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Composite tectocapsules via the self-assembly of functionalized poly(divinylbenzene) microspheres*

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Abstract: Poly(divinylbenzene-55) [poly(DVB-55] microspheres were used as building blocks to form polymer capsule walls consisting of inter-connected microspheres. The microspheres had to be surface-functionalized with maleic acid to facilitate their interfacial assembly. In addition, porous and functionalized poly(DVB-55) microspheres were embedded across interfacial polyurea capsule membranes to form composite tectocapsules where release of core materials is designed to occur through the microsphere pores, rather than by conventional wall diffusion. Electron microscopy and X-ray spectromicroscopy were used to characterize the wall compositions, and release data are presented to illustrate the role of microspheres acting as release portals.

INTRODUCTION

Solid particles assembled at an oil–water interface were first observed independently by Ramsden [1] and Pickering [2], who were interested in preparing colloidally stable pesticide formulations without using soaps. Pickering noted that reducing the particle size increased the stability of his emulsions. He further noted that this only applied to materials that were insoluble in water, but were "wetted more easily by water than by oil" since materials more easily wetted by oil were simply abstracted from the water by the oil, causing coloration of the oil and not emulsification. Stabilization of the oil droplets by the particles was attributed to the fact that particles protruding from the droplet's surface prevented droplet–droplet contact and therefore coalescence. Later, Bancroft [3] developed a rule, which stated that the phase in which the particles were more soluble will become the external or continuous phase. In 1923, Hildebrand's group [4] confirmed this theory by observing mixtures of benzene in water stabilized with lampblack** [5] and stated that "…the powder must collect at the interface in order to be effective" and "…this will occur only when the solid is wetted by both liquids, with a finite angle of contact of the interface with the solid."

Since that time, the ability of fine particles to assemble at the oil–water interface has been exploited for many applications in addition to emulsion stabilization [6,7] such as extraction of fine particles from aqueous suspensions [8,9] and formation of 2-dimensional colloidal crystals [10,11]. Most recently, there has been increased interest in using such assembled colloids to form microcapsules for controlled delivery applications. For example, Caruso et al. [12,13] used layer-by-layer (LbL) assembly of charged SiO_2 particles and polymers on the surface of charged polystyrene latex particles.

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**Lampblack is a finely divided form of carbon that was produced by burning organic compounds in insufficient oxygen. It was typically used as a pigment and filler [5].

Subsequent dissolution of the core template transformed these core-shell composite particles into hollow microspheres. Velev et al. [14–16] reported the multistep ionic assembly of charged polymer particles at the oil–water interface, resulting in capsular structures without the need for a sacrificial core. In addition, microcapsules called colloidosomes [17] have been reported where colloidal particles are assembled at an oil–water interface to form walls with defined porosity.

Our interest in particle assembly at the oil–water interface stemmed from the desire to develop a microcapsule where the rate of release of liquids from the capsule core is independent of the shell polymer.

In current microcapsule diffusion release systems, control over the rate of diffusion of core material is limited to the parameters of the shell material that can be altered during wall formation, such as thickness, porosity, and chemical composition. However, these parameters are often dependent on the environment in which the polymer forms, and are therefore different for every core material used [18]. This dependence on core solvent can be a problem since each new fill may require reoptimization of the capsule wall.

One way to overcome this problem would be to develop a model for solvency effects on release and then, using a mixture of active and solvent, design the core solvent such that the desired release could be achieved. Another way to gain complete control over release from a capsule is to independently prepare the channels through which release occurs. We approach this by introducing preformed polymer spheres into the capsular wall. By designing a system where release occurs only through the polymer spheres, release control may be achieved independently of the core solvent environment (Fig. 1).

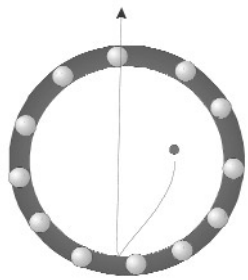


Fig. 1 Illustration of a composite capsule system where release occurs through the embedded spheres and not through the surrounding polymer matrix.

