Scientific paper

Production of Melamine-Formaldehyde PCM Microcapsules with Ammonia Scavenger used for Residual Formaldehyde Reduction

Boštjan Šumiga,[1,2,*] Emil Knez,[2] Margareta Vrtačnik,[1] Vesna Ferk Savec,[1] Marica Starešinič[1] and Bojana Boh[1]

[1] *University of Ljubljana, Faculty of Natural Sciences and Engineering, Vegova 4, SI-1000 Ljubljana, Slovenia*

[2] *AERO, Chemical, Graphic and Paper Manufacturers, Ipavčeva 32, SI-3000 Celje, Slovenia*

* *Corresponding author: E-mail: bostjan.sumiga@aero.si*

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Abstract

Paraffinic phase change materials (PCM) were microencapsulated by *in situ* polymerization of melamine-formaldehyde prepolymers. Partly methylated trimethylolmelamine was used as an aminoaldehyde prepolymer for the microcapsule wall, a styrene-maleic acid anhydride copolymer as an emulsifier and modifying agent, and ammonia as a scavenger for reducing residual formaldehyde. For the determination of residual formaldehyde in a ppm concentration range, EDANA and malachite green analytical methods were studied, and the EDANA 210.1-99 was applied for the determination of residual formaldehyde in 25 samples of microcapsules, produced in a 200-L reactor. A linear correlation was observed between the added ammonia scavenger concentration and the reduction of residual formaldehyde concentration. Compared with 0.45% (4500 ppm) formaldehyde in a non-treated microcapsule suspension, with ammonia scavenger concentrations 0.80, 0.90 and 1.35%, the concentration of residual formaldehyde dropped to 0.27, 0.20 and 0.09% (i.e. 2700, 2000 and 900 ppm), respectively. Morphological characterisation of microcapsules by SEM and microcapsule wall permeability measurements by gravimetry / mass loss at an elevated temperature (135 °C) suggested that ammonia positively contributed to the wall elasticity / durability, while microcapsules with no ammonia scavenger added tended to have more brittle walls, and were more prone to cracking.

Keywords: Microcapsules, phase change materials, melamine-formaldehyde prepolymers, residual formaldehyde, EDANA, ammonia scavenger

1. Introduction

Microencapsulation is a technology of coating small nuclei with protective spherical membranes. The size and shape of microcapsules, chemical properties of microcapsule walls, and their degradability, biocompatibility and permeability have to be considered in the selection of raw materials and microencapsulation processes. Applications of microcapsules are diverse and include both, biomedical and technical domains. One of the fastest growing product areas of microencapsulation applications since 2000 have been textiles for active thermal control, based on microencapsulated phase change materials (PCM) which absorb or emit heat at their phase change transition temperature. An example are paraffinic hydrocarbons with 13 to 28 carbon atoms, and the phase change temperatures ranging from –5,5 °C to 61 °C. Since they are flammable and liquid above the phase transition temperature, microencapsulation is essential for their practical use in various thermal management applications. To remain functional over numerous phase transition cycles, microencapsulated PCMs have to remain encapsulated within the impermeable microcapsule walls for the whole product life. Therefore, PCM microcapsules need to be highly resistant to mechanical and thermal stress. *In situ* polymerisation microencapsulation with aminoaldehyde resins is one the best encapsulation methods to achieve the characteristics needed for PCMs.[1,2]

1. 1. Microcapsules with Aminoaldehyde Resin Walls

Microencapsulation based on amino resins has been described in the literature.[3–10] The processes can start either from monomers (e. g. urea and formaldehyde or melamine and formaldehyde), or from prepolymers (e.g. partially methylated trimethylolmelamine, MTMM, or hexamethoxy-methylolmelamine, HMMM). In microencapsulation by *in situ* polymerisation of amino-aldehyde resins, all materials for the microcapsule wall originate from the continuous (aqueous) phase of the emulsion system, and therefore have to be water soluble. Under ideal conditions, by change of pH and temperature all the mass of the wall material precipitates and distributes evenly over the surfaces of droplets in emulsion. To achieve better process control and improved mechanical properties of microcapsules, modifying agents are added, which at first serve as emulsifiers, and later enable the polymerisation to develop only at the surface of the emulsified microcapsule cores, and not throughout the whole aqueous phase. After microencapsulation, formaldehyde residues can be removed from the suspension of microcapsules by the addition of scavengers, such as urea,[2,11] melamine,[12] ammonia,[12,13] or ammonium chloride.[2,14]

Formaldehyde reacts with ammonium chloride or ammonia to form hexamethylenetetramine.

The reaction between ammonium chloride and formaldehyde is presented in Equation 1,[14] reaction between ammonia and formaldehyde in Equation 2.[15]

$$4NH_4Cl + 6CH_2O \rightarrow N_4(CH_2)_6 + 6H_2O + 4\ HCl \quad (1)$$

$$4NH_3 + 6CH_2O \rightarrow (CH_2)_6N_4 + 6H_2O \quad (2)$$

Kinetic studies of the reaction of formaldehyde with ammonia to form hexamethylenetetramine showed that the reaction was first-order with respect to ammonia and second-order with respect to formaldehyde. The rate increased sharply with the increasing pH to a maximum between 9 and 10.[15] Hexamethylenetetramine vaporises and sublimes at 230 to 270 °C, and decomposes at temperatures above 280 °C. Water solutions of hexamethylenetetramine are relatively stable and show only a slight degree of hydrolysis to formaldehyde and ammonia.[16]

1. 2. Maximum Allowed Concentrations of Formaldehyde

Limits for the maximum allowed concentrations of formaldehyde in several products, including textiles, have been lowered during the last decades. In 1973, Japan became the first country to introduce formaldehyde limits for textiles. Law No. 112 (Control of Household Products Containing Harmful Substances), issued in 1974, set the maximum limit values for five substances, among them also for formaldehyde.[17] Since then, European countries have adopted similar measures. Examples of maximum residue limits for formaldehyde in textiles and similar products are given in Table 1.

