Composite Tectocapsules Containing Porous Polymer Microspheres as Release Gates

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ABSTRACT: Porous and amphiphilic polymer microspheres were incorporated into polyurea capsules in order to control the release of the core solvents independently of wall formation. While nonpolar poly(divinylbenzene-55) microspheres were simply encapsulated along with the xylene core solvent, the amphiphilic poly(divinylbenzene-55-*alt*-maleic anhydride) microspheres, as well as maleic acid functionalized poly(divinylbenzene-55) microspheres, became embedded at the polyurea−water interface. Release of xylene from these microcapsules into air was monitored at room temperature and 50 °C. Release profiles change significantly upon addition of amphiphilic porous microspheres, with the release rates scaling with microsphere loading. Scanning transmission X-ray spectromicroscopy (STXM) indicates that the polyurea is largely excluded from the pores of the microspheres.

Introduction

In current microcapsule systems based on diffusion release, control over the release of fill material requires changing key properties of the capsule wall such as thickness, permeability, and chemical composition. However, these properties are in turn affected by the fill materials, requiring separate optimization of the release properties for each fill.[1] In principle, knowledge of the solubility parameters of the fill allows prediction and adjustment of release properties. Another approach is to separate the encapsulation process from the release controlling process. We are describing here the introduction of preformed porous polymer spheres into nonpermeable capsule walls. By designing a system where release occurs only through the polymer spheres, release may be controlled through microsphere loading and porosity, independent of the solubility parameter of the fill.

This system requires porous, amphiphilic microspheres that could assemble at the oil−water interface and become embedded in the forming impermeable polyurea wall.

Particle assembly at oil−water interfaces was originally reported by Pickering.[2] The concept has since been exploited for emulsion stabilization,[3] removal of fine inorganic particles from aqueous slurries,[4] and the encapsulation of organic materials[5−8] and water.[9] Studies of polymer particle self-assembly have largely focused on electrostatic assemblies of latex particles. In these systems, latex particles assemble at the oil water interface to form capsules,[5,9] in the oil phase of an emulsion to form particles,[6] or on the surface of a solid particle to form core−shell particles.[10] In all these systems the assembled particles are charged and are fixed in place by complexation with a polymer of opposite charge[10] or a salt such as $CaCl_2$.

Recently, Dinsmore et al.[11] reported the formation of colloidosomes, where polystyrene microspheres self-assemble at an interface and are then sintered together at high temperature to form a capsule wall. Microcapsules prepared by the assembly of particles at the oil−water interface often have large pores that result in rapid release of fill material and are likely more suitable for larger fills such as cells than for low molecular weight pharmaceuticals and agricultural chemicals. The composite tectocapsules described here should be suitable for the encapsulation and controlled delivery of low molecular weight fills, since release from these capsules should be governed by the porosity and concentration of the preformed microspheres.

In other work inorganic particles have been incorporated into polymeric membranes as stabilizers,[12] porogens,[13,14] transport channels,[15] and structural agents.[16] Polymeric particles have also been incorporated into polymers[17,18] to increase the mechanical strength of the resulting composite.

We recently described tectocapsules prepared by interfacial self-assembly and cross-linking of highly cross-linked, nonswellable microspheres[8,19] or lightly cross-linked, swellable microgels in the absence of a second polymer. The term "tecto" reflects the use of building blocks that covalently assemble into larger geometries and has precedents in analogous concepts described by Wuest[20] and Tomalia.[21] Here we report the combination of tectocapsule formation with subsequent interfacial polyurea formation to form composite tectocapsules as well as their morphology, composition, and release profiles. We use xylene as model hydrophobic fill, representative of other potential fills with low solubility parameters.

Experimental Section

Materials. Diethylenetriamine (DETA, 99%), divinylbenzene-55 (DVB-55, a commercial mixture of 55% *m*- and *p*-divinylbenzene, with 45% *m*- and *p*-ethylvinylbenzene), methylene chloride (HPLC grade), 2-butanone (methyl ethyl ketone, MEK, 99.5%, HPLC grade), 4-methylstyrene (4-MeSt, 96%), polyethylenimine (M_n ca. 1200, 50% in water), polyethylenimine (M_n ca. 60 000, 50% in water), poly(vinyl alcohol) (PVA, 80% hydrolyzed, M_n ca. 9000), propyl acetate (99%), tetraethylenepentamine (TEPA, tech.), and *p*-xylene (HPLC grade) were purchased from Aldrich and used without further purification. Maleic anhydride (99%) was purchased from Aldrich and was recrystallized from methylene chloride. Mondur ML (a mixture of 2,4- and 4,4-diphenylmethane diisocyanate) was donated by Bayer and used as received. Polyethylenimine (M_n

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ca. 9000, 30% in water) was purchased from Polysciences, Inc., and was used without purification.

Poly(divinylbenzene-55-*alt*-maleic anhydride) Microsphere Synthesis. The microspheres were prepared according to a procedure reported earlier.[23] Maleic anhydride (0.80 g) was dissolved in MEK (8 mL) in a glass scintillation vial (20 mL). Heptane (12 mL) was added, followed by DVB-55 (0.73 g) and 2,2′-azobis(isobutyronitrile) (AIBN) (0.016 g). The vial was closed tightly and placed in the polymerization reactor[22] at 70 °C for 24 h. At the end of the reaction the microspheres were collected by centrifugation and washed with MEK. The microspheres were then dried at room temperature in a vacuum oven overnight and stored in a desiccator. Typical yields are 95%.

