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Emulsion route in fabrication of micro and nanocontainers for biomimetic self-healing and self-protecting functional coatings

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Designing of novel self-healing materials possessing an active feedback on various destructive factors is one of most quickly developing areas in contemporary material engineering. Self-healing and self-protecting coatings represent one of particular classes of these materials that able on damage to recover their anticorrosive or antifouling function. Most established approach to impart to the coating this ability is nowadays the use of container-based structures when the protective agent trapped in containers is embedded in the coating matrix. There are different ways to produce containers for the further incorporation into coating but the role of emulsion route in the containers preparation is probably predominant. Herein, the contemporary achievements in the field of emulsion encapsulation are reviewed. Several types of containers for biomimetic functional coatings synthesized via emulsion as an initial system are presented based mainly on the earlier published and very recently obtained results of our research group. An overview is given of some interfacial physical and chemical methods utilized for the transformation of emulsion droplets into nano- or microscaled containers showing their specific advantages and drawbacks. Successful incorporation of containers in the diverse types of coatings showed is promising for novel materials production in many application fields.

1. Introduction

Human skin as well as the skin of animals has unique abilities to re-establish its integrity after damages by external impacts (self-healing) and deactivate many types of aggressive surface contaminations, first of all, microbial and environmental (self-protecting). Noteworthy that these abilities are always activated only on demand, being triggered by external factors such as integrity damage or contamination occurrence, thus making the corresponding functionality very sustainable.

Being inspired by these properties, many scientific groups all over the world begun in the last three decades to mimic the self-healing and self-protecting functionalities in diverse artificial engineering materials. Usually, a specific design of the material structure on the micro- or even nanolevel enables such an active feedback behavior.

There are some approaches to prepare the microstructurized self-healing materials—containers based, network based (vascular) and intrinsic (Blaiszik *et al.*, 2010). One of the most established now is the approach connected with the use of micro- or nanocontainers (further—“containers”) embedded in the material matrix, whereas these are loaded with diverse active agents and are able to release them on the action of various triggering factors leading to the material damage. Most often, so-called *sealing agents* are used in the three-dimensional case for the encapsulation in the containers imparting to the material bulk, the re-establishment of the structural homogeneity. On transfer of this idea to the coatings (quasi-two-dimensional case), the intrinsic limits for the highest possible volume of the encapsulated sealing agent predestine the predominant use of protective agent (e.g. corrosion inhibitor) instead of former one for the containers loading. In this case, it is better to use the term *self protecting* (Ghosh, 2009) for the coatings with this kind of containers because the physical integrity of the coating is not recovered during the protective action of the encapsulated inhibitor although the protection of the underlaid metallic substrate from corrosion is achieved.

A typical standard coating is composed of several layers possessing different protective functions: thin pretreatment layer B, relatively thick primer layer C and thin but much more mechanically robust topcoat layer D (Figure 1). Frequently, the first layer deposited on the metallic substrate under protection is a sacrificial anode layer A being dissolved during corrosion process and made of electrochemically more active metal (Zn, Cd, and so on) than substrate. In a passive protective coating, the primer and especially the topcoat layers should serve as barrier from corrosive factors as well as from charge and mass transfer occurring as a consequence of corrosion. These polymeric protective systems are however not sturdy enough to withstand diverse damaging impacts, first of all, mechanical damages (scratches, stone chipping etc.) that can occur during its service life. Being damaged, such a passive coating cannot provide satisfactory resistance against the attack of corrosives at the site of damage and the corrosion develops uncontrollably.

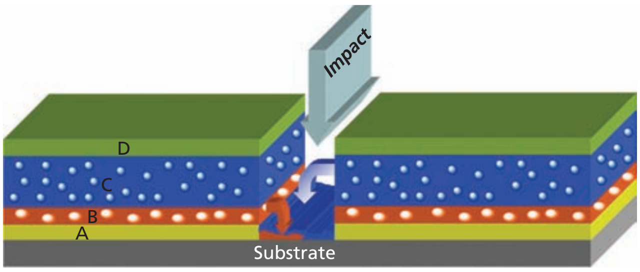

Figure 1. A schematic representation of the active response of the multifunctional self-protecting coating triggered by an external impact. Micro- or nanocontainers with two different types of active agents are incorporated in the thin pretreatment layer B and in the thicker primer layer C and can provide the coating the multilevel protection, for example, inhibition of corrosion (containers in the pretreatment layer B, orange) and water-repelling effect (containers in the primer layer C, blue).

The key element of the above-mentioned self-healing or self-protecting materials or coatings are micro- or nanocontainers with the shells providing the release on demand, triggered by the various naturally or artificially occurring factors. The same external impacts leading to the distortion of the passive protective function of the coating matrix act in the self-healing or self-protecting coatings as stimuli for the release of an active agent from the containers. Functionality of such a protective coating is therefore specified by the compounds entrapped in the containers and can be essentially extended by combination of containers with different loads (Figure 1, containers of one type are embedded in pretreatment layer B, of the other one– in primer layer C).

Containers used in the bulk materials for the purpose of self-healing just have to have enough material inside to fill up at least, partially, the bulky crack areas in the material interior and can be quite large especially compared with the typical thicknesses of conventional polymeric anticorrosive coatings. On the contrary, the size of containers is of crucial importance for their applicability in the coatings because of the natural restrictions dictated by the coating thickness.

In the following paragraphs, the attention of the paper at hand will only be focused on the containers used in the field of corrosion-protection coatings and all types of containers applied for the self-healing bulk materials are out of its scope.

2. Advantages of using emulsions for the preparation of micro or nanocontainers

The methods to prepare the micro- or nanocontainers with the active load could be quite different.

Well-established technique for the fabrication of micro- and nanocontainers with the stimuli-responsive shells made of polyelectrolyte multilayers (PEM; Sukhorukov and Moehwald, 2007) includes some subsequent steps of deposition of oppositely charged polyelectrolytes onto the solid particulate template (melamine-formaldehyde resin (Radtchenko *et al.*, 2002; Voigt *et al.*, 2000), $MnCO_3$ (Antipov *et al.*, 2003), $CaCO_3$ (Antipov *et al.*, 2003), SiO_2 (Mauser *et al.*, 2006) and so on, dissolution of this template in the appropriate medium, swelling of the PE shell by changes of the medium pH or ionic strength to provide it the permeability needed for the penetration of the substance to be loaded into the containers interior, and final closure of PE shell by the opposite changes in the medium properties. This technique becomes especially complicated in case when the container core should be composed of the substance of polarity strongly deviated from the polarity of the dispersion medium where the containers were initially distributed (Moya *et al.*, 1999).

The second group comprises the methods based on the usage of solid hollow or sponge-like colloidal templates such as natural or synthesized micro-, mesoporous or hollow particles, materials or structures of micro- or nanometer scale. Due to their specific internal structure with the high fraction of the empty space, these templates fulfill the function of reservoirs also. After loading, the step of the shell formation finalizes the containers preparation determining in essence, the release properties and colloidal stability of the fabricated containers also (Lvov *et al.*, 2008). Although the number of steps are reduced when compared to hollow PEM containers, the number of steps in the containers assembly procedure remains numerous in these techniques. Moreover, the loading capacity and the complexity of the loading step(s) depend on the scaffold porosity and pores size distribution, especially in the case of narrow pores.

In contrast, the use of emulsion as an initial point for the micro- or nanocontainers preparation demonstrates numerous advantages over the approaches mentioned afore. Most important, this concept is the straightforward one, thus the utilization of liquid particles (emulsion droplets) simultaneously for two purposes—as templates and as container cores allows the significant reduction of steps during the containers fabrication. Also, the liquid state of both the dispersion medium and the dispersed phase decreases substantially the comminution work needed for the preparation of the colloidal system, especially by use of surfactants. The liquid state of the container cores enables the precise control for concentrations of all ingredients and provides on the one hand, the fine adjustment of the active agent content and its distribution in the container and, on the other hand, the flexible regulation of containers size distribution by the addition of surfactants and hydrophobes. Direct encapsulation of emulsions becomes especially important when the formation of containers with core/shell morphology and a liquid core is desired. This situation may for instance frequently occur at the preparation of containers for biomimetic self-healing or self-protecting anticorrosion coatings. Thus, the liquid core of container will play the role comparable with the role of blood in the human skin and, in case of destructive external impact, the strong immediate feedback of the coating will be achieved. Other imaginable cases of the encapsulation of liquid in container core are targeted delivery and triggered release of liquid active compounds or improvement of their shell life, handling and processing.

