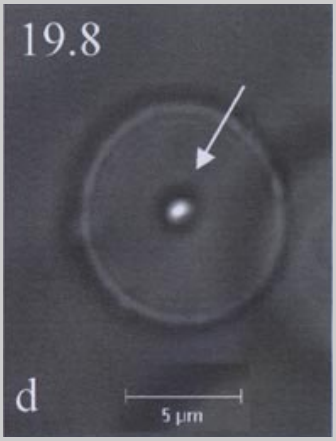
Full Paper: Melamine formaldehyde (MF) colloidal cores were coated with polyelectrolyte multilayers. The core decomposition process at low pH was followed by confocal laser scanning microscopy (CLSM). Transient capsule swelling as a result of the osmotic pressure difference created by the decomposition of the MF resin was observed. The rate of core dissolving and the permeation of decomposition products of the MF core through the capsule walls are discussed in relation to the extent of swelling and capsule wall rupture. The core decomposition products had a diffusion coefficient of 71 $\mu m^2/s$, which corresponds to a hydrodynamic diameter of $\approx$4 nm. Simultaneously with the degradation of MF polymers the hydrolysis at the melamine groups to ammeline groups occurred as was shown by infrared spectroscopy. The size and chemical composition of the reaction products did not depend on the pH. The degradation rate increased with decreasing pH.



CLSM image of core decomposition process as a function of time. Rd-MF colloids with a diameter of 6.4 µm deposited with $(PSS/PAH)_8$. The arrow indicates the residue of the core. The number in the inset indicates the core decomposition time.

The Decomposition Process of Melamine Formaldehyde Cores: The Key Step in the Fabrication of Ultrathin Polyelectrolyte Multilayer Capsules

Changyou Gao,[1,2] *Sergio Moya,*[2] *Heinz Lichtenfeld,*[2,4] *Alain Casoli,*[2] *Harald Fiedler,*[3] *Edwin Donath,**[2a] *Helmuth Möhwald*[2]

[1] Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China
[2] Max-Planck Institute of Colloids and Interfaces, D-14424 Golm/Potsdam, Germany
E-mail: edwin.donath@mpikg-golm.mpg.de
[3] Microparticles GmbH, D-12489 Berlin, Germany
[4] TU Bergakademie Freiberg, D-09599 Freiberg, Germany

Introduction

Recently, a novel technique was introduced for the fabrication of nano- and micrometer-sized capsules. Polyelectrolytes were stepwise adsorbed onto charged decomposable colloidal templates forming a tailored polyelectrolyte film on the surface of the colloidal particles.[1–5] The entropy increase brought about by the release of counter ions as a result of the electrostatic attraction between oppositely charged species is the driving force for film formation.[6] After the film is assembled, a chemical treatment such as pH change, oxidation reaction, etc., is applied to dissolve the core. Hollow capsules are obtained.[5,7] This technique provides a versatile and precise way of controlling the capsule size, shape, and wall composition, as well as the wall thickness. The polyelectrolyte capsules may find many practical applications as containers or reaction vessels.[8–10] They have a great a potential in drug delivery, sensing and catalysis.

Several types of decomposable cores have been employed as templates for hollow polyelectrolyte capsule preparations. Weakly crosslinked melamine formaldehyde (MF) colloidal particles have been often employed. Capsules templated on MF particles of different size were successfully fabricated and subsequently characterized by scanning electron microscopy (SEM), transmission elec-

[a] Additional address: Institute of Medical Physics and Biophysics, University of Leipzig, Liebigstraße 27, D-04103 Leipzig, Germany.

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tron microscopy (TEM), scanning force microscopy (SFM), confocal laser scanning microscopy (CLSM), electrophoresis, electrorotation, and single particle light scattering.[5, 11–14]

The MF cores are usually dissolved in solutions of a pH below 1.6, but they could be also dissolved in *N*,*N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The melamine core dissolution at low pH is routinely performed in our laboratory. However, at present very little is known about the core decomposition process being the key step in the capsule preparation. The core decomposition process may affect many properties of the capsules, for instance, the capsule integrity, the capsule size, the wall permeability, the surface topology and the wall elasticity as a result of adsorption of degradation products or the osmotic induced strain in the wall. For example it was already observed that the size of the capsules made from poly(styrene sulfonate sodium salt) (PSS) and poly(diallyldimethylammonium chloride) (PDADMAC) was larger than that of the templated core.[15] SFM, SEM and CLSM investigations revealed macroscopically detectable pores or holes in some capsules especially in capsules with a larger diameter. Therefore, it is both of practical relevance and theoretical importance to understand the core decomposition process in greater detail.