Poly(divinylbenzene-*alt*-maleic anhydride) Microgel Synthesis. The two types of microgel were prepared according to procedure reported earlier.[23] Poly(DVB55-*alt*-MAn) gels*:* Maleic anhydride (1.90 g) was dissolved in MEK (56 mL) in a Nalgene bottle (125 mL). Heptane (24 mL) was added, followed by DVB-55 (1.6 g) and AIBN (0.064 g). Poly(DVB5-*alt*-MAn) gels: Maleic anhydride (1.90 g) was dissolved in MEK (32 mL) in a Nalgene bottle (125 mL). Heptane (48 mL) was added, followed by DVB-55 (0.16 g), 4-methylstyrene (1.22 g), and AIBN (0.064 g).

In each case, 18 mL of the reaction mixture was transferred to a glass scintillation vial. The vials were closed tightly and placed in the polymerization reactor at 70 °C for 24 h. At the end of the reaction the microspheres were collected by centrifugation and resuspended repeatedly in MEK. Subsequently, MEK was exchanged for reagent grade PrOAc or other fill solvents. Typical yields are 40−60%. Microgels were stored in wet PrOAc for a minimum of 2 weeks prior to use in tectocapsule formation to allow for hydrolysis of approximately 20% of the anhydride functionalities.

Microsphere and microgel diameters were measured using a Phillips ElectroScan 2020 environmental scanning electron microscope (ESEM) and a Coulter LS 230 particle sizer. Infrared spectra were recorded using a Thermo Nicolet FTIR.

Poly(divinylbenzene-55) Microsphere Synthesis. The microspheres were prepared according to a procedure reported earlier.[24] DVB-55 (18.23 g) and AIBN (0.365 g) were added to acetonitrile (950 mL) in a 1 L Nalgene bottle. The bottle was shaken, closed tightly, and placed in the polymerization reactor[22] at room temperature. The temperature was then ramped according to the following profile: 25−60 °C over 1 h; 60−70 °C over 1 h and 40 min. Subsequently, the reaction temperature was held at 70 °C for 24 h. At the end of the reaction the microspheres were collected by vacuum filtration over a 0.2 μm Teflon membrane and washed three times with THF and once each with acetone and methanol. The microspheres were then dried at 40 °C in a vacuum oven for 3 days and stored in a desiccator. Typical yields are 40%.

Porous Poly(divinylbenzene-55) Microsphere Synthesis.[25] DVB-55 (18.23 g) and AIBN (0.365 g) were added to a mixture of acetonitrile (710 mL) and toluene (250 mL) in a 1 L Nalgene bottle, and the reaction was carried out as described above.

Typical Procedure for Maleic Acid Functionalization of Porous and Nonporous Poly(divinylbenzene-55) Microspheres. Porous poly(DVB55) microspheres (2.5 g) were suspended in MEK (40 mL) in a two-neck, jacketed round-bottom flask, using a magnetic stir bar. The temperature of the system was increased to 65 °C, and an excess of maleic acid (MA, 1.2 g) was added. After the system was allowed to mix for 5 min to ensure complete dissolution of the MA, AIBN (0.85 g) was added, and the reaction continued for 24 h. Following the reaction, microspheres were collected by filtration, resuspended in MEK, and left to soak overnight. This collection and resuspension procedure was repeated three times, and the washed microspheres were dried in a vacuum oven at 45 °C and stored in a desiccator (yield: 2.78 g). Diffuse reflectance FT-IR analysis shows the presence of both acid (s, 1731 cm^{-1}) and anhydride functionalities (s, 1786 cm^{-1}). The anhydride groups may be due to anhydride present in the maleic acid monomer or may have been generated during the drying of the particles.

Characterization. Microparticle diameters were measured by environmental scanning electron microscopy (ESEM) as well as by static light scattering using a Coulter LS 230 particle sizer. Chemical composition was monitored using a ThermoNicolet FTIR. ESEM samples were prepared by washing a sample of the capsules several times with distilled water to remove PVA and excess amine, depositing a drop of capsule suspension on a sample stub and gold-coating to 5 nm prior to imaging. Transmission electron microscopy was carried out on microtomed sections of capsules prepared according to the following method. The capsule slurries were first filtered to remove water and dried in air. The dried capsules were then crushed under liquid nitrogen and extracted with *p*-xylene to remove any residual isocyanate. The resulting wall fragments were collected by filtration and dried overnight at room temperature. The capsule fragments were then embedded in Spurr's epoxy resin, microtomed to 100 nm thickness, and mounted on 3 mm TEM grids.

Typical Encapsulation Procedures. (A) Poly(DVB-*alt*-MAn)-based microsphere systems. A solution of Mondur ML (0.24 g) dissolved in 2 mL of PrOAc was prepared in a 20 mL scintillation vial. 0.125 mL of this stock solution was combined with 0.125 mL of microsphere or microgel suspension in a 4 mL glass vial and shaken until well mixed. The aqueous phase consisting of 0.4% w/w PVA in 1 mL of distilled water was added, and the resulting two-phase system emulsified by shaking on a modified laboratory wrist shaker at 384 excursions per minute (epm) for 2.5 min. Subsequently, the rate of shaking was reduced to 215 epm, and TEPA (0.25 mL, 0.95 M in distilled water) was added by syringe over 30 s. After the amine addition the reaction was allowed to continue overnight.