3. Emulsion route for containers preparation: approaches

Generally, starting point for all specific realizations of this concept is the fabrication of "direct" oil-in-water (O/W) or "inverse" water-in-oil (W/O) emulsion. The liquid/liquid interface between the droplets of dispersed phase of emulsion and its continuous phase serves then as the "scene" where the formation of the container shell proceeds. Vast majority of methods finally yielding the containers can be grouped in two broad classes depending on nature of processes used for the container shell formation: (*a*) approaches using the physical phenomena leading to the shell formation and (*b*) techniques utilizing various chemical reactions at the liquid/liquid interface or *in-situ* reactions in the dispersed phase with subsequent merging and segregation of the growing prepolymers at the interface of emulsion droplets (Figure 2).

Several particular methods representing this general classification will be considered in more detail in the later parts of this work. Corresponding examples of concrete systems will help to discuss the mechanisms, benefits and drawbacks of the applied methods, especially, in regards to mimicking of the active feedback properties of living matter employing the obtained containers.

4. Methods based on the interfacial physical phenomena

4.1 Interfacial precipitation

In this method, the emulsion droplets function as soft template particles at whose interface the material forming the shells of the future containers begins to precipitate because of changes in the physical or chemical parameters (composition) of the system. Moreover, the same droplets contain the substance for the containers filling and serve therefore as their future cores. The shell-building component is initially fully dissolved either in the droplets of dispersed phase (emulsion droplets) or in the surrounding dispersion medium, so that both phases of this disperse system (emulsion) remain homogeneous at the beginning. On the changes occurring

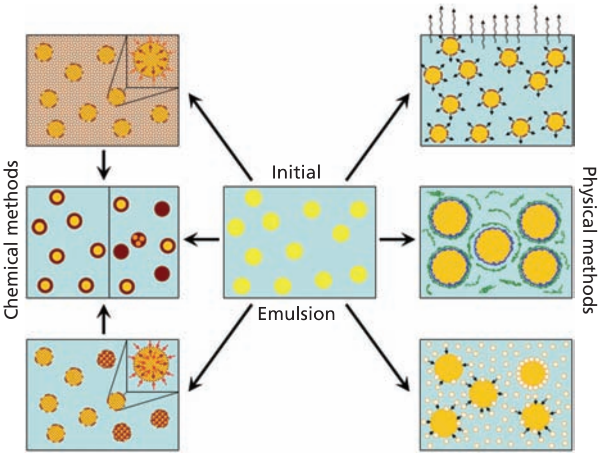

Figure 2. Physical and chemical methods for fabrication of nano- and microcontainers via emulsion route. On the right side from top to bottom: solvent evaporation induced interfacial precipitation, Layer-by-Layer (L-b-L) interfacial adsorption, interfacial attachment–formation of Pickering emulsions. On the left side: upper scheme–interfacial polyaddition/interfacial polycondensation; lower scheme–*in-situ* emulsion polymerization; in the middle–as a result of these polymerization processes solid containers, containers with core/shell or multicompartment morphology can be obtained.

in the system, the solubility of the shell-forming component drops and it starts to precipitate.

In the simplest situation, changes in only one physical parameter of the system such as temperature can cause a serious lowering of the miscibility of the shell-forming component with other components in one phase of the two-phase disperse system leading to its precipitation at the interface between these phases.

The decrease of the solubility of the shell-forming compound with subsequent precipitation can also be induced by changes in the phase composition—either by removal of the solvent having a good solvency for this compound (further–"solvent") from the system or by addition of the solvent possessing a poor solvency for it (further–"nonsolvent") to the system. As the dispersed phase is a nonautonomous one, the phases are unequal against the independent changes of their compositions. If the shell-forming component is initially dissolved in the dispersion medium, its solubility there could be distorted almost without any effects on the composition of the dispersed phase. Moreover, a precipitation from dispersion medium is additionally favored by the presence of the emulsion droplets according to the heterogeneous nucleation mechanism that proceeds at their interface. Typical processes leading to the interfacial precipitation from the dispersion medium are evaporation of the solvent from this phase or its dilution by the nonsolvent, that is, solvent evaporation-induced precipitation (Figure 2) or dilution-induced precipitation.

In the spatially opposite case, precipitation starts from the interior of emulsion droplets and triggers analogous to these, for the dispersion medium can only be activated by involving of the surrounding dispersion medium. Therefore, the solvent or nonsolvent, respectively, should at least be sparingly soluble in the dispersion medium of the emulsion also, to be transferred through it from/to the emulsion droplets with the initially dissolved shell-forming component. Interfacial precipitation from the dispersed phase can additionally be influenced by curvature and confined character of its particles.

Finally, the formation of either containers with the core/shell morphology and liquid core or entirely solid particles is attained.

Solvent evaporation-induced interfacial precipitation technique is widely used in the pharmaceutics (often also called nanoprecipitation technique) for the production of micro- and nanocontainers with entirely solid (micro-or nanospheres) or core/shell morphology (nanocapsules; Desgouilles *et al.*, 2003) when water-insoluble or sparingly soluble drug(s) is incorporated in the containers. As a consequence, solvent to be evaporated is added predominantly into the oily dispersed phase and precipitation begins at the inner side of the liquid/liquid interface in each emulsion droplet. Solvents providing the initial solubility of shell-forming component (as a rule—biologically compatible polymer) in the oily phase such as acetone, ethyl acetate and so on are also either well-soluble or at least sparingly soluble in the aqueous dispersion medium and are first transferred to this medium by diffusion through the phase boundary. To enhance this transfer, the vessel containing emulsion can be intensively stirred, moderately heated or/and purged by air or an inert gas (Couvreur *et al.*, 2002). Other possibility is the use of mild vacuum conditions.

Spray drying, the most frequently used method in the food industry for the encapsulation of various food ingredients, can also be considered as a particular realization of the interfacial precipitation. Indeed, removal of water caused by hot dry air induces the precipitation of surface-active components of mixture such as proteins or polysaccharides at the interface between air and aqueous droplets (Gharsallaoui *et al.*, 2007) and provides simultaneously the segregation of cores of the future containers composed of nonpolar mixture ingredients (oils, fats and so on).

Interesting attempt to use the interfacial-precipitation method with the precipitation induced from the dispersion medium was performed by Voigt and coworkers (Voigt *et al.*, 2000). Initially, shell-forming material that is well-soluble in the dispersion medium—a mixture of two oppositely charged polyelectrolytes—was brought to precipitation at the surface of colloidal templates by two different ways, first, by the slow solvent (acetone) evaporation and, second, by the slow addition of nonsolvent (water) from/to the dispersion medium.

Preparation of micro- and nanocontainers for the self-protecting anticorrosion coating was done in our group, exploiting the solvent evaporation-induced interfacial-precipitation technique for the encapsulation of the water-repelling agent sodium docusate. The oil phase of the O/W emulsion was prepared by the mixing of water-immiscible dodecane with ethyl acetate (EA) sparingly soluble in water at components ratio 5:9. In this composite solvent, approximately 9·5 wt% of polystyrene (PS, M_w = 34 KDa) and 5 wt% of sodium docusate, related to the total oil-phase composition, were dissolved. Phosphate buffer solution with pH 7 saturated by EA at normal conditions was used as an aqueous dispersion medium of the emulsion. To this solution, 135 mg of nonionic surfactant Triton X-100 was added as emulsifying agent. Then, 10 v/v% rough O/W emulsion was prepared by means of Vortex-shaker (stage 7, for 1 minute) and processed finally for 3 minutes with the high speed rotor–stator homogenizer Ultra-Turrax (IKA Werke, Staufen, Germany). After that, this emulsion was either left for the EA evaporation under the fume hood with continuous stirring at 150 rpm for 12 hours or, to accelerate the removal of this solvent, first diluted 10 times with Milli-Q water and then treated by the dry nitrogen bubbling for 5 hours. Volatile EA was completely evaporated and an aqueous dispersion of PS micro- and nanocontainers containing a solution of AOT in dodecane was obtained (Figure 3). The Zeta-average size of containers measured by DLS intensity (Zetasizer Nano ZS Malvern, UK) was 1570 nm

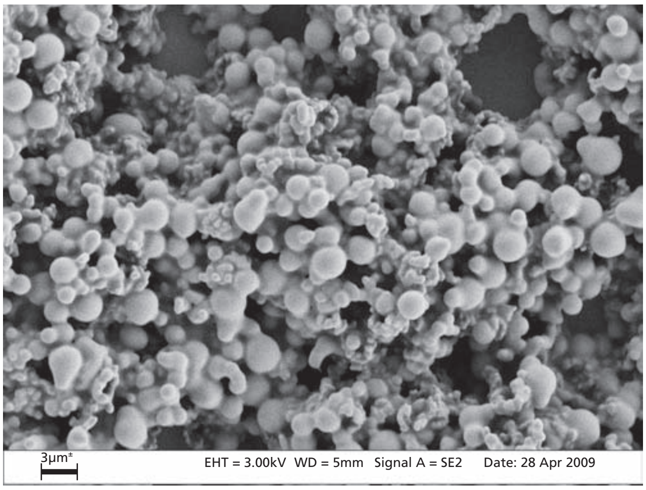

Figure 3. Micro- and nanocontainers with polystyrene shells containing a solution of water-repelling agent sodium docusate in dodecane obtained by the solvent evaporation-induced interfacial precipitation.

with PDI = 0·8 reflecting the strong polydispersity of containers, visible also on the qualitative level in Figure 3. Such a broad container size distribution is a typical consequence of the emulsion preparation by means of a high-speed rotor–stator homogenizer like Ultra-Turrax. Noteworthy, the containers obtained only by the gradual evaporation of EA without acceleration showed lower polydispersity with PDI = 0·6 probably because of the Ostwald ripening in the initial emulsion droplet that kept, in this case, their liquid state longer. Several partially deformed containers with the concavities in the shells observable in Figure 3 can be considered as an indirect argument for their core/shell or multicompartment morphology. However, this container structure may be also deduced from the almost complete immiscibility of the oily container cores (diluted docusate solution in dodecane) in the aqueous dispersion medium.