Such a release system would have a composite wall made of permeable polymer particles embedded in a nonpermeable structural polymer wall. Several factors must be considered when selecting microspheres for such a system: (1) the polarity for the microspheres must permit their self-assembly at the oil–water interface prior to formation of the polymer wall; (2) the microspheres must have pores that can function as release channels; and (3) the microspheres used must be commercially available or easily prepared.

TECTOCAPSULES

Before preparing such composite capsules, it was necessary to understand of how to control particle assembly at the oil–water interface. This led to the development of a family of highly porous microcapsules called "tectocapsules". Tectocapsule walls were prepared from poly(divinylbenzene-*alt*-maleic anhydride) [poly(DVB-*alt*-MAn)] microspheres that were partially hydrolyzed such that they carried some maleic acid groups on the microsphere surface. The microspheres were prepared by precipitation copolymerization of stoichiometric amounts of divinylbenzene-55 (DVB-55) and maleic anhydride in 40 % MEK/heptane mixtures at 2 % total monomer loading, to give poly(DVB-55-*alt*-MAn) microspheres of 550 nm diameter [19]. The maleic acid groups impart sufficient polarity for self-assembly of

the microspheres, whereas the residual maleic anhydride allowed for the microspheres to be linked together using polyamines.

Tectocapsules were prepared by suspending an organic phase, comprised of microspheres and a water immiscible solvent, in a continuous aqueous phase containing poly(vinyl alcohol) as a stabilizer. After self-assembly of the microspheres at the oil–water interface, an aqueous solution of poly(ethylenimine) was added via syringe, resulting in the capsular structures shown in Fig. 2 below.

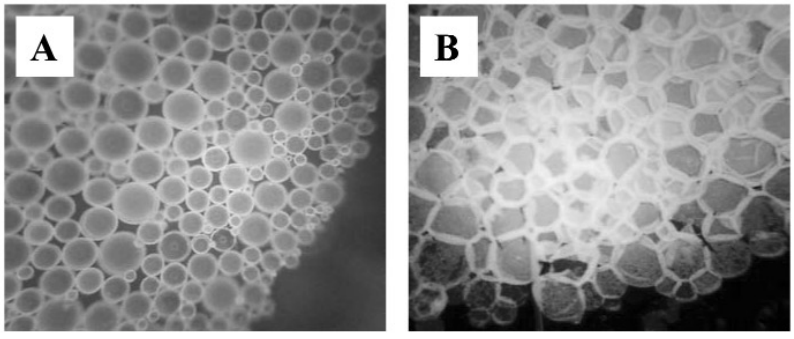
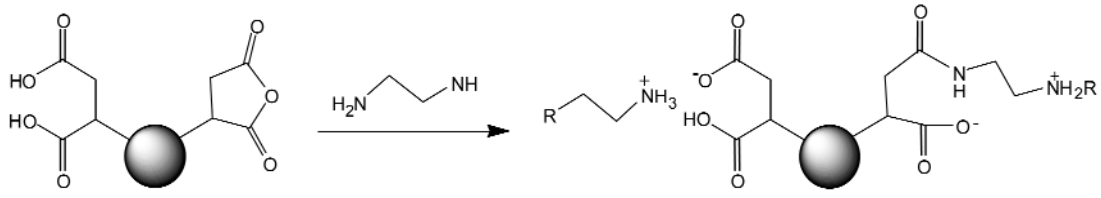


Fig. 2 Optical micrographs of wet (A) and dry (B) tectocapsules.

MECHANISM OF TECTOCAPSULE FORMATION

Several factors were shown to affect the assembly and cross-linking of the microspheres at the interface, including amine molecular weight, core solvent, cross-link density of the microspheres, microsphere loading in the organic phase, and microsphere chemistry or polarity [20–23]. Most importantly, it was determined that acid functionalities arising from partial hydrolysis of the anhydride groups on the microsphere surface, make the microspheres polar enough to self-assemble at the oil–water interface prior to addition of amine to the system. Hence, amine addition forms two different inter-microsphere linkages, covalent linkages via ring opening of the anhydride moiety and ionic linkages resulting from neutralization of the acid groups by the amine. These linkages are shown below in Scheme 1.