Table 1: Examples of maximum allowed residue limits of formaldehyde in textiles and similar products

	Infant garments (ppm)	Garments that contact skin (ppm)	Other garments or fabrics (ppm)
Japan Law No. 112	20	75	
European Union eco-label	30	75	300
Oeko-tex standard 100	20	75	300
EU restrictions on the use of dangerous chemicals	30	100	300
DIN CERTCO certification scheme for textile products	20	75	300
EU eco-label for footwear			textile 75 leather 150
EU eco-label for bed mattresses			mattress 30
EU eco-label for furniture			leather 150

(ppm – parts per million, mg/kg, ng/g)

1. 3. Analytical Methods for Formaldehyde Determination

Several analytical methods have been developed for detecting, measuring and/or monitoring formaldehyde and its metabolites, and further improved to lower the detection limits. The most widely used methods for the detection of formaldehyde are based on:

- colorimetry and spectrophotometry,[2,14,18–31]
- high-performance liquid chromatography – HPLC[28,32–37] and liquid chromatography[38]
- gas chromatography – GC[39–42] and gas chromatography/mass spectrometry – GC/MS[43,44]
- Fourier-transform infrared spectroscopy – FTIR,[45]
- Fluorimetry[46–50] and chemiluminescence[51,52]
- enzyme sensors in FIA systems,[47,53]
- adsorption voltammetry[54,55]
- thin layer chromatography – TLC[56] and
- capillary electrophoresis[57].

Methods for the spectrophotometric determination of formaldehyde are based on reactions with: (a) chromotropic acid (1,8-dihydroxy naphthalene-3,6-disulphonic acid), (b) acetylacetone (2,4-pentanedione) – NASH reagent, (c) 3-methyl-2-benzothiazolone hydrazone – MBTH reagent, (d) phenol phthalein, (e) pararosaniline and sodium sulphite, (f) malachite green–sulphite reaction (inhibitory effect of formaldehyde), and (g) Purpald reagent (Aldrich Chemical Co.).

In our previous work[1] we reported on microencapsulation of higher hydrocarbon phase change materials (PCMs) by *in situ* polymerisation of melamine-formaldehyde prepolymers in a laboratory 2 l and pilot plant 10 l reactor. In the present article, a scaled up microencapsulation process took place in a 200 l industrial reactor. The purposes of our research were (1) to test, optimise and apply two analytical methods – EDANA and Malachite green – to enable a reliable determination of free and/or hydrolyzed formaldehyde in microcapsule suspensions, (2) to reduce formaldehyde residues in aminoaldehyde microcapsule suspensions, preferably by adding ammonia as a scavenger, (3) to investigate the potential effect of ammonia scavenger on microcapsule characteristics.

2. Materials and Methods

2. 1. Microencapsulation by in Situ Polymerisation of Aminoaldehyde Prepolymers

Microcapsules were prepared by in situ polymerisation of aminoaldehyde prepolymers in a 200 l industrial reactor. In a modified *in situ* polymerisation method,[3,8] partly methylated trimethylolmelamine – MTMM (Melamin) was used as a prepolymer for the microcapsule wall, and a paraffinic PCM with melting point 27 °C (Rubitherm) as a core material. A styrene-maleic acid anhydride copolymer – SMA with average mol. weight 350,000 (Hercules) was added as an emulsifier and modifying agent/polycondensation initiator. Analytical grade sodium hydroxide (Kemika) was used for termination of the polycondensation reaction and pH neutralisation. For removing formaldehyde released during the polycondensation, ammonia (Kemika) was added to the suspension of microcapsules as a scavenger, to reach the following concentrations in a final suspension of microcapsules: 0.00, 0.80, 0.90 and 1.35% (mass).

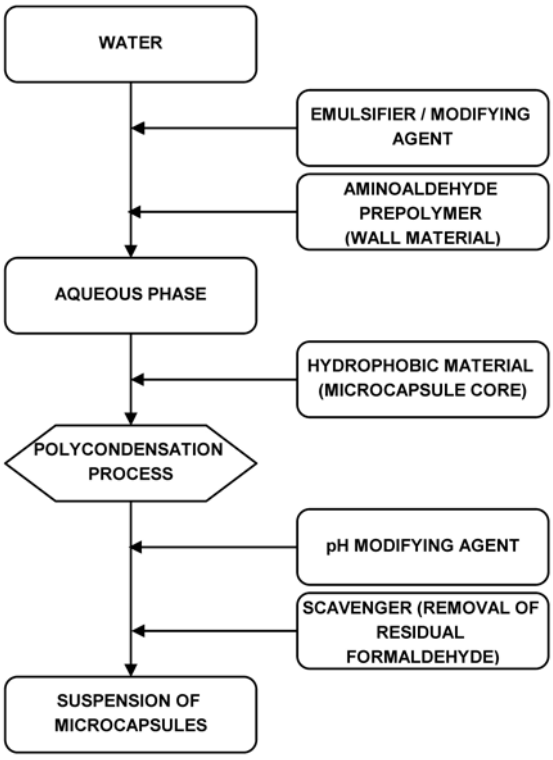


Figure 1: *In situ* polymerisation microencapsulation procedure in a 200 l reactor

The modified *in situ* polymerisation microencapsulation process consisted of the following steps (Figure 1): (1) preparation of an aqueous solution of SMA modifying agent and partial neutralisation with sodium hydroxide, (2) addition of MTMM amino-aldehyde prepolymer for wall formation, (3) emulsification of future cores of microcapsules at a temperature above the melting point of the paraffinic phase change materials, (4) induction of polycondensation reaction by raising the temperature to 70–80 °C; (5) polycondensation process taking place for about 1 hour; (6) termination of polycondensation by raising pH to 7.0, and (7) removal of residual formaldehyde by adding ammonia scavenger at 50 °C, and (8) cooling down to a room temperature.