In spite of the simplicity and relatively low costs of interfacial-precipitation method in its various concrete realizations, there are also a lot of challenges and drawbacks connected with some technical peculiarities of this method and with the properties of containers obtained in this manner related to their embedding into coating matrix. Solvents used for the dissolution of shell-forming component(s) have to be either completely or at least sparingly soluble in the dispersion medium, most often aqueous one. These solvents should be also volatile enough to assure a reasonable time of complete evaporation and formation of the container shell. Therefore, the application of this method in both solvent evaporation-induced precipitation and dilution-induced precipitation types will lead to serious amounts of environmentally dangerous wastes such as VOC or VOC-contaminated water especially when upscaled to the industrial extent. Because of such environmental concerns, the industrial realization of interfacial-precipitation method may be additionally complicated by the necessity to install quite expensive recycling set ups.

Another problem is that polymers used for the formation of containers shell are the preformed polymers, which should be well soluble in several solvents of intermediate polarity ensuring the good miscibility with both aqueous and oily phases. Thus, the relatively low cross-linking degree of polymers employable for this purpose is required. However, the high solubility of shell-forming polymers in the solvents of moderate polarity excludes automatically the incorporation of containers made of these polymers by interfacial precipitation in the coatings on the basis of organic solvents and restricts their use only to water-born coating formulations. Moreover, even in this case, the coating formulations with relatively high curing temperature can also be a subject of doubt as the low cross-linking degree of polymer will cause its melting already on the curing step with subsequent destruction of containers.

4.2 Layer-by-Layer (L-b-L) interfacial adsorption

Although the Layer-by-Layer (L-b-L) interfacial adsorption or interfacial deposition method became well-established worldwide in cases of plane solid (Decher and Schlenoff, 2003) and colloidal solid (Sukhorukov *et al.*, 2004) templates in the last three decades, its extension to the liquid colloidal templates (emulsions) was elaborated relatively recently. Several details of this technique were already partially used in some works issued in the mid-2000s (Guzey and McClements, 2006; Nilsson and Bergenståhl, 2007; Tjipto *et al.*, 2006). These attempts were however seriously restricted either by employing specific chemicals or by application of unique preparation conditions. So, Tjipto and coworkers (Tjipto *et al.*, 2006) have used the special substance (4’-pentyl-4-cyanobiphenyl) forming nematic liquid crystals as material for the droplets of O/W emulsion to be encapsulated. At the encapsulation of various food-relevant emulsions, both amounts of hydrophobic bioemulsifiers and the preparation conditions used evidences that the initial solid or solid-like layer was formed at the interface before the container shell formation by L-b-L polyelectrolyte deposition was started (Guzey and McClements, 2006; Nilsson and Bergenståhl, 2007).

Generalized approach to the preparation of loaded micro- and nanocontainers based on the direct oil-in-water emulsion encapsulation by PE L-b-L adsorption was developed recently in our group (Grigoriev *et al.*, 2008). In this method, the liquid colloidal particles—emulsion droplets—play the role of the template as well as of the loaded container core, simultaneously. To stabilize the dispersed phase of initial emulsion, the oil phase (dodecane) was doped by small amount of cationic surfactant (see Figure 4) dioctadecyldimethylammonium bromide (DODAB). Because of its very low solubility in nonpolar solvents, 30 v/v% of chloroform was added to dodecane to improve the surfactant solubility in the

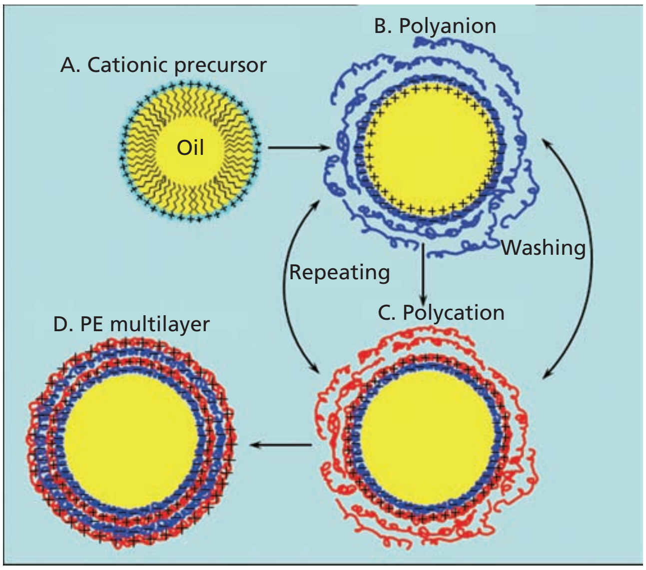

Figure 4. Alternate Layer-by-Layer (L-b-L) polyelectrolyte adsorption on the interface of emulsion droplet–a depiction of deposition steps.

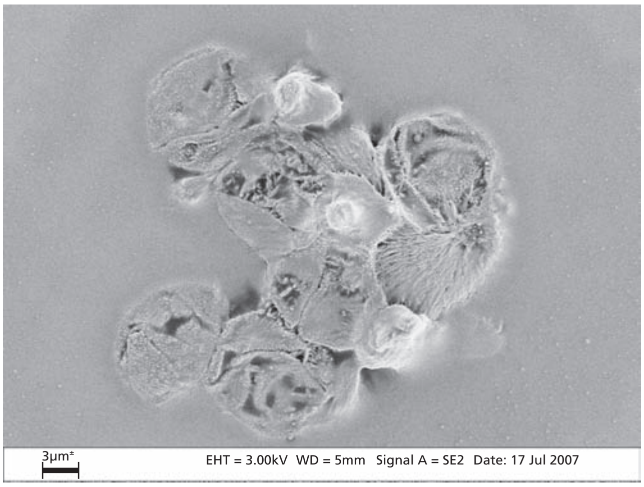

Figure 5. Microcontainers on the basis of dodecane-in-water O/W emulsion with PE shells made of four subsequently adsorbed PSS and PDADMAC layers.

oil phase. However, the O/W emulsion used on the further steps did not contain any detectable residues of chloroform in the droplets of dispersed phase because of the considerable solubility of latter in the aqueous media and relatively high volume of the emulsion dispersion medium (98 v/v%). The colloidal stability of initial emulsion was achieved due to concentrated monolayer of strongly positively charged DODAB (*Zeta*-potential was about +90 mV) at the surface of each droplet. This electrostatically driven emulsion-stabilization mechanism reduced significantly the fractions of droplets occurring because of the partial coalescence of droplets of the original emulsion during and immediately after its preparation and contributing therefore to its moderate polydispersity with Z-average diameter of 2·3 μm and PDI = 0·4.

The L-b-L polyelectrolyte assembly was done by their subsequent adsorption from concentrated (20 mg/ml) aqueous salt-free solutions. The creamed upper layer of the strongly positively charged initial emulsion was added dropwise to 40 ml of the oppositely charged polyelectrolyte solution of (poly(sodium 4-styrenesulfonate, PSS) on continuous stirring at approximately 700 rpm. After this layer was completely brought into polyelectrolyte solution, the mixture was stirred for an additional hour to accomplish the binding of polyelectrolyte at the surfaces of the initial emulsion droplets and to ensure their overcharging. The excess of the remaining free polyelectrolyte was washed out by pure MilliQ water. The second encapsulation step was done in an aqueous solution of positively charged polyelectrolyte (poly(diallyldimethylammonium chloride), PDADMAC or poly(allylamine hydrochloride), PAH) in the same manner (Figure 4). The further repetition of the alternating adsorption steps leads to the formation of containers with desired shell thickness depending on the particular final demand. Because on each PE-coating step, the creamed upper layer was transferred to the oppositely charged PE solution, the fraction of especially small containers with the slowest creaming kinetics was automatically excluded from further treatment, the final containers had larger Z-average size of 4·2 μm and were more monodisperse (PDI = 0.32). The dried droplets of O/W emulsion encapsulated by L-b-L interfacial adsorption technique are presented in Figure 5. Since the procedure of drying leads in the case of PE oil-filled containers to their collapse especially at the following scanning electron micropscopy (SEM) sample-preparation step, the oily container cores cannot be kept intact and only wrinkled PE container shells are observable. High-magnification SEM microphotograph however reveals distinctly the numerous details of the collapsed container shells like folds, overlapped parts, voids between them and so on (Figure 5), supporting the PE multilayered shell assembly around each droplet of the initial O/W emulsion.