(B) Poly(DVB55)-Based Microsphere Systems. A jacketed glass reactor (500 mL) fitted with four-prong stainless steel baffles (length 6 cm, width 1.1 cm) was charged with distilled water (150 g) and PVA (0.15 g). A six-bladed, 2 in. stainless steel stirrer was then inserted into the aqueous phase, and the reactor was closed with a three-neck glass lid. The mixture was stirred at 300 rpm for 15 min to ensure complete dissolution of the PVA. The temperature of the reaction was controlled at 70 °C using a circulating bath. Next, a suspension of microspheres (2.20 g) in a mixture of isocyanate (5.00 g) and *p*-xylene (43.20 g) was added to the reactor. The resulting two-phase system was allowed to emulsify for 10 min at 400 rpm. Following emulsification, the mixing speed was reduced to 250 rpm, and DETA (5.00 g dissolved in a mixture of 0.05 g of PVA in 50 g of distilled water) was added dropwise to the oil-in-water emulsion over about 10 min. After the amine addition the reaction was allowed to continue for 4 h. The mixture was then transferred to a separatory funnel (1 L) and washed three times with distilled water. Samples of the washed capsules were taken and stored in glass scintillation vials. Conversion to polyurea was typically 25−30%.

Fill Release Measurements. Fill release was measured gravimetrically from samples in aluminum weigh dishes stored at room temperature or at 50 °C. Aluminum weigh dishes were prepared for release samples by soaking in Na_2CO_3 solution (~2% w/w) for several hours. After treatment, the aluminum dishes were rinsed three times with distilled water and left to dry for several days. This procedure etches the surface of the aluminum and allows better wetting by the aqueous sample. About 0.5 mL of representative aqueous dispersions of capsules was transferred to a treated dish. Weight loss measurements were carried out in triplicate.

Weight losses were recorded initially every half-hour and later on a daily or weekly basis as appropriate. Room temperature samples were stored uncovered in a fumehood for the duration of the release test. 50 °C samples were stored in an oven set to 50 ± 1 °C.

STXM Measurement and Analysis. Composite tectocapsules were prepared for STXM by first crushing the capsules under liquid nitrogen. The resulting capsule fragments were washed with *p*-xylene on a filter, dried, and embedded in an

aliphatic epoxy resin consisting solely of equimolar amounts of trimethylolpropane triglycidyl ether and 4,4′-methylenebis-(2-methylcyclohexylamine).[26] After room temperature cure for 3 days, the sample was microtomed to a thickness of 100 nm. The polymer STXM[27] on beamline 5.3.2[28] at the Advance Light Source (Berkeley, CA) was used for these analyses. Image sequences were converted to chemical component maps using pixel-by-pixel curve fitting.

Results and Discussion

This work explores using porous microspheres embedded across otherwise impermeable polyurea capsule walls as fill release control devices. First, we used easily prepared poly(divinylbenzene-*alt*-maleic anhydride) microspheres and microgels to study the interfacial assembly and fixation of such polar particles in the presence of isocyanates. Second, we prepared porous and nonporous poly(divinylbenzene-55) microspheres and functionalized their surfaces with maleic acid to enable similar interfacial assembly of these release control microspheres. Here, we studied morphology and fill release profiles, looking for evidence of through-microsphere fill release. Third, we used scanning transmission X-ray spectromicroscopy (STXM) to study the chemical composition of some of these tectocapsules at high spatial and chemical resolution.

Composite Capsules Containing Poly(divinylbenzene-55-*alt*-maleic anhydride) Microspheres and Microgels. Monodisperse poly(DVB55-*alt*-MAn) microspheres and two types of poly(DVB-*alt*-MAn) microgels were incorporated into interfacial polyurea capsule walls. These three types of particles match those used recently to form tectocapsules in the absence of polyurea.[7,8] Their preparation by precipitation polymerization ensures that their surfaces are free of added surfactant and/or stabilizer that might interfere with their interfacial activity.

Composite tectocapsules containing these poly(DVB-*alt*-MAn) particles were prepared by shaking glass vials containing isocyanates and microparticles in the organic phase as well as a 4-fold excess of aqueous phase containing poly(vinyl alcohol) (PVA). During this emulsification process, many of the microparticles self-assembled at the oil−water interface. While shaking, an aqueous polyamine solution was added by syringe to both covalently cross-link the microspheres and commence polyurea wall formation. Some ionic interactions are also expected to occur between the acid groups of the microspheres/microgels and the amine groups.

Propyl acetate (PrOAc) was used as core solvent for the model encapsulations of all three poly(DVB-*alt*-MAn) microspheres and microgels. In addition, a 50/50 (v/v) PrOAc/*p*-xylene mixture, while unable to disperse either of the microgels, was used as core solvent for the encapsulation of the poly(DVB55-*alt*-MAn) microspheres.