Table 2: Main parameters of in situ microencapsulation in a 200 l reactor

	Value
Filling	180–200 l
Concentration of the modifying agent	4.5–6.5%
Concentration of core material	25–40%
Concentration of wall material	20–40 g/100g core material
Dissolver stirrer diameter	200 mm
Emulsification	1500 rpm, 30 min, T= 25–40 °C
Polycondensation	1500 rpm, 60 min, T= 70–80 °C
Diameter of microcapsules	1–10 μm
Viscosity of final suspension	300–800 mPas
Dry matter content	30–35%

2. 2. Preparation of Samples for Free Formaldehyde Determination

Suspensions of microcapsules were treated with 0.5% solution of aluminium sulphate to achieve precipitation of microcapsules. After filtration, free formaldehyde was determined in the filtrate spectrophotometrically according to the EDANA method 210.1-99.

2. 3. Spectrophotometric Determination of Formaldehyde by EDANA 210.1-99 Method –theoretical Background and Analytical Procedure

2. 3. 1. EDANA-theoretical Background

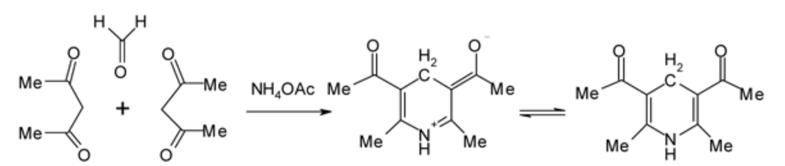
Carbonyl compounds are known to undergo multicomponent reactions. These are convergent reactions, in

which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product.[58] One of the early discovered multi-component reactions is the Hantzsch pyridine synthesis. In the presence of β-ketons or β-keto esters, and a nitrogen donor such as ammonium acetate or ammonia, carbonyl compounds gradually develop a yellow colour due to the formation of dialkyldihydropyridine, which can be oxidized in a subsequent step to pyridine derivatives.[59] The EDANA 210.1-99 method for formaldehyde determination is based on the first step of Hantzsch synthesis. This analytical method can be used for the quantitative determination of free formaldehyde and formaldehyde extracted partly through hydrolysis by means of water extraction. The multi-component condensation reaction occurs between 2 moles of pentane-2,4-dione (Nash reagent) and one mole of formaldehyde in the presence of ammonium salt. The product of the reaction is yellow crystalline diacetyldihydrolutidine or diacetyldihydropyridine (DDL), as presented in Figure 2.

The absorbance of the aqueous solution of DDL is measured at a wavelength of 412 nm. If there is a doubt that the absorbance may not be only due to formaldehyde, but other colouring agents, a conformation test with dimedone is conducted prior to formaldehyde determination. Dimedone (5,5-dimethylcyclohexane-1,3-dione) in a saturated aqueous solution or 10% alcohol solution gives crystalline derivatives with aldehydes, and not with ketones. Therefore, if only formaldehyde is present, it will react with dimedone and no colour will be observed with the Nash reagent. The reported sensitivity of the EDANA 210.1-99 method for formaldehyde determination is >20mg/kg (20 ppm).

2. 3. 2. EDANA Analytical Procedure

Analytical procedures by EDANA (European Disposables and Nonwovens Association, 2002) have been used as described by EDANA standards, summarised in Table 3.



Possible resonance structures of DDL

Figure 2: Formation of the yellow coloured DDL during the first step of Hantzsch reaction

Table 3: Summary of EDANA analytical procedures

	Used for	Determination of	Analytical method description	Reported sensitivity
EDANA 210.1-99 *Free formaldehyde I* (standard EN ISO 14184-1)	Nonwoven textiles, precursor fibres (at normal conditions)	Free and hydrolysed formaldehyde (normal wearing conditions – 40 °C)	Extraction with water at 40 °C. Reaction with Nash **acetylacetone** reagent: ammonium acetate, glacial acetic acid, acetylacetone (=2,4-pentanedione), water. Determination with photoelectric **colorimeter or spectrophotometer** at 412 nm. Confirmation test with dimedone (dimethyl-dihydro-resorcinol or 5,5-dimethyl-cyclohexadione, in ethanol).	>20mg/kg (20 ppm)
EDANA 211.1-99 *Free formaldehyde II under stressed conditions*	Nonwoven textiles, precursor fibres (at stressed industrial applications)	Free and hydrolysed formaldehyde (extraction at 80 °C)	Extraction with water at 80 °C. Further procedure as in EDANA 210.1-99 (**colorimeter or spectrophotometer**)	>20mg/kg (20 ppm)
EDANA 212.1-99 *Free formaldehyde III (HPLC)*	Nonwoven textiles, precursor fibres	Free formaldehyde	Water extraction at 40 °C at 80 °C, **HPLC** on a reversed-phase ODS column, aqueous mobile phase, detector at 412 nm. Post-column: Nash reagent (ammonium acetate, glacial acetic acid, **acetylacetone**, water).	0.5 mg/kg (to 15mg/kg) (0.5–15 ppm)
EDANA 213.1-99 *Free formaldehyde IV*	Aqueous systems in bonding or finishing processes for nonwoven textiles; Solutions of amino-formaldehyde resins	Formaldehyde released by aqueous systems under drying	Apparatus for simulating conditions of film formation and crosslinking of dispersions. Sample preparation, formaldehyde cleaving, colour reaction with **acetylacetone** reagent, **spectrophotometric** determination at 412 nm	>20mg/kg (20 ppm)

After different ways of extracting formaldehyde, the EDANA analytical procedure follows the same main steps: (1) preparation of the acetylacetone reagent (Nash reagent), (2) preparation of formaldehyde solution at approximately 37%, followed by standardisation, (3) preparation of ethanol solution of dimedone, (4) preparation of a standardised stock solution of formaldehyde at approximately 1500 µg/ml, and diluted solutions for calibrations, (5) reacting specimens with acetylacetone reagent, determination of absorbance, (6) preparation of a calibration curve, (7) spectrophotometric measurement of samples, (8) calculation of results. In our work, EDANA 210.1-99 method was used as originally described, with no modifications.