Following the proposed paradigm for the straightforward preparation of the emulsion-based PE containers, (Grigoriev *et al.*, 2008) further developments in this field were done (Lomova *et al.*, 2010; Wackerbarth *et al.*, 2009).

In (Wackerbarth *et al.*, 2009), the microcontainers on the basis of emulsion droplets with six layers of biopolyelectrolytes for the potential application in the food industry were reported. The authors of (Lomova *et al.*, 2010) have presented the successful PE encapsulation of highly unstable polyunsaturated natural oils for the aims of storage and degradation protection by introducing the natural antioxidant compound (tannic acid) as shell constituent in alternation with biocompatible oppositely charged polyelectrolyte.

Container-preparation technique via direct emulsion encapsulation developed in (Grigoriev *et al.*, 2008) can be envisaged as an universal one applicable independent of the nature of the core components used. Due to manifold of polyelectrolytes available for L-b-L container shell assembly, the multifunctionality of containers can be achieved. Moreover, the extension of method towards the use of other, not only macromolecular building blocks for the L-b-L deposition (Caruso *et al.*, 1998) makes this approach even more versatile. Purposeful choice of PEs for the container shells allows their opening by numerous environmental or artificially introduced triggers such as temperature (Köhler *et al.*, 2004), pressure (Shchukin *et al.*, 2006), UV or IR light (Volodkin *et al.*, 2009), changes in pH (Mauser *et al.*, 2006), ionic strength, electrochemical potential and so on and therefore impart them the stimuli-responsive release ability and high sustainability in the load consumption.

Nanometric accuracy provided by PE L-b-L deposition on the each step of the container shell formation allows very fine adjustment of container size and the shell thickness that also can be of high practical importance in many research and industrial fields.

However, some drawbacks of PE containers obtained by the L-b-L interfacial adsorption should be also mentioned here making their utilization in many types of self-protecting coatings problematic. Even at deposition of PEs with lowest Mw, the permeability of shell for low-molecular agents loaded into containers remains very high, disabling the possibility of sustained release for these substances and use of such type of containers in the media with good solvency for the core material. Low mechanical stability of the PE shells at any reasonable number of PE layers in the shell is the other source of sorrow. It can be significantly improved by the increase of L-b-L deposition steps and subsequent annealing at higher temperature (Köhler et al., 2004) but such overcomplication makes the fabrication costs rise and thus unacceptable for many potential application fields. The use of soft emulsion-based containers with L-b-L PE shells may be imaginable in the water-born coating formulations with the quite mild curing conditions and ductile matrix even after this procedure, for instance, in biomedical coatings that are presented in more detail below.

4.3 Interfacial attachment—formation of Pickering emulsions

This method of preparation of emulsion-based nano- and microcontainers relies on the remarkable phenomenon of emulsion stabilization by the partially hydrophobic/lyophilic or partially lyophobic/hydrophilic micro- and nanoparticles due to their spontaneous attachment at the O/W or W/O interface. This “strange” behavior of such particles is known since the beginning of the 20th century (Pickering, 1907; Ramsden, 1903) and can be strictly described in terms of change in the particle energy on its transition from the bulk location to the interface (Binks, 2002):

1. $$\Delta G_{att} = -\pi r^2 \gamma_{\alpha\beta} \left(1 \pm \cos\theta\right)^2$$

Because of huge depth of the energy, well even in the case of small nanoparticles, this transition can be considered as practically irreversible and is therefore commonly called “attachment” and not as “adsorption.” Owing to the above-mentioned thermodynamic reasons, the partially hydrophobic/hydrophilic particles spontaneously form a tight mono- or even multilayer at the emulsion droplets interface, acting as building blocks for the containers shells. Again, the emulsion droplets serve as template for the formation of the particulate shells and work at the same time as reservoirs for the loaded active agent (Figure 2).

The interfacial activity of particles can be an intrinsic property of them connected with their specific affinity to certain types of solvents (Frelichowska *et al.*, 2009). In this case, even the bare unmodified particles are able to concentrate at the interface between droplets of this solvent and surrounding medium. However, more frequently, this peculiarity is imparted to particle by means of corresponding modification of its surface by various types of surfactants (Binks and Lumsdon, 2000; Gonzenbach *et al.*, 2006; Schmitt-Roziéres *et al.*, 2009) bonded electrostatically or covalently to the particle material. Electrostatic mechanism of the modification does not presume the formation of the proper chemical bonds between surfactant molecules and particle surface but is rather a result of the equilibration of the complex physical interaction between these molecules, particles and surrounding medium (solution). Therefore, the small amounts of surfactant in the system persist always in the free state and can occasionally interfere with the corrosion inhibitor or other protective agents contained in the core-forming emulsion droplets and impair the mechanism of the interfacial particle attachment. To avoid this undesired situation, the thorough selection of appropriate nonreacting and noninteracting surfactants and protective components should be done before containers fabrication. The indicated problem will however not arise at all if inhibitor possesses simultaneously the properties of surfactant used for the particle modification. Many corrosion inhibitors are weak organic acids, bases or amphoteric compounds joining both these abilities and can be partially or fully ionized in a certain pH range, thus becoming quite hydrophilic. In case when the residual organic moieties of inhibitor molecule are hydrophobic enough, the whole molecule will demonstrate the amphiphilic behavior in the same pH range, that is, will act as a surfactant. The corresponding ability of the amphoteric multipurpose corrosion inhibitor 8-hydroxyquinoline (8-HQ; Haase *et al.*, 2010) to become considerably protonated at the pH less than 5.5 (pKa = 5·13) and to be adsorbed electrostatically at the surface of negatively charged silica nanoparticles (Ludox TMA) making them partially hydrophobized and therefore interfacially active was utilized. These particles stabilize the O/W emulsion droplets forming the multilayers at their interface that can be considered as particulate container shells (Figure 6). The droplets of dispersed oily phase are composed of Diethyl phthalate (DEP) able to dissolve until 16·5 wt% of 8-HQ and serve as container cores and reservoirs for the loaded inhibitor. As dispersing tool, an ultrasound generated by ultrasonic titanium horn (VCX 505, Sonics

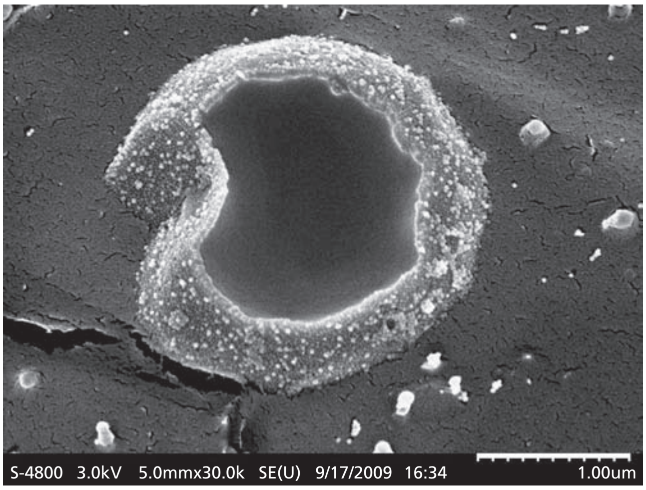

Figure 6. Multilayered nanoparticulate (Ludox TMA) shells of micro- and nanocontainers with liquid core containing corrosion inhibitor 8-HQ. Cryo SEM image.