This study reports for the first time on line observations of the MF core decomposition process in HCl under CLSM. Capsule swelling and shrinking was observed in parallel with the disappearing of fluorescence from the rhodamine labeled cores. Fluorescence correlation spectroscopy (FCS) measurements provided the size of the core decomposition products. It was demonstrated that polymer degradation occurred during the core dissolution process. pH induced chemical changes were further confirmed by infrared spectroscopy. Optimal conditions are suggested for the fabrication of dispersions of highly intact capsules.

Experimental Part

Materials

The source of chemicals were as follows: poly(styrene sulfonate, sodium salt) (PSS), $\overline{M}_w$ 70 kD, and poly(allylamine hydrochloride) (PAH), $\overline{M}_w$ 15 kD, Aldrich; fluorescein isothiocyanate labeled albumin (FITC-albumin), 12 mol FITC/mol albumin, Sigma; melamine formaldehyde particles (MF particles) and rhodamine isothiocyanate labeled MF particles (Rd-MF), 0.5 mg rhodamine/g MF, microparticles GmbH, Berlin, Germany. All chemicals were used as received.

Rhodamine isothiocyanate (Rd) labeled PAH and fluorescein isothiocyanate (FITC) labeled PAH were prepared according to ref.[16] The water used in all experiments was prepared in a three-stage PureLab Plus™ (USF Deutschland GmbH) purification system and had a resistivity larger than 18.2 MΩ · cm.

Methods

Capsule Preparation

Membrane filtration was employed to consecutively adsorb PSS and PAH onto MF particles.[17] The adsorption of polyelectrolytes (1 mg/mL) was conducted in 0.5 M NaCl solution for 5 min followed by 3 washings in H_2O. Then the respective oppositely charged polyelectrolyte species was adsorbed. After the desired number of layers was adsorbed the coated particles were subjected to a HCl treatment to conduct the decomposition of the MF cores. The products of core decomposition and excess HCl were washed off in H_2O by filtration with gentle agitation until a neutral pH was established.

Confocal Laser Scanning Microscopy

Confocal micrographs were taken with a Leica TCS NT inverted confocal systems (Leica, Germany) equipped with a 100 × oil immersion objective, numerical aperture 1.4. Rd-MF particles were used for time-dependent observations of the core decomposition process with CLSM. A drop of the particle suspension was put onto a glass cover slip. After the water had evaporated the focus was adjusted to the equatorial plane of the particles. A drop of HCl solution was then applied to the particles. The reaction was followed and a series of fluorescence images as a function of time were taken using the 'Series Scan' function. Images in transmission mode were taken in parallel. The capsule sizes were obtained from the images. Fluorescence intensity profiles along a line were calculated using the 'Profile' function provided with the TCS NT program.

Förster Energy Transfer (FRET)

The Förster energy transfer between FITC labeled PAH and Rd labeled PAH was recorded by means of a Fluorolog Spex device. Excitation was set at 488 nm, i.e., the FITC absorption maximum.

The apparent efficiency of FRET is defined as $E = (I_a - 0.4\ I_d)/(I_d + I_a - 0.4\ I_d)$, where I_a is the maximum intensity of the acceptor (i.e. Rd PAH) and I_d is the maximum intensity of the donor. The factor of 0.4 I_d takes into account the intensity of the donor at the maximum of the acceptor.

Fluorescence Correlation Spectroscopy (FCS)

Diffusion coefficients of the core decomposition products were determined by FCS. Measurement was conducted by means of the Confocor (Carl Zeis, Jena, Germany) connected to an Ar^+ laser (514 nm). The microscope was equipped with a Zeiss* 63/1.2 objective. The measuring volume was 0.6 fl.

Rhodamine 6G at a concentration of 10^{-7} M was used as a standard. A diffusion coefficient of 300 $\mu m^2/s$ was obtained for the pure dye. Rd-MF particles were decomposed with HCl or dissolved in DMF. In the case of HCl treatment a homogeneous solution with a Rd concentration of about 10^{-6}–10^{-7} M was prepared. All samples were measured immediately after preparation.