2. 4. Malachite Green Method – Theoretical Background and Analytical Procedure

2. 4. 1. The Malachite Green – Theoretical Background

The malachite green (IUPAC name 4-[(4-dimethylanophenyl)-phenyl-methyl]-N, N-dimethylaniline) method has been developed for colorimetric determination of very low concentrations of formaldehyde.[22] The malachite green chromatic form is a green dye. In the presence of sulphurous acid, a nucleophilic addition of HSO_3^- occurs, resulting in the formation of a colourless leuco form of malachite green, known as Schiff's reagent (Figure 3).

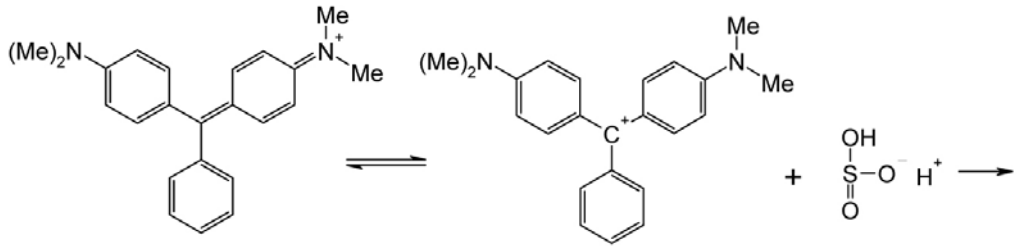
Schiff's reagent reacts with aldehydes, and through a series of reactions (the first being a nucleophilic addition of Schiff's reagent to the formaldehyde molecule) the chromophore system is regenerated via a carbinolamine, from which upon elimination of water an imine is formed, which further reacts with sulphurous acid to give rise to a resonance stabilized coloured cation (Figure 4).

The reaction in Figure 3 is kinetically controlled; therefore the absorbance of the samples must be measured in a very short time span (within 1 minute). Prolongation of the reaction results in a thermodynamic controlled competitive reaction – the addition of bisulphite to formaldehyde, and in the formation of a colourless adduct. A drawback of this method is that malachite green was found to be toxic to human cells, and that there was a possibility of causing the formation of a liver tumour.[61] When absorbed into the body, it is converted into the carbinol form, which spreads across cell membranes faster. Inside the cell the carbinol form is metabolized into leuco malachite green, which is toxic and remains in the body for a longer period of time than the chromatic form. Therefore, safety handling during the whole analytical procedure must be ensured.

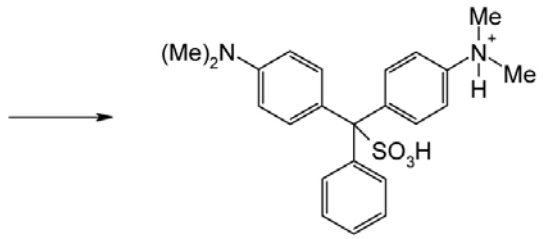
2. 4. 2. The Malachite Green Analytical Procedure

In our work, the basic procedure by Afkhami and Rezaei[22] was modified and used as follows.

Reagents. A 1500 µg/ml solution of formaldehyde was prepared by diluting 1.9 ml of 36.5% formaldehyde solution (Riedel-de Haën) with water to 100 ml. Working solutions were prepared before each experiment by dilution from the stock solution. A working solution of sulphite (0.37 mg/ml) was prepared before each experiment by dissolving 3.7 mg of anhydrous sodium sulphite (Fluka)



I. Malachite green - coloured chromatic form



II. Malachite green sulphite - colourless Schiff's reagent

Figure 3: Nuclephilic addition of sulphurous acid to malachite green – formation of colourless Schiff's reagent

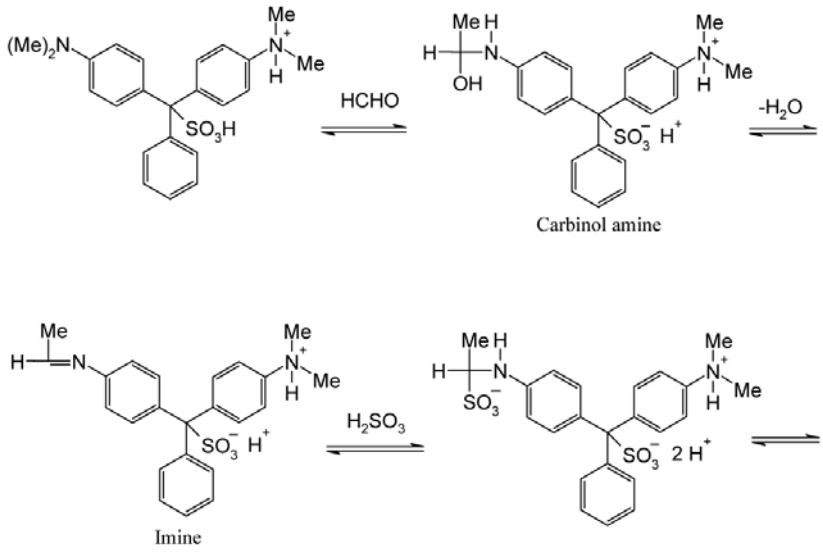


Figure 4: Regeneration of the chromophore system of malachite green (adaptation of a mechanism based on Keuch60)

in distilled water, followed by dilution with water to the mark in a 10-ml volumetric flask. The sulphite solution can be used only for 2 hours, due to its instability at room temperature (24.5 °C). Malachite green solution (10^{-4} g/ml) was prepared daily by dissolving 0.0100 g of malachite green (Riedel-de Haën) in distilled water and diluting to 100 ml with water. A borate, sodium hydroxide buffer solution (pH 8, Itrij) was used for pH adjustment.

Apparatus. A Shimatzu UV-VIS spectrophotometer UV-2401 PC, with a 1 cm glass cell, was used for absorbance measurements; Mettler Toledo AG204 for precise determination of the mass of reagents; VoluMate Liquidsystems stactometer for determination of volumes 500–5000 µl, and Finnpipette, Thermo Labsystems, for volumes 20–200 µl.