& Materials Inc. Newton, USA) with tip area 0·785 cm^2 and power 40 W was used. The container size distribution and the amount of nanoparticles in the container shells were well-expressed function of pH in the range from approximately 4·4 to 5·6. At pH 5·6, the maximum in the monomodal volumetric size distribution lies at 12 µm with PDI of about 0·6 and shell built of almost monolayer of silica nanoparticles. On the opposite end which is considered pH window, that is, at pH 4·4, another monomodal distribution was achieved with however essentially smaller and more monodisperse containers (volumetric average size of 4·5 µm and PDI of about 0·4) possessing the multilayered nanoparticulate shells. In the intermediate cases of pH 5·3 and 5·1, the bimodal containers size distributions were observed (Haase *et al*., 2010) with two main container fractions at 12 µm and 5·5 µm as well as at 10 µm and 5 µm, respectively, with the decrease of the fraction of larger particles on decrease in pH. This behavior can be related to the continuously increased interfacial activity of silica nanoparticles hydrophobized by the gradually growing amount of the adsorbed 8-HQ on pH drop. The attempts to use the ultrasound of higher intensity or a high speed rotor–stator homogenizer for the container fabrication led to the much higher polydsipersity of them in whole pH window discussed. The stability of containers is also satisfactory only in the same narrow pH window between 5·6 and 4·4. Below this window, the protonation degree and subsequently the concentration of 8-HQ in the dispersion medium attain the values enabling the formation of an 8-HQ bilayer at the surface of silica nanoparticles. The interaction of the overlapping aromatic rings, for example, π-π stacking or van der Waals attraction could be suggested as a driving force for this effect. As a result, the positively charged protonated groups of 8-HQ molecules in the outer part of bilayer are oriented towards dispersion medium and rehydrophilize the particles from which the container shells are built. The rapid destruction of the containers is observed in this pH region leading to the immediate burst-like release of the encapsulated inhibitor. This pH sensitivity together with the mechanical rupture of containers could be utilized as triggers for the containers opening and stimulated inhibitor release when the containers become embedded in the matrix of an anticorrosion coating.

Emulsion-based containers fabricated by means of interfacial attachment of nano- or microparticulate building blocks forming the container shell reveal several advantages in the preparation routine and in the following handling fashioning them as potential candidates for the use in the various self-protecting coatings. Fabrication of micro- and nanocontainers by means of interfacial-attachment method is usually a simple procedure that includes as a rule, only two steps—(a) preparation of particles as building blocks for the shells of future containers via their partial hydrophobization (O/W) or hydrophilization (W/O), and (b) addition of them to the two-phase system containing all components of containers during or immediately before the emulsification with subsequent processing leading to the ready containers. Sometimes, this procedure can be even further simplified to practically one-pot process (Frelichowska *et al.*, 2009). Because of its simplicity, this preparation pathway may often be economically sound and has a high practical relevance. Wide variety of particles of different chemical nature and of immiscible solvents with diverse polarities available facilitates an almost unlimited number of achievable container types, thus making the method very comprehensive. Compared with the emulsion-based container types described above, containers prepared by the interfacial attachment of particles demonstrate much higher robustness (Ferri *et al.*, 2008) and are therefore more suitable for incorporation into self-protecting coatings with hard coating matrices. However, the main problem in the application of containers prepared by interfacial attachment is the heterogeneity of their shells comprised of many fine particles joined at the surface of each emulsion droplet to a mono- or multilayer with lot of gaps between individual building blocks. This discontinuous structure of the container shell reduces its mechanical properties considerably, especially compared with those of the individual particle in the shell and increases its permeability drastically. The latter could be very critical when the containers loaded with the oil-soluble protective agent are mixed with a liquid coating formulation on the basis of the organic solvent(s) able to wash out the container load immediately after their addition into coating mixture.

To enhance the mechanical strength of containers and to make them more seamless, single particulate elements of the container shells should be locked at the interface and joined together. It can be done, for instance, by the local high-energy treatment as was shown in (Grigoriev *et al.*, 2007) where the high intensity ultrasound was used for this purpose. The second possibility is the interlinkage of particles in the shell by the deposition of additional PE layer(s) above it. This, on the one hand, complicates the process of the container preparation by one more step but on the other hand, can

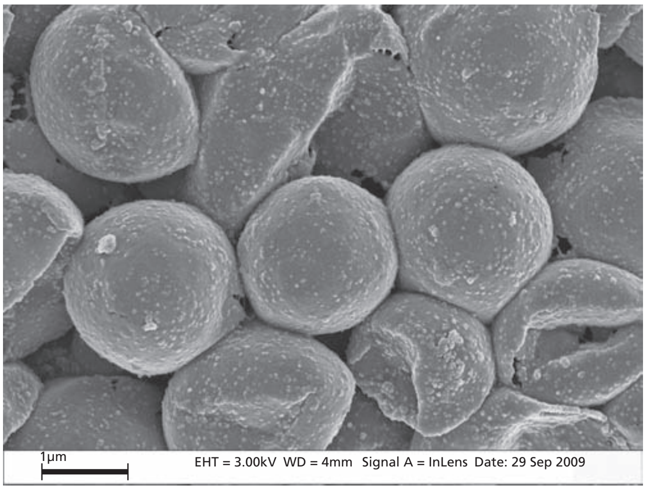

Figure 7. Core/shell microcontainers with nanoparticle shells obtained by interfacial deposition locked subsequently with the L-b-L adsorption of six polyelectolyte monolayers (PSS/ poly(allylamine hydrochloride, PAH).

significantly improve some drawbacks reported for the containers obtained by pure interfacial deposition such as undesired high permeability. Moreover, the PE deposition could impart to shells certain additional valuable features connected with the properties of polyelectrolyte layer, like selective pH sensitivity and so on. Figure 7 shows containers on the basis of Pickering emulsion droplets made of 1.5 M solution of 8-HQ in dimethyl phthalate (DMP) coated with three PE bilayers composed of pairs PAH/PSS or PAH/PAA. Polyelectrolyte alternate deposition did not disturb the initial containers size distribution with volume average size of 2·5 μm and PDI = 0·35 and but also led to the significantly higher stability of containers that remained almost undeformed during the SEM sample preparation (Figure 7). Another way to fix particulate elements in the container shell is their locking via liquid container core due to its solidification, for example, by polymerization of some core components as is presented in the next section of this work.

5. Techniques utilizing the interfacial or bulk chemical reactions

In the chemical methods of containers fabrication, containers form in the course of a chemical reaction proceeding either at the interface between emulsion droplets and dispersion medium around them or in the droplets interior.

Following this natural division related to the reaction location, the methods using the corresponding reactions could be classified in two big groups: one group of methods using the interfacial polyaddition or polycondensation reactions and another one exploiting *in-situ* emulsion polymerization proceeding in the bulk of emulsion droplets.

5.1 Interfacial polyaddition/interfacial polycondensation

In this case, at least one of reactants is located outside the droplets in the continuous phase of emulsion whereas the other are dissolved in the droplets. The reactants have very different polarities initially and are soluble only in one particular phase, excluding their interpenetration in the coexisting phases and premature reaction between them. Moreover, reactants have to remain phase separated all the time when reaction goes on and meet each other only at the interface of emulsion droplets. If the product of such an interfacial reaction is neither soluble in the droplets of the emulsion nor in the medium around them, containers with the core/shell morphology will be synthesized. More frequently however, the resulting product is soluble or swellable in the material of dispersed phase and particles with the solid bulk structure occur. Depending on the release of low-molecular side products, the interfacial polyaddition (without side products) or interfacial polycondensation (with) reactions can be discriminated.

The encapsulation of the mixture of protective agents with two functionalities—corrosion inhibitors and simultaneously water repellents—was performed recently (Latnikova *et al.*, 2011) by the interfacial polyaddition technique for the further application in the self-protecting anticorrosion coatings. The oil phase of the future O/W emulsion was composed of mixture of two protective agents, trimethoxy(octadecyl)silane (TMODS) and trimethoxy(octyl)silane (TMOS), Poly[(phenyl isocyanate)-co-formaldehyde] trifunctional prepolymer participating in the reaction of shell formation as well as solvent (DEP) enabling the miscibility of all components, see also (Latnikova *et al.*, 2011) for more details. This mixture was first dispersed in an aqueous medium by means of nonionic polymeric emulsifier polyvinyl alcohol (PVA) under intensive stirring for 3 minutes with high speed rotor–stator homogenizer Ultra-Turrax (IKA Werke, Staufen, Germany).