Propyl Acetate/*p*-Xylene Mixed Core Solvent. Stable composite capsules were formed from poly-(DVB55-*alt*-MAn) microspheres using the PrOAc/*p*-xylene mixed core solvent. Transmission (TEM, not shown) and environmental scanning electron microscope images (ESEM, Figure 2) of the resulting composite tectocapsules showed the microspheres just piercing the outer polyurea membrane, suggesting that the particles assembled at the interface prior to the bulk of polyurea wall formation, which occurs mainly after amine is added to the system. This is consistent with the self-assembly of microspheres and microgels prior to amine addition, as observed earlier in absence of polyurea.[7,8]

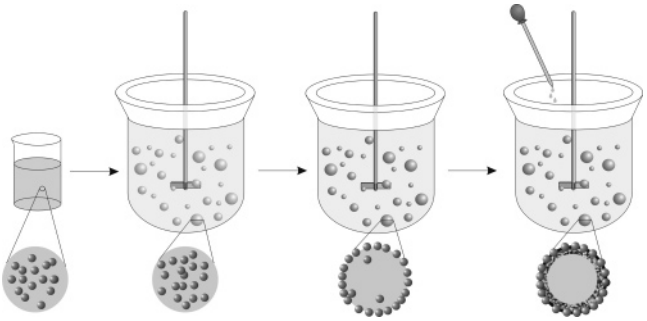

Figure 1. Composite tectocapsules formed by self-assembly of porous amphiphilic microspheres at the oil−water interface, followed by embedding in an impermeable polyurea film formed between oil-soluble isocyanates and added amines.

These composite capsules retain their fill for several days, an order of magnitude longer than those prepared with 100% PrOAc as the core solvent described below. This is attributed to a denser, less permeable polyurea membrane formed in the presence of 50% xylene. Still, the presence of 50% MEK ensures some permeability of the wall and thus should enable slow fill release by diffusion through the polyurea wall.

Propyl Acetate (PrAc) as Single Core Solvent. Composite tectocapsules involving all three poly(DVB-*alt*-MAn) microspheres and microgels were prepared using PrOAc as the core solvent. All three composite tectocapsule systems released their fill within hours of removal from the aqueous phase. Fill release may happen by diffusion through the highly permeable polyurea walls formed in a polar core solvent[1] as well as by diffusion through the microgels located at the interface. The resultant capsule systems were studied by optical microscopy (Figure 3) as well as by both ESEM (Figure 4) and TEM (Figure 5).

The optical microscope images (Figure 3) show spherical capsules. The microspheres and microgels are too small to be resolved by this technique.

The ESEM images clearly show the poly(DVB55-*alt*-MAn) microspheres and the large poly(DVB5-*alt*-MAn) microgels protruding through the polyurea wall (Figure 4D,F). Although the small poly(DVB55-*alt*-MAn) microgels are not clearly visible in the ESEM image (Figure 4E), the hexagonal close packing of the other particles strongly suggests that they assemble at the interface prior to amine addition. Amine addition then leads to rapid interfacial polyurea formation, with fixation of the microparticle arrays at the interface.

TEM images of the cross section of collapsed composite capsules embedded in Spurr's[29] epoxy resin are shown in Figure 5. These images indicate that the microspheres and microgels are predominantly located at the edge of the cross sections, which corresponds to the outside of the capsules, located at the oil−water interface during synthesis.

Composite Tectocapsules with Porous Poly(divinylbenzene-55) Precipitation Microspheres. The poly(DVB-*alt*-MAn) microspheres and microgels described above are good model particles for developing composite tectocapsules. However, they are not porous and too polar to be dispersed in core solvents containing 50% xylene or more. As described above, the proposed separation of wall formation from release control requires a combination of porous amphiphilic microspheres, with nonpolar core solvents such as xylene that form impermeable polyurea walls.[1] To address these

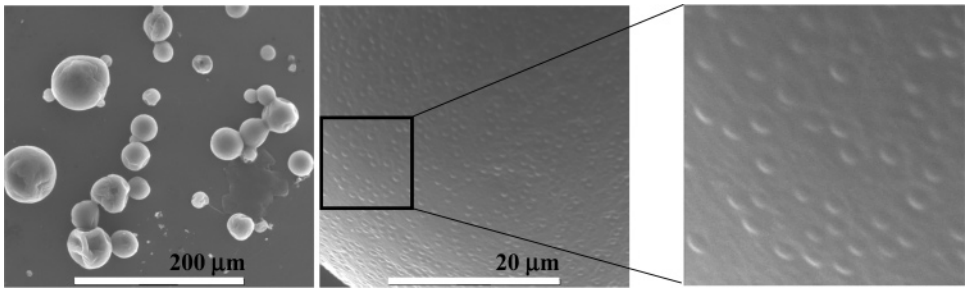

Figure 2. Environmental scanning electron micrographs of composite tectocapsules prepared with 50/50 (v/v) PrOAc/*p*-xylene as mixed core solvent. The tops of poly(DVB55-*alt*-MAn) microspheres can be seen protruding from the polyurea wall.

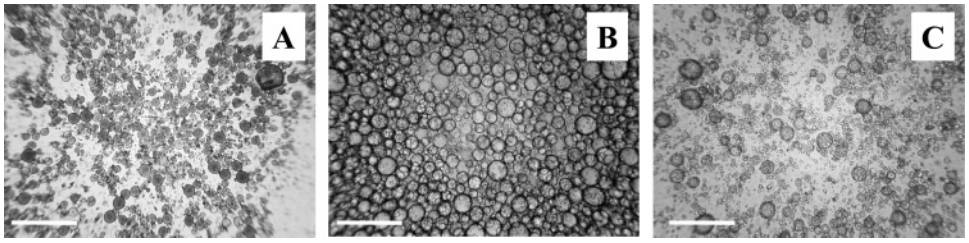

Figure 3. Optical micrographs of wet composite propyl acetate-filled tectocapsules made with poly(DVB55-*alt*-MAn) microspheres (A) or microgels (B) and with poly(DVB5-*alt*-MAn) microgels (C). The scale bar is approximately 250 μm.