Infrared Spectroscopy

A Bruker Equinox 55/s infrared spectrometer was employed for obtaining the infrared (IR) spectra with the KBr pellet method. The MF particles were treated in HCl solution with a pH value of 2.2 for 5 min, followed by 3 washings and centrifugation. HCl solutions with pH values ranging from 0.7–1.5 were employed to decompose the MF particles. Homogenous solutions of the decomposition products were obtained. The solutions were dried at room temperature (23 °C). A powder was obtained.

Single Particle Light Scattering

The intensity of the scattered light from single particles was recorded with a custom made photometer equipped with an Argon laser operating at a wavelength of 488 nm. Hydrodynamic focusing was applied. For each particle the intensity of forward scattering within an angle 10–15° is recorded. An intensity distribution is obtained. Details of the method are given elsewhere.[3, 17]

The Rayleigh-Debye-Gans Theory was used for evaluating the scattering data. The refractive index of the melamine core was assumed as 1.53. This value was obtained by extrapolating concentration dependent measurements of the refractive index of melamine formaldehyde solutions by means of an Abbé refractometer. The refractive index of the polyelectrolyte multilayer was taken as 1.47.[21] The scattering intensity distribution of the core particles $\varphi(I)$ is converted into a distribution of the particle radius $\varphi(r)$ by taking into account $I \propto r^6$. To this aim the recorded intensity is calibrated with that of a standard monodisperse latex of 480 nm in diameter. For core-shell particles and capsules the intensity is calculated as the superposition from the scattered light from the interior and the shell wall.

Results and Discussion

For the on line observation of the core decomposition process, four layers pairs of PSS/PAH were deposited on Rd-MF particles. The labeling of MF cores with rhodamine has the advantage that the intensity of fluorescence is almost unaffected by the low pH. The core decomposition process followed by CLSM is shown in Figure 1. Upon addition of the acid (HCl, pH 1.1), the core (Figure 1a) started to decompose immediately. Its size decreased rapidly along with time. The complete decomposition of the MF cores required about 20 s. The diameter of the remaining small core, such as shown in Figure 1d in transmission, is plotted against time in Figure 2. The core decomposition kinetics shows a linear decrease in diameter until the core completely vanishes. The linear decrease in the core diameter as a function of time is remarkable. From this linear decrease in diameter it can be concluded that the rate-limiting step of the dissolution process is the outermost "layerwise" degradation and desorption of the core constituents. If permeation would be the rate limiting step a saturation of the degradation products inside the capsules could be expected. This would

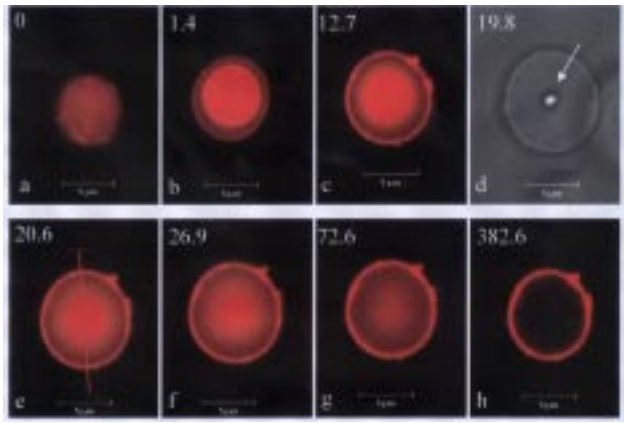


Figure 1. CLSM images of core decomposition process as a function of time. Rd-MF colloids with a diameter of 6.4 μm deposited with $(PSS/PAH)_8$. The arrow in (d) indicates the residue of the core, and the line in (e) indicates the position of profiles presented in Figure 3. The numbers in the insets indicate the core decomposition time, respectively.

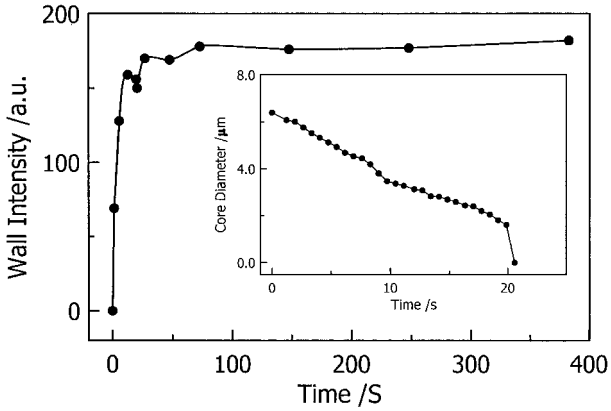


Figure 2. Fluorescence intensity from the capsule wall as a function of the core decomposition time. The position is shown in Figure 1e. The inset is the core diameter as a function of core decomposition time.

lead to a situation where the volume and not the radius of the remaining core should decrease in proportion with time.