Resulting emulsion was added to the phosphate buffer solution containing the second water-soluble reactant glycerol and polyaddition reaction catalyst 1,4-diazabicyclo[2.2.2]octane (DABCO). The formation of polyurethane (PU) containers shells at the interfaces of droplets was occurred according to the following reaction scheme:

$$nOCN-R-NCO+nHO-R'-OH \rightarrow [-R-NHC(O)OR'-]_n \quad (2.)$$

This mixture was stirred for 1 hour at 65°C and stirred continuously and subsequently left overnight without heating and stirring for the completion of container formation. Suspension of obtained micro- and nanocontainers was dialyzed to remove residual glycerol and PVA and finally separated by centrifugation at 13 000 rpm. The prepared containers were polydisperse and have well-expressed core/shell morphology (Figure 8). The size distribution of PU containers demonstrated two peaks representing two main fractions of containers

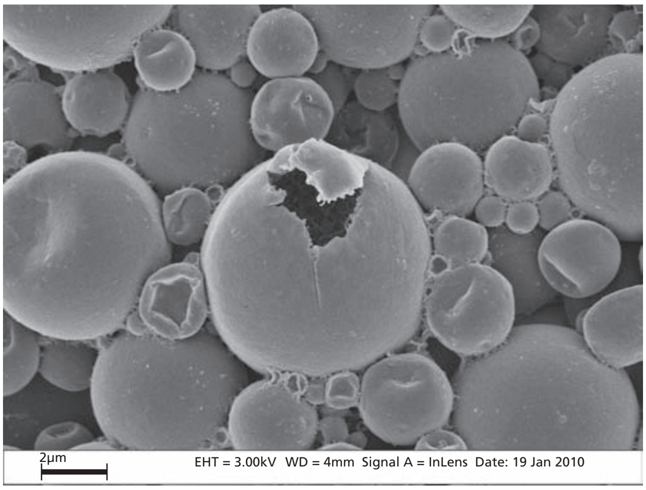

Figure 8. SEM images of microcontainers synthesized by interfacial polyaddition technique with encapsulated mixture of bifunctional protective agents and polyurethane shells.

in the mixture—one at 1·0 µm and the second one—at 5·5 µm. At the increasing of rate of the high-speed rotor–stator homogenizer from 11 000 rpm through 16 000 rpm to 22 000 rpm, the area of the first peak was continuously increased with the subsequent reduction of the second one, however, still remaining bimodal. Such a bimodal particle size distribution can be considered as polymerized replica of an initial O/W emulsion predestined by its droplet size distribution (Barrére and Landfester, 2003), almost always showing a very high polydispersity if the high speed rotor–stator homogenizer was applied for the emulsification process. Utilization of ultrasound for this purpose leads as a rule to narrower and frequently monomodal droplet size distribution in the original emulsion (Abismaïl *et al.*, 1999). Application of this comminution method in the considered case of containers with PU shells was unfortunately impossible because of numerous sonochemical effects accompanying the collapse of cavitation bubbles on ultrasound propagation. Reactive isocyanate functional groups in the prepolymer molecules quickly underwent side reaction with water molecules and highly reactive products of the water thermolysis (free radicals, hydroxyl-carrying species and so on, see below).

The incorporation of small amount of these containers into the conventional coating (approximately 6 wt% microcontainers in relation to the total mass of the dry coating) provides to it self-healing and self-protecting features: being mechanically damaged, the modified coating reveals not only recovered corrosion protection at the site of scratch but also dewetting ability for the aqueous media as seen from Figures 3(s) and (Latnikova *et al.*, 2011).

Similarly, the containers of other compositions for the self-protection purposes with either core/shell or solid bulk morphology were obtained by the interfacial polyaddition method. Figure 9 shows, for example, the coexistence of containers with core/shell, multicompartment and bulk morphology made of PU and filled with the corrosion inhibitor mercaptobenzothiazole (MBT) for the self-protecting anticorrosion coatings on the aluminum substrate. Core/shell containers with the PU shells and biocide filling for the self-protecting coatings against biofouling are presented in Figure 10 as already embedded into the polyepoxy coating matrix. The preparation routine for these microcontainers was similar to the pathway described above for the alkoxysilanes-filled PU containers. Only difference was that instead of alkoxysilanes mixture, the dispersed phase of the initial O/W emulsion contained about 55 v/v% of 10 wt% solution of biocide 4·5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in the mixture of octyl- and nonylbenzene. The minimal stirring rate and short duration of the comminution step (Ultra-Turrax, 11 000 rpm) led to the large size and broad size distribution of the initial emulsion and subsequently of synthesized containers (Zeta-average 8 µm, PDI = 0·8).

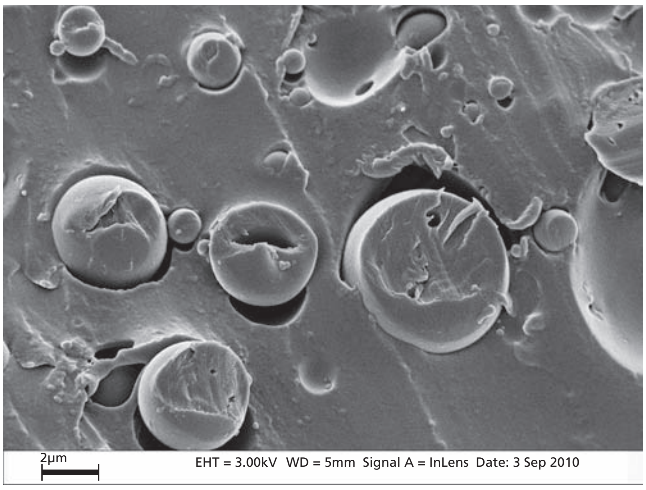

Figure 9. Influence of the nature of encapsulated protective agent/solvent on the morphology of micro- and nanocontainers obtained by the interfacial polyaddition method: coexisting of core/shell, multicompartment and bulk containers.

Containers filled with many other corrosion inhibitors and biocides and shells made not only of polyurethane but also polyurea (PUa) and polyepoxy resins were synthesized as well by the interfacial polyadditon method. The latter two polymers are especially suitable as materials for the container shells as both of them are sensitive to the reduction of pH to low or middle-low values, that is, the release of protective agents can be triggered by this factor accompanying corrosion and stop the further development of the process.

Figure 11 demonstrates an example of containers obtained by the interfacial polycondensation technique. The containers presented here have polyamide shells and are filled with the corrosion inhibitor

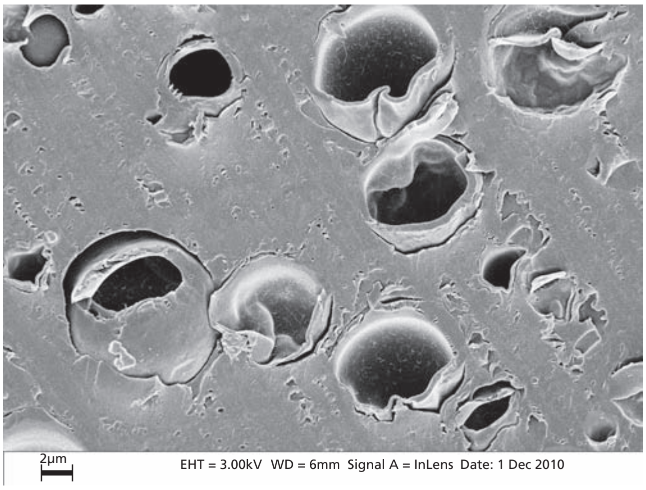

Figure 10. Cross-section biocide-filled core/shell containers with the PU shells in the dried polyepoxy coating matrix. Liquid core contained 10 wt% solution of 4·5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) in aromatic hydrocarbons.

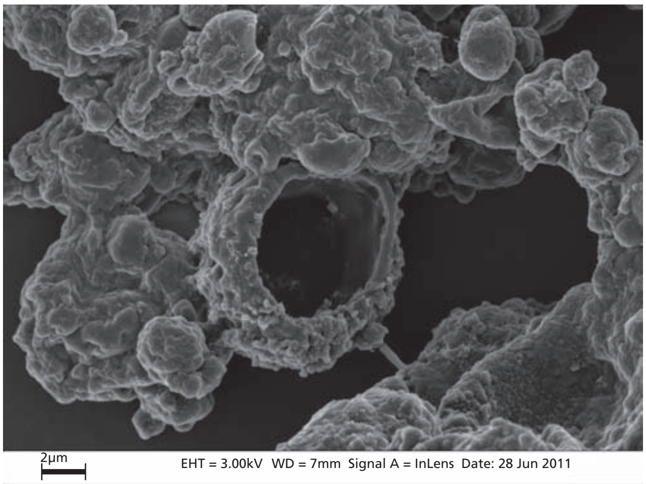

Figure 11. Micro-and nanocontainers filled with the corrosion inhibitor Ce(III)-tris-(bis-2-ethylhexyl) phosphate dissolved in the organic solvent dibutylphosphate and possessing the polyamide shells prepared by the interfacial polycondensation technique.

Ce(III)-tris-(bis-2-ethylhexyl) phosphate dissolved in the organic solvent dibutylphosphate. These two compounds along with the shell-forming component terephthaloylchloride (TPC) were mixed together in the weight ratio 2:13:5 for inhibitor, solvent and TPC, respectively to form the oil phase of the future emulsion. Oil phase was dispersed in the MilliQ water using the nonionic emulsifier PVA and the resulting emulsion was then added to the second aqueous phase containing combination of bi- and pentafunctional amines—ethylenediamine and tetraethylenepentamine in the ratio ensuring the average trifunctionality of the final mixture. The rapid formation of container shells according to the reaction:

3. $$\begin{gathered}\mathrm{nH_2NRNH_2 + nClOCR'COCl \leftrightarrow} \\ \mathrm{[-NHRNHCOR'CO-]_n + 2nHCl}\end{gathered}$$

was accomplished by the release of HCl as the low-molecular side product and was therefore conducted in a highly basic medium containing fivefold excess of amines relating to the TPC amount. The obtained containers had a mean size of 6 μm and were highly polydisperse (PDI = 0.7) because of very cautious conditions during their preparation (use of high speed rotor–stator homogenizer at lowest stirring rate, short comminution time and so on).