Scheme 1 Linkage reactions of amines with acid and anhydride groups present in the poly(DVB-55-*alt*-MAn) (DVB-*alt*-MAn/MA) microgels and microspheres. L. M. Croll et al. *Langmuir*, in press [21]. Copyright © 2003 American Chemical Society.

COMPOSITE TECTOCAPSULES

Following the above study of the basic tectocapsules, a range of composite materials were designed that include microspheres embedded in polyurea capsule walls. Two of these designs will be discussed below.

First, we used the same poly(DVB-*alt*-MAn) microspheres described above for the formation of tectocapsules, to study the interfacial assembly and fixation of such polar particles in presence of isocyanates. This allowed us to evaluate if the presence of particles at the oil–water interface would disrupt polyurea wall formation or vice versa.

Second, we prepared porous and nonporous poly(DVB-55) microspheres, and functionalized their surfaces with maleic acid to enable similar interfacial assembly of these microspheres as was observed for the poly(DVB-*alt*-MAn). Here, we studied morphology and fill release profiles, looking for evidence of through-microsphere fill release. Finally, these composite tectocapsules were characterized by 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(DVB-55-*alt*-MAN) MICROSPHERES

Composite tectocapsules containing monodisperse poly(DVB-55-*alt*-MAn) particles were prepared by shaking glass vials containing isocyanates and microparticles in a 50/50 (v/v) mixture of PrOAc and *p*-xylene, as well as a four-fold excess of aqueous phase containing polyvinylalcohol (PVA). During this emulsification process, many of the microspheres 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 and the amine groups.

Environmental scanning electron microscope images (ESEM, Fig. 3) 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. These composite capsules retain their fill for several days. In this case, the microspheres are nonporous, however, the presence of 50 % PrOAc in the core ensures some permeability of the polyurea wall, therefore slow fill release occurs by diffusion through the polyurea wall rather than through the microspheres.

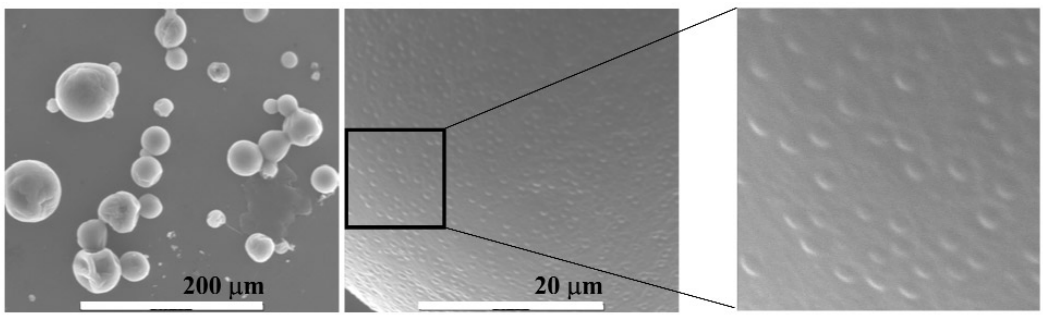


Fig. 3 Scanning transmission electron micrographs of composite tectocapsules prepared with 50/50 (v/v) PrOAc/*p*-xylene as mixed core solvent. The tops of poly(DVB-55-*alt*-MAn) microspheres can be seen protruding from the polyurea wall. L. M. Croll et al., submitted for publication in *Macromolecules.* Copyright © 2003 American Chemical Society [23].

COMPOSITE TECTOCAPSULES WITH POROUS POLY(DVB-55) PRECIPITATION MICROSPHERES

The poly(DVB-55-*alt*-MAn) microspheres described above are good model particles for developing tectocapsules. However, they are not porous. The proposed separation of wall formation from release control requires a combination of porous microspheres, with nonpolar core solvents such as xylene that form impermeable polyurea walls [18]. We accordingly prepared nonporous and porous poly(DVB-55) microspheres by precipitation polymerization of DVB-55 in acetonitrile, and in a mixture of acetonitrile and toluene, respectively. These microspheres were subsequently surface-functionalized by radical reaction with maleic acid in order to facilitate their assembly at the oil–water interface.

Three types of polyurea composite tectocapsules were prepared, containing nonfunctionalized, as well as both porous and nonporous functionalized DVB-55 microspheres. All three capsules were pre-

pared using Mondur MRS, an aromatic isocyanate, and tetraethylenepentamine (TEPA). They were studied by optical and environmental scanning electron microscopies (OM and ESEM, respectively).