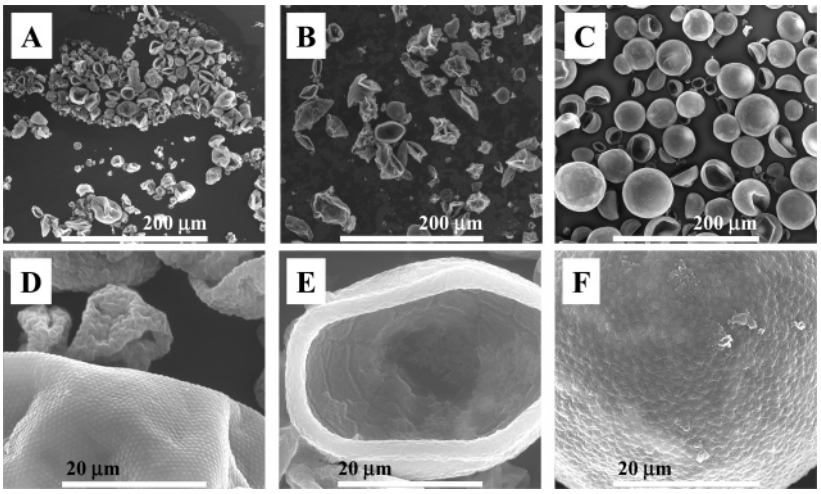

Figure 4. Environmental scanning electron micrographs (ESEM) of dry tectocapsules prepared with poly(DVB55-*alt*-MAn) microspheres (A, D) and microgels (B, E) and poly(DVB5-*alt*-MAn) microgels (C, F).

issues, we prepared nonporous and porous poly(DVB55) microspheres by precipitation polymerization of divinylbenzene-55 in acetonitrile and in a mixture of acetonitrile and toluene, respectively.[25] These microspheres were subsequently surface-functionalized by radical grafting of maleic acid onto the residual double bonds in the presence of AIBN to ensure their assembly at the oil−water interface.

Optical microscopy of polyurea capsules prepared with both functionalized and nonfunctionalized porous poly(DVB55) microspheres revealed very different interfacial properties (Figure 6). Capsules prepared with nonfunctionalized microspheres featured distinct opaque patches (Figure 6A), while the capsules formed with maleic acid functionalized microspheres showed less internal contrast, suggesting a more even distribution of microspheres within the capsule wall (Figure 6B). The inset in Figure 6B is an expanded view of the microcapsule contained in the box on the main image and clearly shows microspheres in the capsular wall.

ESEM images of the tectocapsules prepared with nonfunctionalized porous microspheres showed smooth outer surfaces, suggesting that these microspheres remained in the core of the microcapsules (Figure 7A,C). In contrast, the maleic acid functionalized microspheres clearly breach the polyurea capsule wall (Figure 7B,D), suggesting that they self-assembled at the oil−water interface prior to polyurea formation. Representative TEM images of wall fragments similarly show the maleic acid functionalized microspheres breaching the polyurea capsule wall (Figure 8B), while the nonfunctionalized microspheres stay in the interior of the polyurea capsules (Figure 8A). The nonfunctionalized microspheres also appear fuzzy, suggesting they are coated with polyurea.

Fill Release from Composite Tectocapsules. Release of xylenes from three different types of composite tectocapsules was monitored gravimetrically, both at room temperature and at 50 °C. Release data shown (Figure 9) represent the average of three different release samples and are normalized to the initial weight of the samples.

At room temperature, the tectocapsules containing the nonfunctionalized poly(DVB55) microspheres show

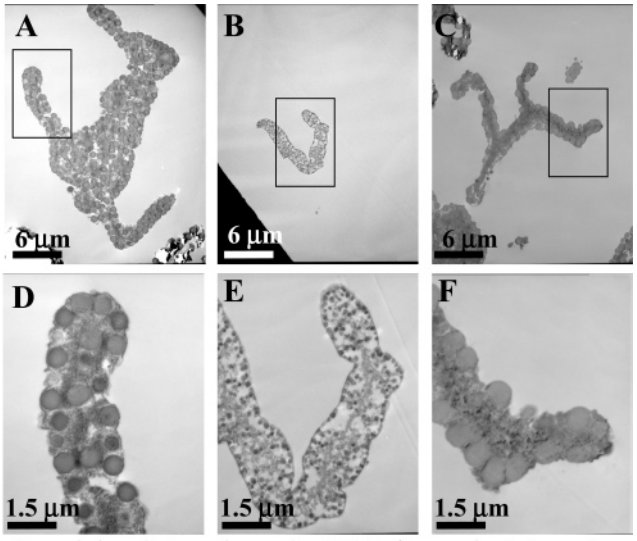

Figure 5. Transmission electron micrographs (TEM) of composite tectocapsules prepared with (DVB55-*alt*-MAn) microspheres (A, D) and microgels (B, E) and poly(DVB5-*alt*-MAn) microgels (C, F). embedded in Spurr's resin and sectioned. The box shown on the upper images indicates the field of view for the lower images.