The series of images in Figure 1 show clearly that the capsule swells after addition of the acid, and shrinks afterwards, as it can be seen by comparing Figure 1h and Figure 1e. The change of the capsule diameter as a function of time is quantitatively shown in Figure 2. Within 2 s after acid addition the capsule radius rapidly increased to approximately 120% of its original size (Figure 1b). After this steep rise the capsule radius increased almost linearly to about 140% until the core was completely decomposed (Figure 1e) as indicated by the arrow in Figure 2. The capsule thus swelled to a maximum size of 9.1 μm and initially maintained this size. Finally, capsule shrinking took place and lasted until the initial diameter was recovered. From these observations one can conclude that the polyelectrolyte multilayer film of the PSS/PAH

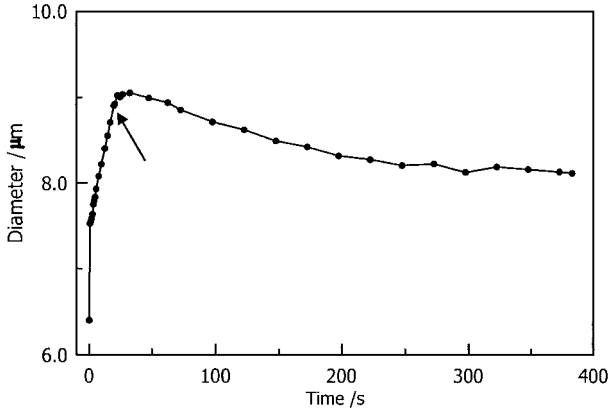


Figure 3. The variation of capsule diameter as a function of core decomposition time. The arrow indicates the time of complete core decomposition.

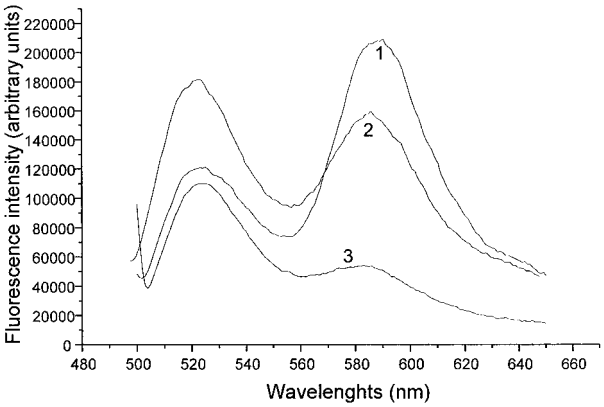


Figure 4. Energy transfer from FTCPAH to RdPAH in melamine capsules. (1) 1 polyelectrolyte layer in between, (2) 3 layers in between, (3) 5 layers in between.

capsule wall is stretched by a factor of 3 in area compared with the initial state just after deposition. This capability to stretch is a remarkable new feature of a free polyelectrolyte film not reported before.

The capsule swelling is understood as a result of the osmotic pressure difference created by the decomposition of the core. The MF polymers constituting the core are degraded to smaller soluble units by the low pH. The concentration of the core dissolution products inside capsules becomes almost instantaneously quite large since the available volume is very small.

A large tension is created as the result of the appearing hydrostatic pressure difference. The extent and duration of the osmotically induced tension onto the capsule wall depends on the interplay between the rate of core dissolution and the permeation of the core degradation products through the capsule wall. A larger permeability would be favorable for releasing the tension. It is also worth to note that smaller capsules should thus have a higher stability against swelling. Indeed, at a given pressure difference Δp the tension in the wall, γ, becomes $\gamma = \Delta pr/2$, where r is the capsule radius. On the other hand the characteristic time of the concentration decay is $V/AP = r/3P$, where P is the wall permeability and V and A are capsule volume and surface area, respectively. Hence, it can be expected that capsules with smaller radii and otherwise the same wall properties should be more resistant towards area increase during the core dissolution process;[20] because, i) due to Laplace's law the tension is smaller, and ii) the oligomer concentration in the interior decreases faster as a result of the more advantageous ratio between capsule volume and surface. For smaller capsules the relatively large area per unit volume increases the flux of the core degradation products out of the capsules.