ESEM images clearly show the need for maleic acid functionalization. Tectocapsules prepared with nonfunctionalized microspheres have a smooth outer surface (Figs. 4A and 4C), indicating the microspheres are buried below the outer, release-controlling capsule surface. In contrast, the maleic acid-functionalized microspheres breach the outer polyurea wall, suggesting that they self-assembled at the interface prior to formation of the polyurea wall.

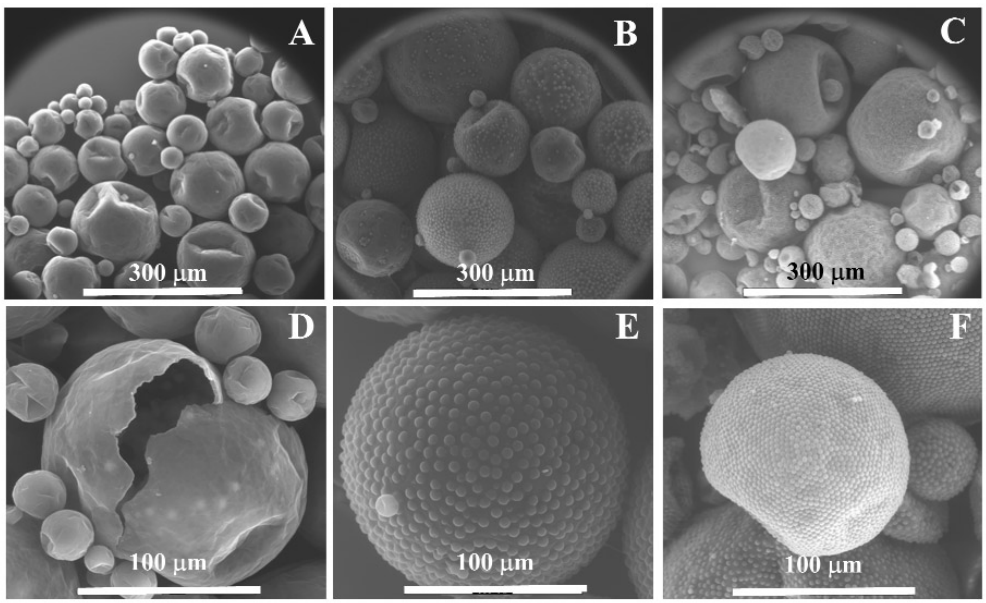


Fig. 4 Environmental scanning electron micrographs (ESEM) of composite tectocapsules made with nonfunctionalized porous poly(DVB-55) microspheres (A, D), as well as maleic acid-functionalized porous (B, E), and nonporous (C,F) microspheres. L. M. Croll, A, B, D, and E submitted for publication in *Macromolecules.* Copyright © 2003 American Chemical Society [23].

RELEASE OF *P*-XYLENE FROM COMPOSITE TECTOCAPSULES

Release of xylenes from three different types of composite tectocapsules was monitored gravimetrically at room temperature. Release data shown (Fig. 5) 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(DVB-55) microspheres show little mass loss until 20 days, at which point mass decreases rapidly. This step-wise release profile is similar to release profiles seen in traditional polyurea capsules containing xylenes as fill, which was expected since the microspheres are contained within the core of the capsules and therefore, do not affect the capsule wall. This step-wise release behavior has been attributed to the superposition of two release mechanisms: slow, diffusion-controlled release through intact capsule walls, and a much faster wall strain-induced release from capsules that adhere to each other [18].