Procedure. All solutions were kept at a constant temperature (24.5 °C) before starting the reaction. An aliquot of 1 ml of solution containing 310–9000 ng/ml formaldehyde was transferred into a 10-ml volumetric flask, then 1 ml of buffer solution (pH 8) and 0.1 ml of 0.37 mg/ml sodium sulphite solution was added. The solution was diluted to 8 ml with water, thereby also the residual sulphite was washed into the solution. After 60 s, 1 ml of 10^{-4} g/ml malachite green solution was added, the solution was diluted to the 10 ml mark with water and mixed. The time was measured from the starting point when malachite green was added (initiation of reaction), and at the fixed time of 60 s the decrease in absorbance at 613 nm was measured. A blind sample was prepared by following the above described procedure, but instead of 1 ml of formaldehyde solution, 1 ml of distilled water was added.

2. 5. Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used for morphological determination of microcapsules. Samples of microcapsule suspension were coated with an ultra thin coating of carbon, gold and platinum, by high vacuum evaporation. The observations were performed by JEOL JSM 6060LV SEM microscope at 10kV, which gave bright images of microcapsules.

2. 6. Measurement of Microcapsules Permeability by Mass Loss

For a quick determination of microcapsules permeability by mass loss, an industrial (AERO d.d.) internal method for a quantitative evaluation of microencapsulation performance was applied, which was previously used for a rapid evaluation of microencapsulated antimicrobials[62], essential oils and fragrances[63]. Samples of aqueous suspensions of microcapsules (2–3 g each) in a thin layer were placed to aluminium vessels, and put into an oven, equipped with a ventilation system (Sterimatic ST-11, Instrumentaria), and set to a constant elevated temperature of 135 °C. After the evaporation of initial free suspension water (first 30 minutes), further changes in mass loss of dry microcapsules were determined by a precise analytical balance (Mettler Toledo AG204) after 30, 90, and 150 min at 135 °C. Each sample of microcapsules was investigated in two parallels, and the average values were calculated.

3. Results and Discussion

3. 1. Evaluation of Methods for Residual Formaldehyde Determination

3. 1. 1. Testing of EDANA 210.1-99

Testing of the EDANA 210.1-99 method with standardized formaldehyde solutions and measurements of

samples in 3 parallels confirmed its reported sensitivity >20 mg/kg (>20 ppm). Furthermore, when using freshly prepared reactants, the method showed good sensitivity and repeatability even below this value, down to 1 ppm. Standard deviation of measuring formaldehyde concentration in 3 parallels in sixteen samples between 1–20 ppm was 30%, and in five samples between 20–200 ppm it was 4%.

3. 1. 2. Testing of the Modified Malachite Green Method by Standardised Formaldehyde Solutions

Low amounts of formaldehyde inhibit the malachite green–sulphite reaction in neutral media. This property was used for kinetic determination of low amounts of formaldehyde in aqueous media. The reaction was monitored spectrophotometrically by measuring the decrease in absorbance of the solution at 613 nm (Figures 5,6). A linear calibration graph was obtained in the concentration range 31–900 ng/ml. The detection limit, defined as $A_{LOD}=A_B+3S_B$, where A_B is the average absorbance change for blank solution and its standard deviation respectively, was 31 ng/ml. The relative standard deviations for 10 replicate determinations of 100 and 500 ng/ml of formaldehyde were 2.6 and 1.8%, respectively.

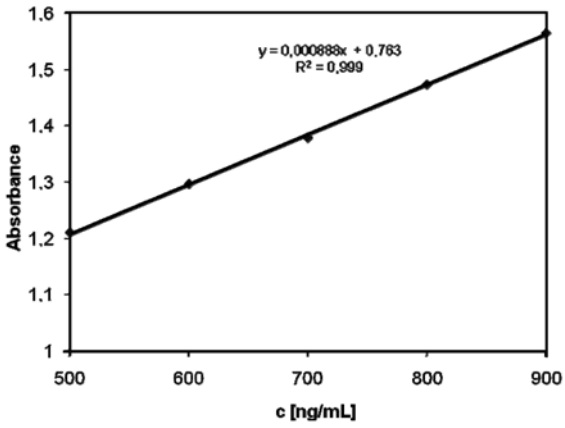


Figure 5: Malachite green method, higher concentration range: the absorbance of the reaction mixture 60 s after the initiation of reaction for concentrations of formaldehyde 500–900 ng/ml (0–500 ppm). Conditions: 0.37 mg/ml sulphite, 10^{-4} g/ml malachite green, pH = 8, T = 24.5 °C

The results proved that low amounts of formaldehyde could be efficiently detected and quantified by the adapted malachite green method by Afkhami and Rezaei[22], if optimized with regard to the sulphite concentration and the fixed time of measuring the decrease in absorbance at 613 nm (see details in materials and methods). However, research by several authors[64–66] using malachite green, has demonstrated its high toxicity to bacteria, fish species and mammalian cells. Therefore, safe handling during the analytical procedure is highly important, and/or the use of other available analytical methods, which seemed to be a better choice.

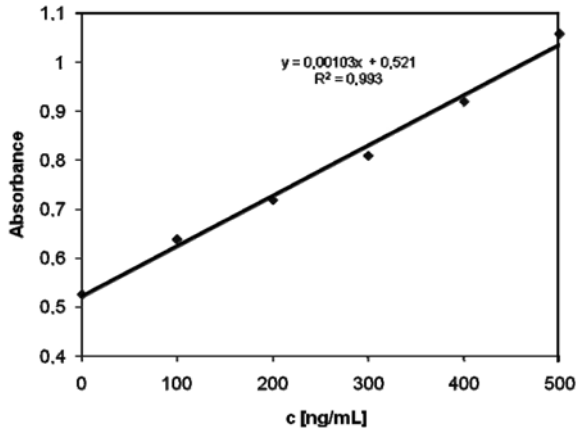


Figure 6: Malachite green method, lower concentration range: the absorbance of the reaction mixture 60 s after the initiation of reaction for concentrations of formaldehyde 0–500 ng/ml (0–500 ppm). Conditions: 0.37 mg/ml sulphite, 10^{-4} g/ml malachite green, pH = 8, T = 24.5 °C

3. 1. 3. Comparison of the Two Methods

Parallel analyses of 15 microcapsule samples in the range of 10 to 1100 ppm of formaldehyde, measured independently with both EDANA *210.1-99* and malachite green methods, showed a good overlapping of results with 15% standard deviation (Figure 7). More precisely, standard deviation for four samples between 10–20 ppm of formaldehyde concentration was 31%, and for eleven samples between 20–1100 ppm it was 9%. Due to the toxicity of malachite green, the EDANA method was chosen and applied for formaldehyde determination in further analyses of samples described in Figures 9 and 10.