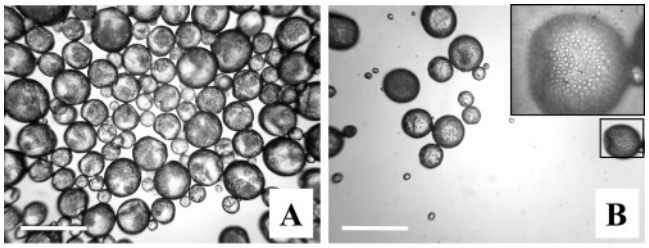

Figure 6. Optical micrographs of wet composite tectocapsules containing nonfunctionalized (A) and maleic acid functionalized (B) porous poly(DVB55) microspheres. The inset in image B is an expanded view of the capsule in the box on the main image. Scale bar is 100 μm.

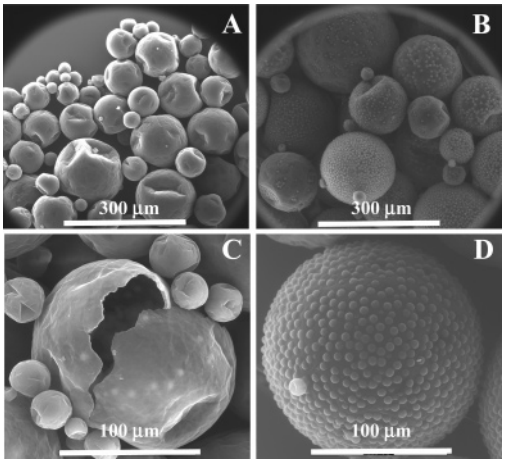

Figure 7. Environmental scanning electron micrographs (ESEM) of composite tectocapsules made with nonfunctionalized (A, C) and maleic acid functionalized (B, D) porous poly(DVB55) microspheres.

little mass loss until 20 days at which point mass decreases rapidly. This discontinuous release profile is similar to those seen previously for polyurea capsules containing xylenes as fill.[1] It is attributed to the superposition of two release mechanisms: very slow, diffusion-controlled release through intact capsule walls,

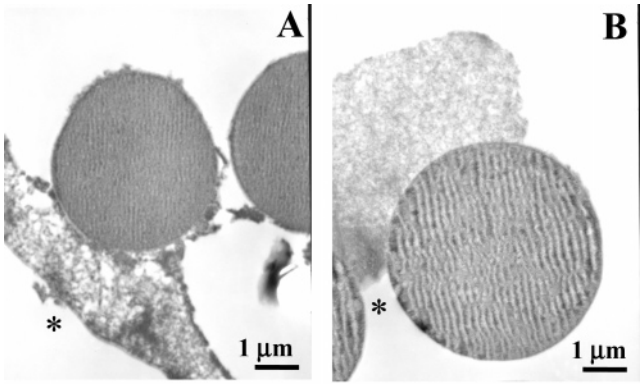

Figure 8. Transmission electron micrographs of sections of composite tectocapsules made with nonfunctionalized (A) and maleic acid functionalized (B) porous poly(DVB55) microspheres, embedded in Spurr's resin. The asterix indicates the outer, aqueous side of the capsule wall.

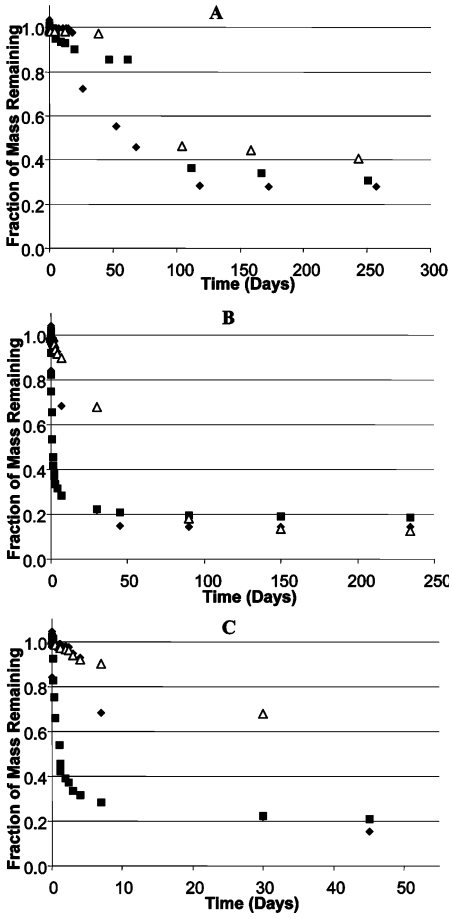

Figure 9. Release curves at room temperature (A) and 50 °C (B, C) for tectocapsules prepared with nonfunctionalized (◆) and functionalized (■, 2.2 g particles; △, 0.2 g) porous poly(DVB) precipitation microspheres. (C) is an expansion of the 0−50 days region of (B).

and a much faster wall strain-induced release from capsules that adhere to each other.[1] A similar stepwise release profile is observed at 50 °C. In these capsules, the nonfunctionalized microspheres do not play a role in wall formation and hence do not influence the release process.

