermal and micromechanical studies led to the same conclusion. Performed with the STA technique, the higher amount of denser crosslinking of the MF resin during the synthesis of particles was proven by high weight loss detection in the temperature region significant to the breakdown of methylene bridges also for the particles produced with 23 h reaction time. In comparison to the particles synthesised with shorter microencapsulated reaction time, the total weight loss was by only 0.5% higher. Although

small, the difference points to the achieved thermal stability of particles produced with prolonged reaction time. The nano-identification results with higher hardness and Young's modulus also proved higher curing density and stiffness of particles produced with 23 h reaction time.

The results obtained with the scanning electron microscopy revealed the surface roughness of all samples regardless of the duration of their synthesis with visible solid bridges between particles, which are a consequence of the surface tension and capillary forces among them formed during the drying of the suspension of particles.

The volume size distribution results also showed that prolonged reaction time does not have any influence on the average size of microspheres. Only the volume size distribution of the particles became narrower with lower dispersion of particle sizes at time prolonged to 23 h.

The study showed the similarity of characteristic properties of MF spheres with MF microcapsules, i.e. size and size distribution, curing mechanism of MF resin, density and thermal stability of particles with prolonged reaction time. The only difference found was the surface roughness of particles which was noticed only at 1 h reaction time in the case of microspheres, while in the case of microcapsules, it occurred only at prolonged reaction time.

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