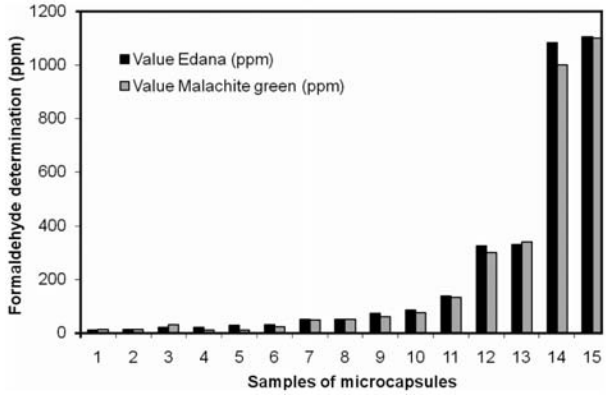


Figure 7: Comparison of EDANA 210.1-99 and malachite green methods: results of parallel independent analyses of 15 microcapsule samples in the formaldehyde concentration range of 10 to 1100 ppm

3. 2. Measurement of Residual Formaldehyde Content in Final Suspensions of Microcapsules

Residual formaldehyde concentrations were measured by the EDANA210.1-99 method in 25 batches of microcapsule suspensions, prepared in a 200 l reactor, at the end of the microencapsulation process, after the addition of ammonia scavenger. In all samples, paraffin with melting point 27 °C was used as a PCM in the microcapsule core. Ammonia was added to the final microcapsule suspension to reach three concentrations in the continuous phase: 0.80% (batches 2–7), 0.90% (batches 8–16) and 1.35% (batches 17–25). In the control (batch 1), no ammonia was added.

Residual formaldehyde in final microcapsule suspension derives from two sources: (1) free formaldehyde present in melamine-formaldehyde prepolymers, which are added to the reactor as microcapsule wall material, and (2) free formaldehyde released during the polycondensation process (Figure 8)

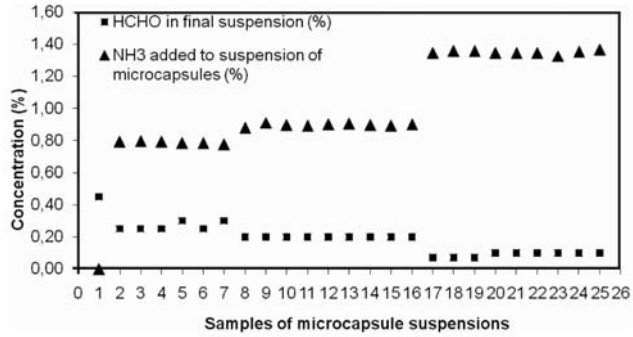


Figure 9: Effect of ammonia scavenger concentration on the residual formaldehyde concentration, measured in 25 batches of final microcapsule suspensions produced in a 200 l reactor

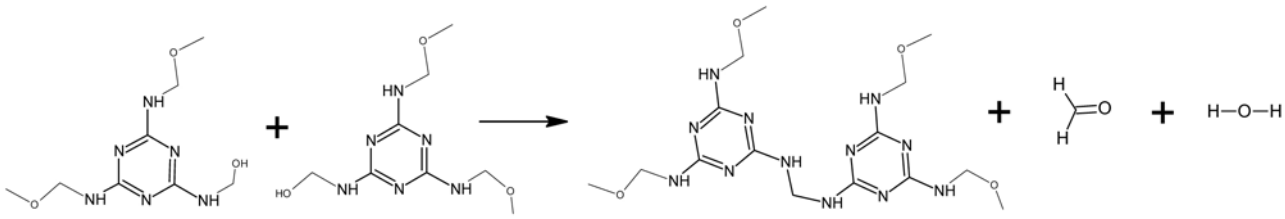


Figure 8: Mechanism of formaldehyde release during the polycondensation reaction of melamine-formaldehyde prepolymers

According to the added raw materials and process parameters used in our microencapsulation process, the contribution of free formaldehyde, deriving from melamine-formaldehyde prepolymers, could be up to 400 ppm in the continuous phase in a reactor. According to the molar ratio between melamine, formaldehyde and methanol, used for the preparation of melamine-formaldehyde prepolymers, one mol of a prepolymer releases up to one mol of free formaldehyde during the polycondensation reaction, if all reactive groups react, and the reaction is completed. Based on these assumptions, the maximal theoretical quantity of free formaldehyde in the final microcapsule suspension could reach up to 6500 ppm, i. e. 400 ppm from the melamine-formaldehyde prepolymers, and up to 6100 ppm from the polycondensation process.

The results of measuring residual formaldehyde concentrations (Figures 9 and 10) revealed that in final microcapsule suspension with no added ammonia, the concentration of residual formaldehyde was 0.45% (4500 ppm). The addition of ammonia as a scavenger reduced the concentration of residual formaldehyde in all cases. With the increasing ammonia scavenger concentrations 0.80, 0.90 and 1.35%, the residual formaldehyde concentrations in the final microcapsule suspensions dropped to 0.27, 0.20 and 0.09%, respectively (i.e. 2700, 2000 and 900 ppm).