The series of images in Figure 1 also reveal that the decay of the fluorescence inside the capsule was delayed compared with the rate of the core decomposition. Some fluorescence in the capsule interior remained even after the core was completely decomposed as can be seen in Figure 1f at a time of 26.9 s. It required about 400 s to achieve equilibrium between the fluorescence intensity in the capsule interior and the bulk (Figure 1h). Since the reduction of the fluorescence intensity is caused by the diffusion of the Rd-MF decomposition products from the capsule interior to the bulk, this means that the existence of the capsule wall considerably slowed down the permeation of MF oligomers. This is consistent with the result shown in Figure 2 and explains why the capsules continue to shrink even after core decomposition.

In a previous work it was shown that Förster Energy transfer measurements could be used to characterize the layer structure on colloidal particles.[21] It was interesting to study whether the stratified polyelectrolyte layer structure is preserved after the core dissolution. For this purpose the energy transfer before and after dissolution was compared. Rd PAH and FITC PAH were assembled on melamine particles of a diameter of 3.2 μm, with 1, 3 and 5 layers of polyelectrolyte between the donor and acceptor layers. Three layers of polyelectrolyte were always assembled underneath the first labeled polymer, FITC-PAH; two layers were assembled on the top acceptor polymer. Fluorescence spectra were recorded before and after the core dissolution. The spectra of capsules are shown in Figure 4. The transfer diminishes progressively with the increase of layer numbers between the Rd and FTC labeled PAH, as in the case of the coated cores. This decrease is consistent with an increase of layer thickness with the number of polyelectrolyte layers and a stratified film structure. This film topology structure is preserved after core dissolution. No mixing of layers as a result of the tension induced swelling-deswelling occurred. Apart from the similarity in the behavior, a small quantitative difference in the transfer was observed for colloids and capsules. The Förster energy transfer was higher for the capsules than for the colloids. In the case of three intercalated layers the transfer increased from 22% before disso-

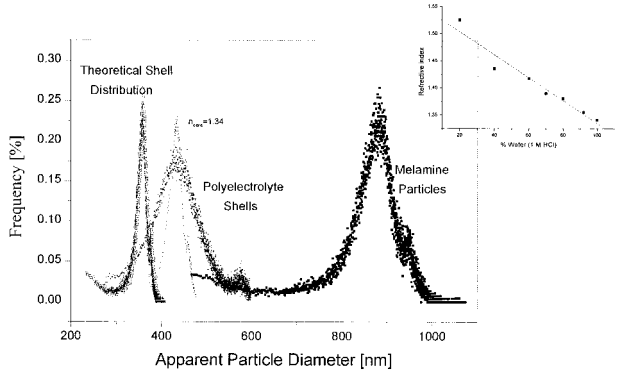


Figure 5. Experimental and theoretical single particle light scattering distribution as function of capsule radio.

lution to 32% after core removal. This increase in the transfer is currently understood as a consequence of the osmotic pressure generated tension during core dissolution and the subsequent swelling as described above. During the swelling the individual layers may have come closer to each other as a result of the capsule wall thinning.

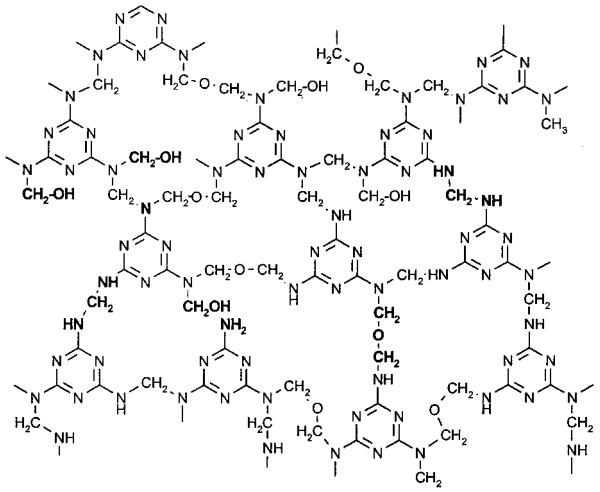
The decomposition products of the MF cores can adsorb on the capsule wall as it can be inferred from the fluorescence of the capsule wall. The appearance of fluorescence in the wall in parallel with the core decomposition process is easily distinguished as shown in Figure 1c to Figure 1h. To quantify this adsorption of the MF degradation products in the capsule wall, profiles of fluorescence intensity through the capsule wall were evaluated, as shown in Figure 1e. The fluorescence intensity from the capsule walls was obtained and averaged. Figure 2 shows that the fluorescence intensity coming from the capsule wall steeply increased during the wall decomposition process. After the core was completely decomposed the fluorescence remained constant. It can be thus concluded that some remains of the core become irreversibly adsorbed in the capsule wall.