These containers can be also successfully applied in the anticorrosive self-healing and self-protecting coatings in cases when the corrosion is caused or followed by the pH decrease. The dissolution or strong swelling of the polyamide shell in this pH range will lead to the corrosion-triggered release of inhibitor.

5.2 *In-situ* emulsion polymerization

Realization of this container-preparation technique presumes that all reactants needed for the synthesis are contained in the emulsion droplets. These play the twofold role of reservoirs for reactants and protective agents as well as of liquid colloidal reactors and are only kinetically stabilized against the premature reaction start. After the O/W or W/O emulsion with desired properties such as stability, concentration, droplet size distribution and so on is prepared, the chemical (initiator substance, catalyst) or physical (T, UV-light and so on) triggers are activated to switch on the reaction and it runs until the attainment of the real equilibrium state corresponding to the completion of the polymerization reaction.

The polyepoxy containers filled with the corrosion inhibitor methylbenzothiazole (Me-BT) for the self-protecting anticorrosion coatings on the aluminium substrates were prepared by *in-situ* polymerization method by the following steps. The mixture of reactants needed for the formation of polyepoxy shells of containers was initially prepared composed of the 1:1 combination of aromatic and aliphatic epoxy-monomers trimethylolpropane triglycidyl ether and tris(4-hydroxyphenyl)methane triglycidyl ether, respectively. A 20% of Me-BT related to the total mass of the mixture was then added. The final step in the preparation of oil phase of the future emulsion was the addition of the second reactant for the *in-situ* polymerization reaction—diethylenetriamine in the amount ensuring the slight excess of the stoichiometric equivalence with the sum of both epoxy components. The oil phase was dispersed in the 2 wt% aqueous solution of the nonionic emulsifier PVA using Ultra-Turrax at 16 000 rpm for 5 minutes. The obtained O/W emulsion was then doped with a small amount of polymerization catalyst tetrabutylphosphonium bromide to increase the reaction rate to a reasonable level. The mixture was left overnight under moderate stirring to complete the polymer formation. The resulting containers are very polydisperse (see Figure 12) with the volume-average size of 2·3 µm (PDI = 0·96) and have obviously the core/shell morphology revealing the phase separation in the emulsion droplets in the course of the polymerization reaction leading finally to the segregation of core and shell parts of containers. Again, the significant improvement of the container size distribution by the creation of the more monodisperse initial O/W emulsion via ultrasonication was not possible because of the immediate reaction of monomers with water and especially with the products of sonochemical processes. Because of the presence of free amino groups in the structure of the epoxy polymer that is obtained, the containers reveal high positive surface charge (Zeta-potential of about +45 mV) and are therefore well dispersible in various aqueous media, for instance, in the water-based liquid coating formulations. Moreover, the introduction of epoxy monomers with the functional groups easily hydrolyzable in the acidic or basic medium (like ester groups) allows their opening in these media and finally acid- or base-triggered release of protective agents from the containers.

Sometimes, the combination of several emulsion-based methods of container fabrication leads to better results than the application of each of these methods alone. Solid micro- and nanocontainers for the self-protecting anticorrosion coatings were prepared via interfacial deposition of droplets-stabilizing SiO_2 nanoparticles with subsequent *in-situ* polymerization of their liquid cores (Haase *et al.*, 2011 submitted). Oil phase of the initial Pickering emulsion was composed either of styrene with dissolved corrosion inhibitor 8-HQ, hydrophobe hexadecane (HD) and polymerization initiator azo-bis-(isobutyronitril; AIBN) or of styrene, corrosion inhibitor MBT, 4-vinylpyridine (4VP) as a solubilizing agent for MBT, HD, and AIBN. The weight percent ratios of all components were 193:45:10:2 or 255:90:130:20:4, respectively. The silica nanoparticles (Ludox TMA, Sigma) were used for the creation of particulate shells of the future containers. Noteworthy, that no additional steps for making silica partially hydrophobic and therefore interfacially active were needed: 8-HQ acts as SiO_2 particle hydrophobizing agent and as, simultaneously, the encapsulated inhibitor, 4VP also hydrophobizes silica, acts as a MBT cosolubilizer and becomes copolymerized with styrene. Variation of the amount of silica introduced in the liquid/liquid system on the comminution step (ultrasonication, VCX 505, Sonics & Materials Inc. Newton, USA, see above) allowed the size controlling of the interim containers with the oily liquid core, simply by almost complete consumption of particles due to their interfacial deposition. The higher was the ratio of nanoparticles mass to the oil volume R, the smaller were the droplets of corresponding Pickering emulsion, independent of the ultrasonication power (W = 40 W) applied to the system. The size distribution of the nanosilica-stabilized emulsion droplets was always satisfactorily narrow: at R = 0·09, the number-average size was 2·3 µm with PDI = 0·45; at R = 0·32, the number-average size was 600 nm with PDI = 0·35; and at R = 0·91, the number-average size was around 260 nm with PDI = 0·2. It is also important to underline here that before und during the ultrasonic treatment, the system was purged for 7 minutes by the nitrogen flow and ultrasonication was carried out under continuous cooling in the ice bath. These measures allowed the complete avoidance of the undesired premature polymerization on the dispersion step. Finally, the polymerization of the liquid cores was initiated by heating the whole mixture up to 65°C for 24 hours. These solid containers (Figure 13) were introduced in the conventional water-based alkyd coating formulation that was then deposited on the aluminum specimens. The coatings with entrapped containers showed considerably better corrosion resistance than unmodified one, as

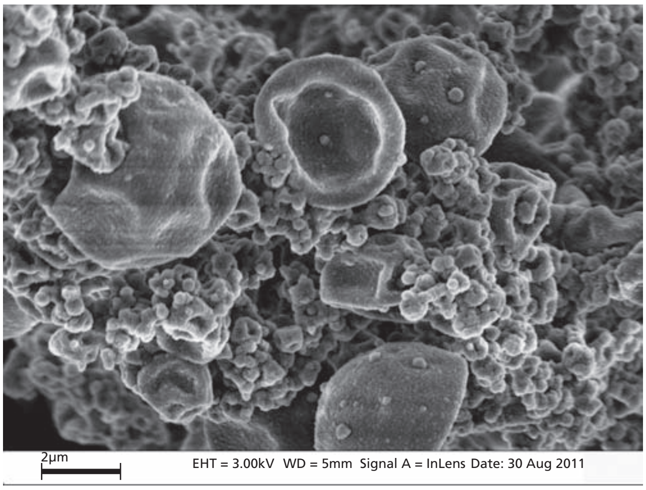

Figure 12. The polyepoxy micro- and nanocontainers filled with the corrosion inhibitor methylbenzothiazole (Me-BT) obtained by *in-situ* polymerization method of O/W emulsion.

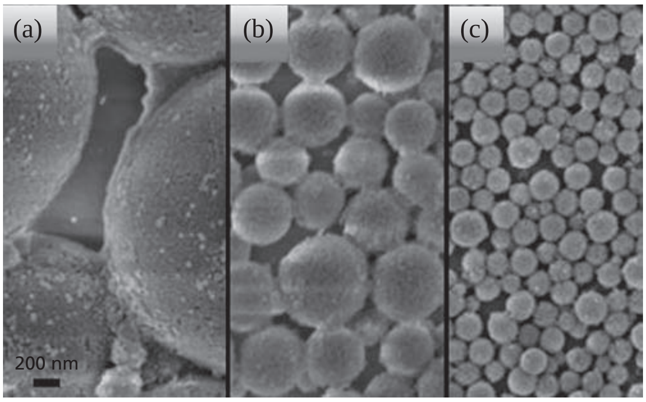

Figure 13. SEM micrographs of silica-PS/8-HQ micro- and nanocontainers stabilized initially by the interfacial deposition and finally synthesized by *in-situ* polymerization method at different silica-mass to oil-volume ratios ($m_{particle}/V_{oil}$) (a) 0·09 (b) 0·32 (c) 0·91g/ml (Haase *et al.*, 2011 submitted).

was confirmed by the electrochemical impedance spectroscopy (EIS) and scanning vibrating electrode technique data (Figure 14).