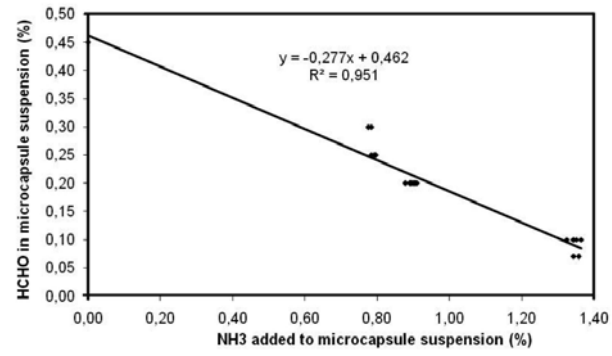


Figure 10: Correlation between the added ammonia scavenger concentration and the residual formaldehyde concentration; measurements from 25 batches of final microcapsule suspensions produced in a 200 l reactor

Measurements of residual formaldehyde concentrations in microcapsule suspensions proved that ammonia was a suitable scavenger for formaldehyde removal. Furthermore, addition of ammonia caused a rise in pH value of the microcapsule suspension to 8.0, which further stabilised the formaldehyde bound in hexamethylenetetrami-

ne, and prevented the potential hydrolysis, which could occur under acidic conditions, as mentioned by Ogata and Kawasaki[15].

3. 3. Permeability and Morphology of Microcapsules in Relation to Ammonia Scavenger Concentration

Suspensions of microcapsules were dried for 30 minutes at 135 °C to remove water from the samples. Then, diffusion of core material from dry microcapsules at an elevated temperature was detected as a mass loss at 135 °C. Two parallels were measured for each sample, and the average value was used. Figure 11 shows the influence of ammonia scavenger concentration on the permeability, measured as a mass loss of microcapsules. After 150 min, microcapsules, treated with 0.00, 0.80, 0.90 and 1.35% ammonia lost 6.40, 4.28, 2.35 and 1.11% of their initial mass due to the diffusion and evaporation of paraffinic PCM from the microcapsule core.

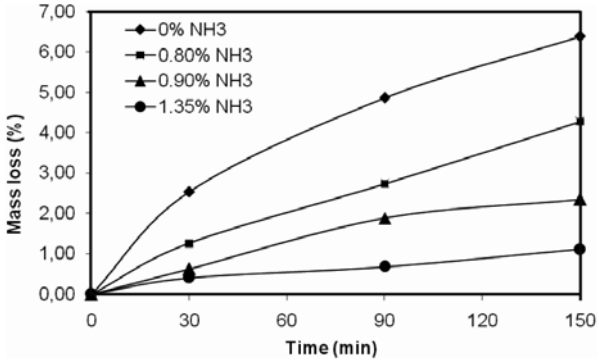


Figure 11: Mass loss of microcapsule samples from four different batches: with 0.00%, 0.80%, 0.90% and 1.35% ammonia scavenger in the microcapsule suspension after the polycondensation process

The results showed that the loss of paraffinic core material from microcapsules at an elevated temperature was reduced by the addition of ammonia scavenger. This observation could be explained by improved aminoaldehyde polymer microcapsule wall permeability. While the addition of ammonia scavenger to the microcapsule reaction suspension rised the pH above 7, the higher pH value possibly influenced the polymerisation equilibrium towards the degradation of dimethylene ether bridges and the formation of methylene bridges, thus forming stronger crosslinking bonds. A similar observation was reported by[67] who studied the synthesis of melamine–formaldehyde resins as a system of complex reversible parallel and consucetive reactions. Their results suggested that the hydroxy-methylamines were converted to methylene and dimethylene ether bridged compounds by acid- and base-catalyzed reactions. A similar effect was also reported by,[68] where an addition of ammonium chloride was found to be important in the process of preparation of urea-formaldehyde microcapsules. According to,[69] by adding ammonium salt in preparing of urea-formaldehyde microcapsules, the strength, hea-