SPLS was applied to quantify the total amount of MF remaining in the polyelectrolyte capsules after core removal. The distribution $\varphi(r)$ of MF particles employed as the templates are measured and shown in Figure 5. Accordingly, a theoretical distribution of the polyelectrolyte capsules templated on these MF particles can be predicted. When using the relative refractive index of 1.47 for the capsule wall material and 1.333 for water in the capsule interior one can predict theoretically the scattering light intensity distribution $\varphi(I)$. To compare this with the experimental distribution of the templates it was converted to an apparent radius distribution of melamine spheres, which would have the same scattered light intensity distribution. However, the experimental result shows that the capsules had a higher scattering than expected. In addition, a broadening of the distribution was observed. When a refractive index of 1.341 was used for the capsule interior instead of 1.333 to anticipate the presence of remains of the core, the theoretical position becomes superimposed with the experimental one. This refractive index change is consistent with assuming that on average 4% of the original core material were not removed. Elemental analysis confirmed this interpretation since it was found that as much as 20% of the capsule mass were provided by the remaining decomposition products of the MF cores.[20] The broadening of the scattered light intensity can be explained by a distribution of the refractive index of the capsules as a result of a different amount of remains of the core present in the capsule after dissolution as shown in the inset in Figure 5.

In order to characterize the degradation of the MF resin during the core decomposition procedure, diffusion coefficients D were measured by means of FCS. It is remarkable that the diffusion coefficient of products from the MF core decomposition in acid is 4 times bigger than that of the MF polymers obtained after dissolving the cores in DMF/H_2O (1:9 v/v). This demonstrates that polymer degradation occurs when the MF resin is treated at low pH. An equivalent hydrodynamics radius r can be calculated from the diffusion coefficient the Einstein-Stokes equation: $D = kT/6\pi\eta r$, where k is the Boltzmann constant, T is the absolute temperature and η is the viscosity of the solution. The hydrodynamic radius of the products from MF core decomposed in acid is 3.4 ± 0.8 nm (distribution 2.6–4.2), while for the MF polymers obtained after dissolving the cores in DMF/H_2O an average radius of 16.3 nm (distribution 8.7–27.2 nm) was obtained. Taking into account that the volume of a MF monomer is around 2 nm^3 and approximately 50% of the polymer coil volume is water it can be estimated that the MF polymers and the degradation products are composed of about 4000 and 60 monomer units, respectively.

A possible structure for the melamine resin is provided in Scheme 1. The amine groups of the melamine monomers are partially or totally substituted. The substitute is always a methoxy group or a linkage with another melamine monomer. The linkage between melamine monomers can come from ether or methylene bridges. The bridges are formed during the polymerization by addition of either two methoxy groups or one methoxy and a primary amine. It is important to emphasize that not all the amino groups are substituted and that the polymerization is not complete, as it can be observed in the Scheme.

It is conceivable that the ether bound is broken by hydrolysis as a result of the pH treatment. The chemical changes of MF resin induced by the treatment with acid were studied by IR spectroscopy. The IR spectra show no structural difference for the derived products as a function of the pH value during treatment. Regardless of whether a pH value of 0.7, 1.1 and 1.5 was used, in all the cases a new absorbance peak around 1645 cm^{-1} appeared as shown in Figure 6. According to literature this mean peak can be attributed to the absorbance of the amide



Scheme 1. Schematic sketch of a weakly crosslinked melamine formaldehyde resin. Some typical structure units are highlighted in bold letters:

ether linkages	—CH_2—O—CH_2—
primary amino groups	—NH_2
secondary amino groups	—NH—CH_2—
tertiary amino groups	—NR_3
methylene bridges	=N—CH_2—N=
primary hydroxyl groups	—CH_2—OH