Tectocapsules prepared with porous poly(DVB55) microspheres functionalized with maleic anhydride showed different release profiles depending upon microsphere loading. Capsules prepared with 0.2 and 2.2

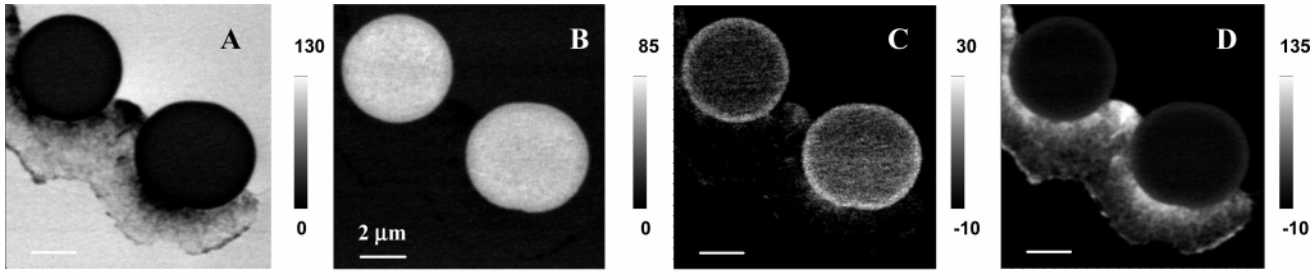

Figure 10. STXM individual component maps of a wall fragment of a composite tectocapsule having porous maleic acid functionalized microspheres embedded in the polyurea capsule wall: (A) epoxy, (B) poly(divinylbenzene-55), (C) succinic acid; (D) polyurea matrix. The intensity in the images is the thickness (in nm) of each component at the given point in the sample.

g microspheres both show evidence for significant diffusion release during the first 40−60 days. These initial release rates are much faster than those seen in polyurea capsules not containing interfacial microspheres and appear to scale with microsphere loading. Following this initial, diffusion release period, both capsule samples show rapid weight loss reminiscent of wall strain-induced release. At 50 °C, these two capsules show rapid, near-linear release over approximately 100 and 10 days, again in agreement with their different microsphere loading. At this higher temperature there is no evidence of discontinuous release attributable to wall strain-induced release.

After approximately 120 days at room temperature, release from all three types of capsules slows dramatically. This could be due to the end of wall strain-induced release and a return to diffusion-controlled release. Alternatively, it may be due to slow release from capsules containing few microspheres or having stronger polyurea walls.

These results show that interfacially active, porous microspheres can strongly enhance the release of xylene from polyurea capsules. At the same time, they raise several new questions: (1) Is the enhanced release due to a mechanical weakening of the capsule walls, leading to more pronounced strain-induced release? (2) Is the enhanced release from tectocapsules due to diffusion through the microsphere pores or due to diffusion through the microsphere−polyurea interface? (3) What is the nature of the microsphere−polyurea interface, and does polyurea form within the porous microspheres? No cracks associated with the polyurea−microsphere interfaces were seen in ESEM images, leading us to discount a mechanical weakening of the embedded microspheres.

The microsphere−polyurea interface is likely composed of a finite hydrophilic gel layer. The poly(divinylbenzene-55) microspheres are known to have a ∼50 nm thick surface layer of lightly cross-linked poly(divinylbenzene).[30,31] Functionalization with maleic acid would convert this organogel layer into a polar layer containing a mixture of succinic acid as well as some succinic anhydride groups formed by dehydration during microsphere workup. Reaction with polyamine during the capsule formation would lead to a combination of electrostatic and covalent bonding and form an amphiphilic interfacial film. During release, xylenes could diffuse through this lightly cross-linked, amphiphilic interfacial layer between microspheres and impermeable polyurea. Therefore, while the release rates appear to scale with microsphere loading, at the present time we cannot distinguish between through-pore and interfacial layer release of xylenes. This issue will be addressed in future work based on a series of suspension polymer microspheres that do not have this gel surface layer but have porosity controllable over a wide range of pore diameters.

In the final section below we map the chemical distribution in the composite tectocapsules, in an attempt to answer the third question.

STXM Analysis of Composite Tectocapsules. While electron microscopy offers superb spatial resolution and good contrast, it cannot provide the chemical composition distribution of these nanocomposites prepared with the succinic acid functionalized porous poly(DVB55) microspheres. To this end we used scanning transmission X-ray spectromicroscopy (STXM),[32] a technique based on near-edge X-ray absorption spectroscopy that combines high spatial and high chemical resolution. We have previously used STXM to study core−shell microspheres.[33] The technique involves raster-scanning a ∼130 nm thin microtome section of the sample through the ∼50 nm wide focal point of a synchrotron-derived, monochromatic X-ray beam. Successive images are measured using a sequence of highly resolved X-ray photon energies covering the C 1s spectral region from 280 to 320 eV. The resulting image stack can be viewed as a set of sample images taken at different X-ray energies or as a set of X-ray absorption spectra taken at each raster pixel.