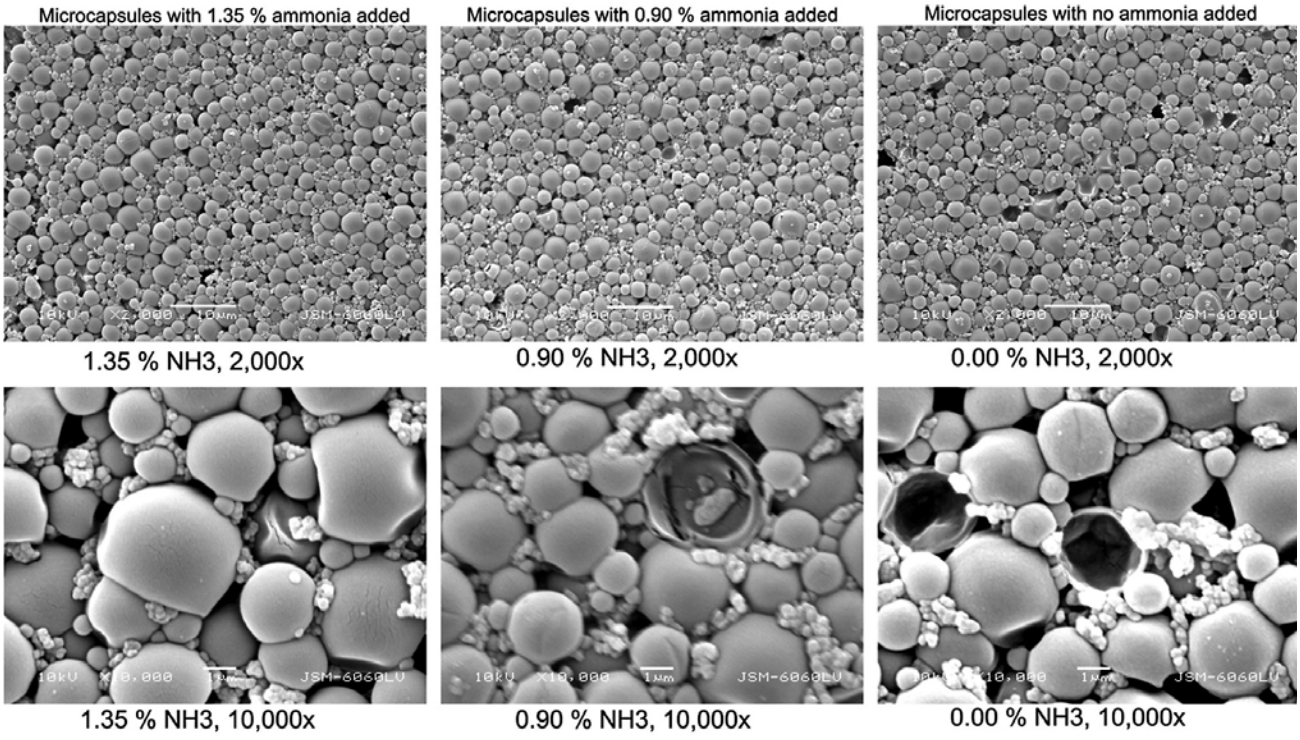


Figure 12: Comparison of microcapsule morphology and damage in relation to ammonia scavenger concentration (1.35%, 0.90%, 0.00%); cracking and opening of microcapsule wall appeared more frequently in a sample with no ammonia added (SEM 2000x, 10000x)

ting resistance and sealing performance of the microcapsule were improved.

SEM micrographs of microcapsules (Figure 12) also supported the observation that ammonia scavenger affected microcapsule wall characteristics, including the morphology. Increased concentrations of ammonia resulted in microcapsules with more elastic/durable walls, while microcapsules with no ammonia scavenger tended to have more brittle and pressure-sensitive walls, and were prone to cracking. The latter would be a desirable characteristic for pressure-sensitive applications (e.g. pressure-sensitive copying papers, sniff and scratch fragrances, etc.), but not for microencapsulated PCMs. In order to remain functional over numerous phase transition cycles, microencapsulated PCMs have to remain permanently encapsulated within the impermeable microcapsule walls for the whole product life. PCM microcapsules therefore need to be highly resistant to mechanical stress – a property which was improved by the addition of the ammonia scavenger.

In our previous work[1] a mathematical model was developed for comparing the mechanical resistance of different batches of aminoaldehyde resin wall microcapsules, produced at different ratios of prepolymers and modifying agents. Mathematical data were confirmed by a modified smudging colouration test at an elevated temperature, and illustrated by SEM. For a more precise quantitative evaluation of mechanical strength of individual microcapsule walls, direct mechanical testing could be carried out, such as described by[70,71]. However, this exceeds the scope of the present study and remains one of the objectives for our further research work.

4. Conclusions

Most countries have applied strict measures and determined the maximum allowed concentrations of formaldehyde in various products, including textiles. The main two purposes of our research were to study and test EDANA and the malachite green analytical methods for a reliable determination of residual formaldehyde in microcapsule suspensions, and to reduce the quantity of formaldehyde residues in aminoaldehyde microcapsule suspensions by the addition of ammonia as a scavenger. Based on experimental results, the following conclusions can be drawn:

Low amounts of formaldehyde (ppm range) can be effectively detected and quantified by both analytical methods: the malachite green method by Afkhami and Rezaei,[22] if optimized with regard to sulphite concentration and fixed time of measuring the decrease in absorbance at 613 nm, and by the EDANA method. Both methods gave comparable results, with 15% standard deviation in the range 10 to 1100 ppm of formaldehyde in the analysed samples. However, due to the reported toxicity of the malachite green reagent, the EDANA method seems to be more appropriate for routine determination of residual formaldehyde concentrations in microcapsule suspensions.

Determination of residual formaldehyde in 25 samples of microcapsule suspensions, prepared by in situ polymerisation of aminoaldehyde prepolymers in a 200 l reactor, without and with ammonia scavenger, confirmed that ammonia can be used as a reagent for lowering the concentration of residual formaldehyde in microcapsule suspensions after the in situ polymerisation process. A linear correlation was observed between the added ammonia scavenger concentration and the reduction of residual formaldehyde concentration in a suspension of microcapsules.

Furthermore, morphological characterisation of microcapsules by SEM and microcapsule wall permeability measurements by gravimetry / mass loss at an elevated temperature (135 °C) suggested that ammonia positively contributed to the wall impermeability / durability and thermal resistance, while microcapsules with no ammonia scavenger added tended to have more permeable walls, and were more prone to cracking.

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Povzetek

Parafinski fazno spremenljivi materiali (PCM) so bili mikrokapsulirani z *in situ* polimerizacijo melamin-formaldehidnih predkondenzatov. Delno metilirani trimetilolmelamin je bil uporabljen kot aminoaldehidni predkondenzat za tvorbo stene mikrokapsul, kopolimer stirena in malein anhidrida kot emulgator in modifikator ter amonijak kot dodatek za odstranjevanje ostankov formaldehida. Za določanje ostankov formaldehida v območju ppm koncentracij so bile preučene analizne metode EDANA in metoda malahit zeleno. EDANA 210.1-99 je bila uporabljena za določitev ostankov formaldehida v 25 vzorcih mikrokapsul, proizvedenih v 200-L reaktorju. Ugotovljena je bila linearna korelacija med koncentracijo dodanega amonijaka in zmanjšanjem koncentracije ostankov formaldehida. V primerjavi z 0,45% (4500 ppm) formaldehida v neobdelanih suspenzijah mikrokapsul, je z dodajanjem amonijaka v koncentracijah 0,80, 0,90 in 1,35% koncentracija ostankov formaldehida padla na 0,27, 0,20 in 0,09% (t.j. 2700, 2000 in 900 ppm). Karakterizacija morfoloških lastnosti mikrokapsul s SEM in merjenje prepustnosti sten mikrokapsul z gravimetrijo / izgubo mase pri povišani temperaturi (135 °C) sta nakazala, da je amonijak pozitivno prispeval k elastičnosti / vzdržljivosti stene mikrokapsul, medtem ko so bile stene mikrokapsul brez dodanega amonijaka večinoma bolj krhke in nagnjene k poškodbam.