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# Slow release of a biocidal agent from polymeric microcapsules for preventing biodeterioration

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ABSTRACT

Water-soluble biocides are prone to excessive leaching and high concentrations are therefore required in surface coatings for successful protection of a surface against biodeterioration. Encapsulation prolongs the lifetime of biocides in different matrices by protecting them from leaching and by releasing them slowly. In this study, sodium benzoate as a model water-soluble biocidal agent and Congo Red dye as an capsulation indicator were incorporated into branched polyethyleneimines (PEIs) with molecular weights of 1300 and 5000 g/mol. Microscopic investigations verified that the Congo Red dye and sodium benzoate were entrapped within the capsules. The encapsulation capacity, release behaviour and efficiency of the encapsulated model biocide against two brown rot species *Coniophora puteana* and *Serpula lacrymans* were determined. The encapsulated water-soluble model biocide inhibited the growth of the decay fungi. The release of the biocide was based on slow diffusion from the capsules. The molecular weight of the encapsulated agent and the polyethyleneimine affected the release rate.



## 1. Introduction

Exterior wood coatings have a life expectancy of 5–10 years. The actual service life of a coating exposed to outdoor weathering depends on the specific properties of the coating – such as its ability to protect against moisture and to prevent photochemical surface degradation and microbiological degradation – as well as the wood species and the exposure conditions [1–5]. Biocides are incorporated into coatings in order to prevent the growth of microbes on the dried coating surface; the biocide concentration in paint, for instance, is normally 0.5 wt.%. In theory, the protection time of a coating could be prolonged simply by increasing its biocide concentration. However, this would alter the mechanical properties of the coating [6]. Conventional biocides are very often subjected to environmental stresses, such as rain, temperature extremes, and UV radiation, which reduce the efficacy of the biocide [7]. Biocide leaching due to such stresses renders material surfaces vulnerable to growth of microorganisms such as algae, mould, blue stain and decay fungi, where moisture and temperature conditions are favourable [8–11].

Encapsulation provides a potential environmentally acceptable and controlled means of prolonging biocidal activity in coatings. Encapsulation protects against biocide leaching and UV-induced degradation, which in turn increases the lifetime of the coating [12]. Microencapsulation also provides a method to introduce into wood biocides that have very poor solubility in water-based matrices [13]. In addition, controlled release of certain biocides has resulted in a reduction in the threshold levels of biocides to prevent microbiological attack [7,13–15]. Blends of biocides are often used to enhance coating performance, as one biocide alone cannot always provide the desired results under demanding and varying climate conditions. Encapsulation of different biocides inside different microcapsules enables combinations of various biocide-capsule systems within a coating matrix, which then release the biocides at different rates [16].

The active compounds are encapsulated into nano/microcontainers with controlled shell permeability, and the capsules can be introduced into pre-treatment, primer, or topcoat matrices. The release of the biocide from the containers can be free, controlled [7,17], or triggered [18]. Most of the studied applications are based on slow, controlled diffusion of active agents through the container shell. Bioactive agents have been embedded in polymeric nanoparticles [13–15], microspheres [6], porous silica microparticles [12], inorganic silica framework [7], sol–gel matrices [17] or in modified nanoclay [4].

When paints or coatings are formulated with microcapsules, the mechanical stability of the capsules must withstand the shear forces during the mixing processes as well as the compression forces during application (e.g. brushing). If the capsule wall is not strong enough, the capsule may break during the application

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process. Microcapsules were found to have no effect on the physical or mechanical properties of paints when the size was optimized to 0.2–20 μm in diameter [19]. On the other hand, Samadzadeh et al. [20] have shown that coating adhesion may be negatively affected by the addition of microparticles. In addition, the distribution of capsule size, shell wall thickness, morphology and porosity, capsule shape, and loading within the binder matrix must be optimized in order to attain adequate release rate, formulation, storage, application and performance properties. In typical coating applications, the biocide loading of the capsule varies between 10 and 25 wt.% [19]. In general, when the critical pigment volume concentration (CPVC) in a paint system is exceeded, the appearance and behaviour of the paint change considerably. For instance, the permeability of paint clearly increases above the CPVC point, whereas gloss values decrease. When adequate interaction between a binder and fillers/pigments is ensured, the additives have a reinforcing effect on the paint film at concentrations below the CPVC point. Typical pigment volume concentrations (PVCs) vary from 15% to 45%; however, higher quality flat paints generally have PVCs in the 38–50% range [21]. These figures and results give some guidelines and limits for the loading capacity of coatings with microcapsules.

Polyethyleneimines (PEIs) offer one type of polymeric shell matrix. PEIs are polymers with primary, secondary and tertiary amine groups as well as with varying molecular weight and shape (linear, branched or combined structures). At low pH, the amine groups are protonated and thereby the polymer appears as a highly positively charged polyelectrolyte, whereas in high pH conditions the polymer is neutral. Polyethyleneimines are used widely as adhesives or dispersion and flocculating agents in pharmaceuticals, foods, and household and personal care products, for example [22].