Past analyses of divinylbenzene methacrylate core−shell particles taught us that STXM can distinguish easily between aromatic bands at 285 eV and carbonyl bands at about 288 eV and even between Spur epoxy carbonyl and methacrylic carbonyl bands at 288.2 and 288.4 eV, respectively.[33] The challenge in the present system was to distinguish the succinic acid groups at the microsphere−polyurea interface from the strong polyurea carbonyl signal, both absorbing around 288 eV. Replacing the commonly used four-component Spur embedding resin[31] with a new purely aliphatic two-component system helped by removing any interfering carbonyl and aromatic signals arising from the embedding resin.[26]

Maps of the distributions of the epoxy, polyurea, poly(divinylbenzene-55), and succinic acid/anhydride were derived from the image sequence (Figure 10). The gray scale in these maps is thickness in nanometers. To depict the spatial relationship of these species, we have combined the poly(divinylbenzene-55), polyurea, and succinic acid/anhydride maps by assigning 8-bit red, green, and blue scales to each, respectively. Summing leads to a color-coded composite map that depicts the distribution of all three species within the sample region imaged (Figure 11).

The STXM results indicate that polyurea is mostly excluded from the microspheres pores, although there does appear to be a small amount of polyurea penetra-

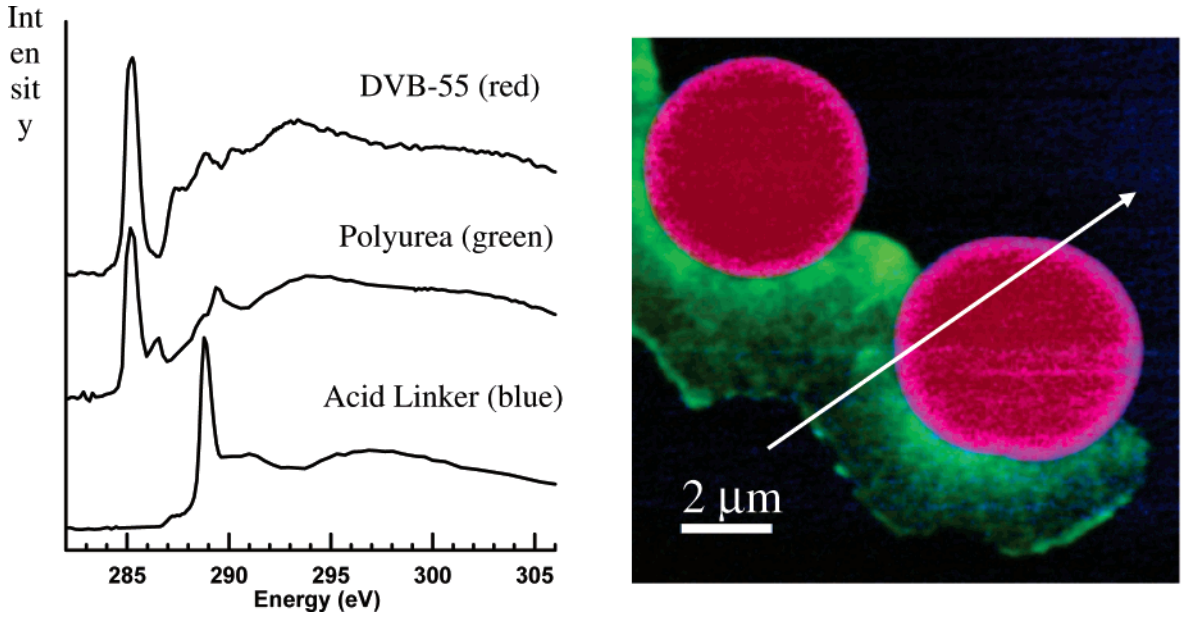

Figure 11. STXM composite component map and the corresponding X-ray spectra, with the DVB55, polyurea and acid linker components shown quantitatively in red, green, and blue, respectively.

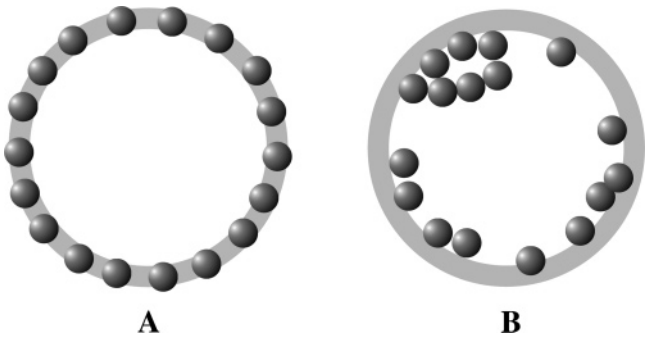

Figure 12. Two types of composite capsules that result from encapsulations in the presence of functionalized (A) or nonfunctionalized (B) poly(divinylbenzene) microspheres.

tion in the outer 10% of the porous poly(DVB-55) microspheres (Figure 10D). Since both the isocyanates and amines used are smaller than the pore exclusion molecular weight of 500 Da, the absence of polyurea from the pores is attributed to slow diffusion of the wall former, especially amine, through the pores. Any oligomers formed would be too large to enter the pores. Second, no polyurea could be seen on the outer surface of the microspheres, once again suggesting that the microspheres self-assemble at the interface prior to significant polyurea formation.

Summary and Conclusion

Shown here are new types of controlled release microcapsule, called composite tectocapules. They incorporate porous, interfacially active microspheres embedded in nonpermeable polyurea walls (Figure 12A) and permit controlled out-diffusion through or around the microspheres. These composite tectocapsules exhibit enhanced diffusion release and partial suppression of wall stress-induced release. Release rates scale with microsphere loading.

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