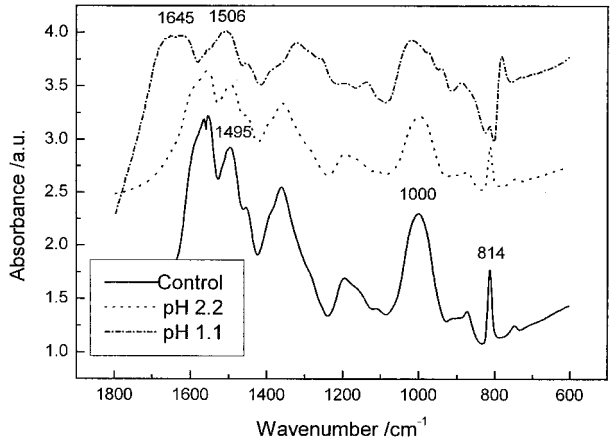


Figure 6. Infrared spectra of MF resins treated with HCl with different pH value. The numbers in the insets indicate the absorbance peaks.

group in ammeline.[22, 23] This means that during the process of core decomposition not only the MF resin is degraded to MF oligomers, but also the melamine is hydrolyzed to ammeline. It should be mentioned that, although there is neither a size nor a chemical difference for the MF degradation products obtained at pH values between 0.7–1.5, the degradation rate is largely different, the lower the pH value, the faster core degradation takes place. Because the permeability of the degradation products and the capsule wall strength are the limiting factors, the optimal pH value should be carefully adjusted. The study of the influence of pH values as well as other factors on the capsule integrity during dissolution is subject of a forthcoming study.

A remarkable feature is that the MF resin could not be dissolved in DMF or decomposed as described above if it was treated beforehand with acid at a pH value higher than 1.7. Through comparison of the relative intensity of absorbance in Figure 5 it becomes possible to explain the pH induced chemical changes of the MF-resin. The absorbances at 3300 (not shown), 1495, 1000 and 814 cm^{-1} are assigned to the vibration of hydroxy/amino, amino, ether (C—O—C) and C—N—C groups,[24] respectively. The absorbance ratio of $A_{OH,NH}/A_{NH}$, $A_{C\text{-}O\text{-}C}/A_{NH,OH}$, and $A_{C\text{-}N\text{-}C}/A_{C\text{-}O\text{-}C}$ are 0.477, 1.411 and 0.596 for the control, and 0.397, 1.855 and 0.65 for the sample pretreated at pH2.2, respectively. These data indicate that the amount of hydroxy groups decreased in parallel to an increase of the ether groups and the C—N—C groups. This result implies that a higher pH above the decomposition threshold is able to catalyze the dehydration of hydroxy groups to form the ether linkage, or C—N—C groups. The ether linkage can be hydrolyzed by the acid, whereas the C—N—C groups cannot. These structure alterations should be responsible for the loss of the ability to dissolve the cores once they were pretreated with a pH higher than 1.7. It is deduced that at lower pH the rate of C—N—C formation should be slower than the hydrolysis rate, otherwise the MF resin could not be dissolved. The conclusion is that in the core decomposition protocol the pH value in the bulk should be lowered to less than 1.7 as fast as possible. It is worth to note that a very low pH value is disadvantageous for the core decomposition either. Incomplete core decomposition was observed under CLSM when acid at pH 0 was employed. The reason is not clear, probably at this pH value the repolymerization rate is even faster than the degradation.

Conclusion

It has been shown that the core decomposition procedure is a key step for capsule fabrication.

The on line observation of the core decomposition process under CLSM revealed for the first time that the capsules swell due to the osmotic pressure difference created by the decomposition of the MF core. The extent and duration of the osmotically induced tension onto the capsule wall depends on the interplay between the rate of core dissolving and the permeation of the oligomer through the capsule walls.

The MF oligomer size measured by FCS verified the degradation of the MF polymers induced by an acid treatment at low pH.

In addition to the degradation of the polymer chain at low pH the melamine ring was also partially hydrolyzed to ammeline as was shown by IR spectroscopy. IR spectra also demonstrated that further polymerization might

occur leading to a higher degree of crosslinking when the MF resin was treated with acid just above the degradation threshold, in this situation insoluble MF colloids were obtained. This suggests that for an optimal MF core decomposition the pH value in the bulk should be always below 1.7.

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