Release from the microcapsules prepared with maleic acid-functionalized microspheres differs from those described above. The microcapsules with porous microspheres breaching the polyurea membrane show much faster release of xylene over the first 50 days, after which a period of rapid weight loss reminiscent of wall-strain induced release is seen (not shown). Interestingly, release from the capsules prepared with functionalized nonporous microspheres release much faster than either of the other composite tectocapsules systems. These capsules empty completely within a few hours. This rapid re-

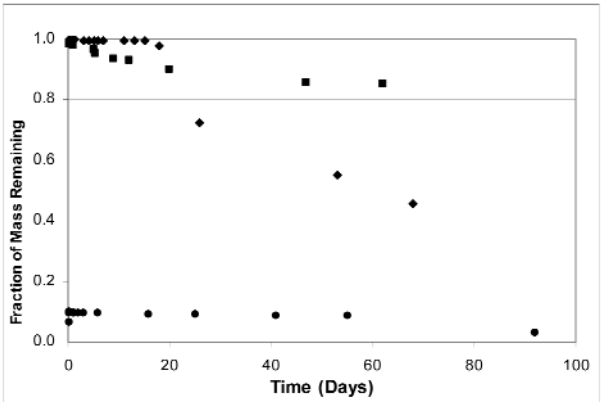


Fig. 5 Release curves at room temperature for tectocapsules prepared with nonfunctionalized (◆), functionalized porous (■), and nonporous (●) poly(DVB) precipitation microspheres.

lease suggests that the microspheres-polyurea interface contributes to release from composite microcapsules and that porous microspheres are perhaps better anchored in the surrounding polyurea.

These results show that interfacially active, porous microspheres can alter xylene release from polyurea capsules. However it was not possible to determine if xylene release actually occurred through the pores of the microspheres embedded in the polyurea wall. One step toward determining if release through the microspheres pores was possible was to determine if polyurea had formed in those pores. If polyurea was found blocking the pores it could be assumed that the pores were no longer available to function as release channels.

STXM ANALYSIS OF COMPOSITE TECTOCAPSULES

Chemical characterization of the composite membranes was carried out using STXM [24], an emerging technique that allows for chemical speciation of nanoscale materials. STXM is based on near-edge X-ray absorption fine structure (NEXAFS). Images of the cross-section of materials are created by raster scanning the X-ray beam, focused to ~50 nm, across the microtomed sample, and measuring energy-selective X-ray absorption using an X-ray detector located behind the sample. Images obtained at many X-ray energies can be combined to give an image stack, having a NEXAFS spectrum at each pixel of the image.

Capsules were crushed under liquid nitrogen, washed with xylenes, dried and embedded in epoxy resin*. The cured resin containing the tectocapsule fragments was then microtomed to give 200 nm thick sections that were supported on copper grids.

Figure 6 shows an STXM image of a wall fragment of composite tectocapsule taken at 285 eV. The regions in the boxes correspond to the areas from which the spectra on the right were taken. Spectrum A corresponds to the polyurea wall of the tectocapsules and has two predominant peaks: one at ~289 eV resulting from the π to π^* transition of the urea carbonyl and a second one at ~285 eV, which can be attributed to the π to π^* transition of the phenyl rings of the polyurea.

The NEXAFS spectrum taken from the region of the poly(DVB-55) microspheres shows no signals attributable to polyurea, but only a single absorption peak at ~285 eV.

These STXM results indicate that polyurea is excluded from the microsphere pores, within the detection limit of about 10 %. 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 diffu-

*Spurr's resin is a common embedding medium, comprised of: nonenyl succinic anhydride (NSA), the diglycidyl ether of poly(propylene glycol) (DER 736), vinylcyclohexene dioxide (ERL 4206), and 2-dimethylaminoethanol (DMAE).