Polyethyleneimines have also been used for encapsulation of organic molecules as well as metal ions [23–27]. Polyethyleneimines used for enzyme immobilization have resulted in capsules with a semipermeable membrane having a porous structure, which maintains the enzyme inside but allows substances to diffuse out of the capsule [28–30]. Bioactive paper with high water resistance and high enzyme lifetime was provided by encapsulation of laccase [30].

The aim of this study was to develop a method for encapsulation of water-soluble model biocidal additives to limit their leaching. In the study, sodium benzoate was used as a model biocide for a water-soluble biocidal agent. Sodium benzoate was encapsulated via interfacial polymerization into polyethyleneimine (PEI) capsules. The chosen method and materials were envisaged to be a potential combination for biocide applications based on previous results with laccase encapsulation showing adequate mechanical properties, including compression forces as high as 100 N [30]. The synthesis time of the PEI capsules is only 2 h, compared to many other encapsulation processes, which require one or several days. The encapsulations were carried out with two different molecular weight polyethyleneimines. Congo Red dye was used as a model substance in confocal microscope analyses to verify encapsulation within the PEI microcapsule. The encapsulation capacity and release behaviour were studied with capsules containing Congo Red dye and sodium benzoate. The efficacy of the capsules containing sodium benzoate against decay fungi was studied by means of an agar diffusion test.

## 2. Materials and methods

### 2.1. Chemicals

Polyethyleneimine (PEI, $M_w$ = 1300 g/mol), cyclohexane, Congo Red, sodium benzoate, Span 85, Tween 20 and FITC (fluorescein isothiocyanate) were purchased from Sigma–Aldrich. Sebacoyl chloride was purchased from Fluka. The chemicals were of analytical grade. The polyethyleneimine (PEI, $M_w$ = 5000 g/mol) was kindly donated by BASF.

### 2.2. Preparation of the PEI microcapsules

Polymer microcapsules were prepared by interfacial polyaddition using sebacoyl chloride as a cross-linker. The described method was developed by Poncelet et al. [31]. An aqueous phase (PEI and Milli-Q water) and organic phase (cyclohexane and 1% (v/v) Span 85 surfactant) were mixed together by agitating at 1100 rpm to produce a miniemulsion. In the final stage of encapsulation, sebacoyl chloride was added to the emulsion as a cross-linker for PEI. During the crosslinking reaction, primary and secondary amines on highly branched poly(ethyleneimine) react with the acid group at each end of the sebacoyl chloride through nucleophilic substitution to covalently link the PEI chains together. The capsule is thus built around the aqueous phase [32]. Microcapsules containing the encapsulated substance (Congo Red or sodium benzoate) were prepared by dissolving the dye or biocidal agent in the aqueous phase, which was added to the organic phase to form an emulsion. Finally, the microcapsules were rinsed with water.

Fluorescence tagged microcapsules were produced by preparing FITC–PEI before microencapsulation by diluting 2 mg FITC into 0.2 ml dimethyl sulfoxide (DMSO). 120 μl of this mixture was added to a solution containing PEI and 50 mM sodium succinate buffer (pH 4.5). Microencapsulation was performed as described above by using FITC–PEI instead of regular PEI. Prepared microcapsules containing Congo Red and sodium benzoate were dissolved in the water phase (containing PEI) at 0.5 wt.% and 11 wt.%, respectively. The capsules were either air-dried or freeze dried.

### 2.3. Confocal laser scanning microscopy

The FITC- and Congo Red-tagged PEI microcapsules were analyzed by confocal laser scanning microscope (CLSM) setup consisting of a Bio-Rad Radiance Plus confocal scanning system (Bio-Rad, Hemel Hempstead, UK) attached to a Nikon Eclipse E600 microscope (Nikon Corp., Tokyo, Japan). A water suspension of microcapsules containing 1% Tween 20 surfactant was analyzed using a 488 nm argon laser line for excitation and a band-pass emission filter at 500–560 nm or a long-pass emission filter above 570 nm for detection of FITC (green fluorescence) or Congo Red (red fluorescence), respectively. Images of the optical sections were captured with both emission filters using a 20× objective (Nikon Plan Apo, numerical aperture 0.45) to a depth of 10 μm at 2.0 μm *z*-steps.

Capsules containing sodium benzoate and the corresponding empty capsules were visualized with an Olympus BX-50 microscope (Olympus Corp., Tokyo, Japan) using epifluorescence at 420–480 nm and fluorescence at >480 nm. Micrographs were obtained using a PCO SensiCam CCD colour camera (PCO AG, Kelheim, Germany) and the CellP̂ imaging software (Olympus). The capsule sizes were determined from calibrated epifluorescence and confocal microscopy images using the measuring application of the CellP̂ software.

### 2.4. Release properties of the PEI microcapsules

Diffusion of the encapsulated substances (Congo Red and sodium benzoate) through the capsule walls in an aqueous environment was evaluated by soaking the capsules in Milli-Q water under constant stirring and by determining the amount of leached substances at set times using a UV spectrophotometer (Hitachi U-2000). In addition, the effect of pH on the release rate of sodium benzoate was evaluated by soaking the capsules (loaded with the two model biocides) in water with a pH of 5 (pH adjustment with