6. Use of ultrasound for the preparation of emulsion-based containers (and physicochemical aspects of ultrasonic emulsion treatment)

All the methods of containers preparation via emulsion route considered above, physical as well as chemical, include generally two subsequent steps, in the first, the emulsion was preformed and in the second—encapsulated, either chemically or physically. Ultrasonication is, in this sense, a unique technique that allows the unification of these stages in only one procedure. The application of this method for the fabrication of micro- and nanocontainers is based on the specific physical and subsequently chemical phenomena accompanying the propagation of ultrasound wave inside a liquid medium. On periodic density oscillations with a typical frequency between 20 kHz and 5 MHz, the gas-/vapor-filled microbubbles (so-called *caviation bubbles*) are created in the medium bulk. The implosive collapse of these bubbles at almost adiabatic conditions leads to the very fast energy release causing locally tremendous values of pressure (≈10^8 Pa) and temperatures (≈5000 K; Suslick *et al.*, 1986). These extremely harsh physical conditions in turn lead to the formation of free radical species occurring at the gas-/liquid-interface of cavitation bubbles. Highly reactive free radicals react immediately with other species in their vicinity inducing various sonochemical reactions. These extraordinary features of ultrasonic treatment in liquid media have been effectively exploited for the container fabrication. For the first time, this ability of ultrasound was demonstrated on the two-phase oil/water system containing protein bovine serum albumin in the aqueous phase (Suslick and Grinstaff, 1990). Application of the high-intensity ultrasound led to the formation of oil-filled proteinaceous microcontainers with protein shells stabilized by interprotein disulfide cross-linking of cysteine residues. Other type of intermolecular interactions promoting the containers formation on ultrasonic treatment is the hydrogen bonding or ion pairing, for example, as shown in (Dibbern *et al.*, 2006) or, more recently, in work performed in our group (Teng *et al.*, 2007). In the latter publication, the stability improvement of the polyglutamate oil-filled nanocontainers by the subsequent PEs L-b-L interfacial adsorption (see section 4·2 of this work) was presented. Moreover, the addition of surfactant (SDS) into the aqueous phase prior to ultrasonication led to the smaller and more monodisperse containers with volume-average size of 350 nm and PDI = 0·32. The nanocontainers that were obtained possess obviously core/shell morphology, for example, from the observation of numerous hollows in the container monolayer occurring when they break or of darker concavities on the surface of individual randomly distributed containers in the middle part (Figure 15).

Due to high versatility of L-b-L adsorption approach, the modification of protocontainers obtained by ultrasound can be done not only by the L-b-L deposition of PEs but also of other species, for example, nanoparticles as was reported in (Han *et al.*, 2008). Herein, the initial microcontainers formed by the high-intensity ultrasound treatment and possessing shells comprised of the interlinked human serum albumin were subsequently coated by three PE layers deposited by L-b-L adsorption. The L-b-L

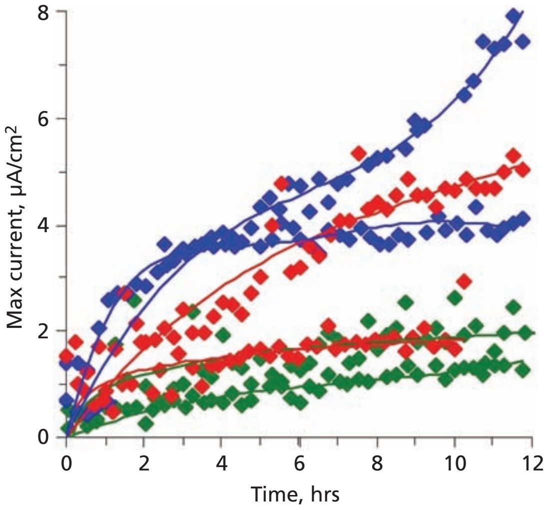

Figure 14. Results of measurements by the scanning vibrating electrode technique (SVET) obtained for scratched blank and modified alkyd coatings on aluminum in 0·1 M NaCl solution. Coatings: without containers–blue, with 10 wt% of containers–red, coating with 20 wt% of containers–green. (Haase *et al.*, 2011 submitted).

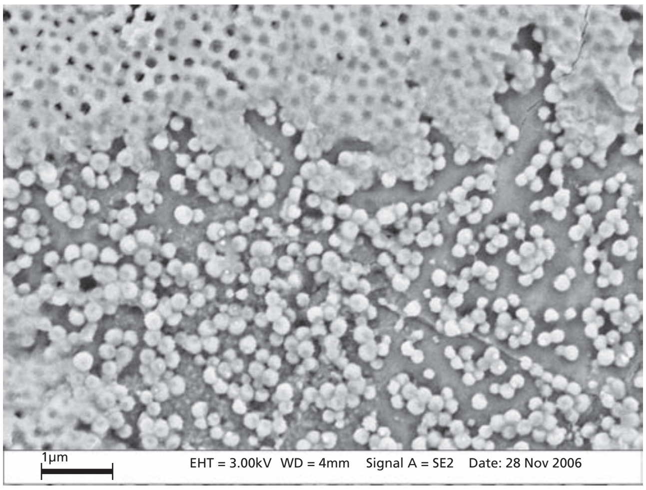

Figure 15. Polyglutamate oil-filled nanocontainers fabricated by ultrasonication of O/W two-phase system with sodium dodecyl sulfate as surfactant and subsequent L-b-L interfacial adsorption of three polyelectorlyte bilayers–$(PEI/PAA)_3$.

deposition was also extended to the formation of a fourth layer made of citrate-stabilized magnetite nanoparticles. Finally, another PE layer was brought over to stabilize the particle deposition onto polyelectrolyte shell. Presence of the magnetic nanoparticles in the shell composition imparts to the containers an additional ability to be controlled and triggered by an external magnetic field, for example, for the protective or targeted delivery purposes.

Further development of this idea was demonstrated very recently in (Borodina *et al.*, 2011). The stable microcontainers filled with the oily vitamin E solution and the shells made of polysaccharide gum acacia (GA), were produced using an ultrasound treatment of a two-phase liquid system. The initially coarse 10 v/v% O/W emulsion was sonicated at the intensity of 23 W.cm^{-2} and 20 kHz frequency for 2 minutes in the ice-cooled water bath. Ultrasonic treatment yielded a dispersion of stable nanocontainers, whose size was only slightly varied on storage at room temperature for more than 2 months. This high stability of containers was explained by the sonochemical effect of high-intensity ultrasound on the GA biomacromolecules—cross-linking between the polymer chains of polysaccharides and glycoproteins in GA that contributed to the formation of stable nanocontainer shells. The surface of the microcontainers obtained was subsequently coated by the natural polyelectrolyte poly-L-lysine and demonstrates the possibility of their future functionalization with various active substances for several biomedical applications.

The microcontainers loaded with the vitamin E were then homogeneously embedded into a biocompatible coating made of calcium alginate hydrogel matrix. The measurements of kinetics release of vitamin E from microcontainers entrapped in the gel coating were performed in the artificial model release medium (50 wt% aqueous ethanol solution). The character of release from the biocompatible protective coating was much more sustained compared with the case of free-loaded vitamin, demonstrating approximately 20 times longer release period. The synthesized coatings may find their application for protecting skin cells from impacts producing free radicals (due to the antioxidant activity of vitamin E), help prevention and treatment of sunburns as well as for the protective antiaging and wound-healing treatments.

By extension of the polymers used for the shell formation to the other types of biopolymers and by use of various classes of biologically relevant protective agents, the developed bioactive coatings could open new applications in many fields, particularly these concerning medicine, pharmacy and cosmetics.

7. Conclusions

The biomimetic self-healing and self-protecting coatings are a new class of active feedback materials with multifunctional properties. Aggressive system-external or internal factors serve as triggers for the switching of protective effect of these systems, providing a very economical and sustained and consumption of active agents making such types of coatings especially environment friendly.

The crucial element of self-healing and self-protecting coatings is the micro- and nanocontainers embedded in the coating matrix and impart to it various protective features. This is only possible due to sophisticated construction of the containers joining the specially designed stimuli-responsive shells and cores filled with diverse types of protective agents like corrosion inhibitors, biocides, and so on. Encapsulation of O/W or W/O emulsion is the straightforward and most economically sound approach to prepare the micro- or nanocontainers with core/shell or solid-bulk morphology. Different physical and chemical methods suitable for this purpose are discussed in detail in this paper, the concrete practically relevant examples of their realization are shown and the advantages as well as drawbacks of container prepared are considered.

The choice of containers appropriate for each particular application is dictated by the requirements to the substrate or coating protection (i.e. against corrosion, biofouling and so forth) and is additionally complicated by the multilateral interactions in the system substrate/coating matrix/containers/protective agent. Some prototypes of self-protecting materials relevant for the both technical and biomedical applications are demonstrated.

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