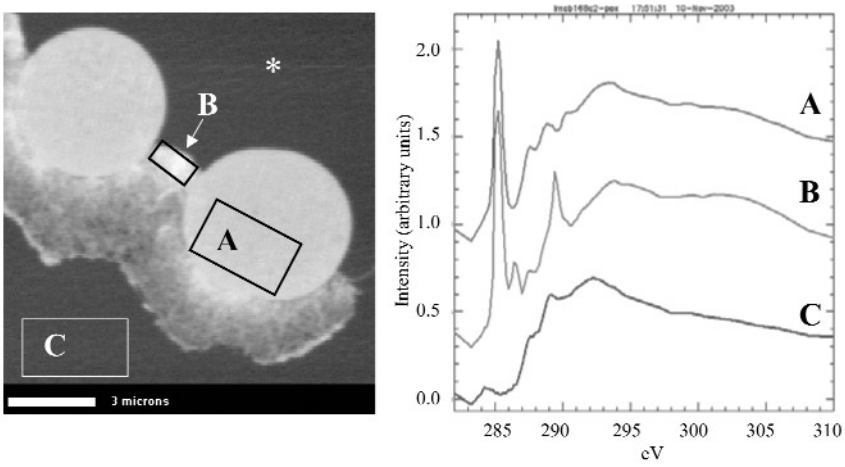


Fig. 6 STXM image of the cross-section of a composite tectocapsules prepared with porous maleic acid-functionalized poly(DVB-55) microspheres. Note: * indicates the outside of the microcapsule, in contact with the aqueous phase during formation, and the boxes indicate the regions from which the spectra at the right were extracted.

sion of the wall former, especially amine, through the pores. Any polyurea oligomers formed would be too large to enter the pores.

CONCLUSIONS

This paper summarizes the development of two new types of microcapsule: highly porous tectocapsules with walls comprised of self-assembled poly(DVB-55-*alt*-MAn) microspheres, and composite microcapsules, which incorporate self-assembled microsphere arrays into a dense polyurea capsule wall. It has been shown that porous microspheres breaching this polyurea wall show a more controlled release of core solvent at room temperature compared to systems where the microspheres are simply encapsulated within the core. STXM analysis of the composite tectocapsules revealed that polyurea is excluded from the microsphere pores. Therefore, release is proposed to occur via two possible routes: through the microcapsule pores and through the microsphere–polyurea interface.

EXPERIMENTAL

Materials

Diethylenetriamine (DETA, 99 %), divinylbenzene-55 (DVB-55, a commercial mixture of 55 % *meta* and *para*-divinylbenzene, with 45 % *meta* and *para*-ethylvinylbenzene), heptane (HPLC grade) methylene chloride (HPLC grade), methyl ethyl ketone (MEK, 2-butanone, HPLC grade) 4-methylstyrene (4-MeSt, 96 %), polyethylenimine (Mn ca. 1200, 50 % in water), polyethylenimine (Mn ca. 60 000, 50 % in water), PVA (80 % hydrolyzed, Mn ca. 9000), propyl acetate (99 %), TEPA (tech.), *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. 2,2′ Azobisisobutyronitrile (AIBN) was donated by DuPont Canada and was recrystallized from methylene chloride prior to use. Polyethylenimine (Mn ca. 9000, 30 % in water) was purchased from Polysciences, Inc. and was used without purification.

Poly(DVB-55-*alt*-MAn) microsphere synthesis

The microspheres were prepared according to a procedure reported earlier [19]. 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 AIBN (0.016 g). The vial was 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 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(DVB-55) microsphere synthesis

The microspheres were prepared according to a procedure reported earlier [25]. DVB-55 (18.23 g) and AIBN (0.365 g) were added to actonitrile (950 ml) in a 1 l Nalgene bottle. The bottle was shaken, closed tightly, and placed in the polymerization reactor at room temperature. The temperature was then ramped according to the following profile: 25 to 60 °C over 1 h, 60 °C to 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(DVB-55) microsphere synthesis

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 carried out as described above.

Typical procedure for maleic acid functionalization of porous and nonporous poly(DVB-55) microspheres

Porous poly(DVB-55) 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 FTIR 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 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.

*The polymerization reactor is a modified commercial hotdog roller. The temperature in the reactor can be controlled (±1 °C) and vials roll at a rate of approximately 5 vial rotations per minute.

Typical encapsulation procedures

Poly(DVB-55-alt-MAn)-based microsphere systems

A solution of Mondur ML (0.24 g) dissolved in 2 ml 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 not stirred until well mixed. The aqueous phase consisting of 0.4 w/w% PVA in 1 ml 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.

Poly(DVB-55)-based microsphere systems

A jacketed glass reactor (500 ml) fitted with 4-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″ 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 PVA in 50 g of distilled water) was added drop-wise 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 were 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 °C ± 1°.

STXM 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, embedded in an epoxy resin designed to contain no aromatic or carbonyl groups, and microtomed to a thickness of 200 nm. The Polymer STXM Beamline 5.3.2 at the ALS in Berkeley was used for these analyses.

ACKNOWLEDGMENTS

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