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Microcapsule-protected actives reduce leaching

Microencapsulation enhances anti-fouling coating performance

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Polystyrene was studied as a novel encapsulating polymer to reduce the release rates of biocides in coatings and so extend their useful life. PS microcapsules containing IPBC biocide were compared with 'free' IPBC and commercial microcapsules containing it. The experimental microcapsules were as effective as the commercial products, despite a slower biocide release rate. The hindered release of biocide is expected to provide a longer service life.

Improved durability and long-term performance of outdoor coatings are required in various industrial and domestic applications. In particular, these include func-

tional coating performance, such as easy-to-clean, self-cleaning, anti-fouling or anti-mould finishes [1].

Fouling of surfaces and its prevention using anti-fouling materials have been a subject of study for decades [2]. Both biocidal and non-biocidal approaches have been presented. Currently, the biocidal control of living organisms such as bacteria, fungi or algae consists of adding large enough amount of biocides or fungicide to the coating, which has both environmental and efficiency problems [2].

Toxic anti-fouling materials, such as organo-tin (TBT) previously used are today prohibited. New generation marine paints exists though, based on self-polishing systems, usually containing slowly dissolving pigments such as ZnO or Cu₂O included in a self-hydrolysing binder [2]. When added to the coatings in this way, the biocides may dissolve in the service environment, which reduces the efficacy of the coating and leads to even larger amounts of active agents being added. In addition, some questions have arisen concerning the use of zinc and copper, as they also have some toxicity, with the potential to affect eco-systems and accumulate in sediments.

Non-biocidal approaches, such as surface nanostructuring, have been studied to prevent the adhesion of organisms [3]. Nanostructuring may not alone adequately prevent fouling and therefore, it has been studied in combination with biocides or acoustic pulsing [4].

Encapsulation of anti-fouling active agents has received much attention [5, 6]. Some slow release anti-fouling coatings based on encapsulated active agents have been launched on the market and are said to provide long-term performance.

Polystyrene studied as a microcapsule shell

3-iodo-2-propynyl n-butylcarbamate (IPBC) is a biocide originally developed for use in metalworking fluids and wood preservatives. The toxicity in aquatic ecosystems of IPBC and other fungicides has been studied widely [7]. Microencapsulation of IPBC can be beneficial, to further control its release rate and to protect it against degradation by UV or heat exposure [8]. In addition, microencapsulation may reduce the total amount of active agent needed in the coatings, hence minimising the cumulative release to the environment.

Polystyrene (PS) is an easily processable, inexpensive, hard, brittle and biologically stable polymer with low water absorption (about 0.1 wt % at room temperature). In this respect, PS would be an interesting shell material to study, although it has not been commonly utilised in controlled release systems.

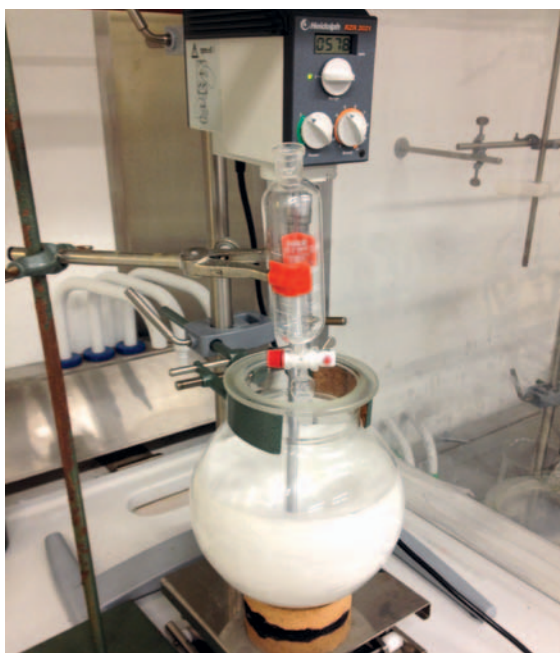


Figure 1: Lab-scale setup for the synthesis of PS microcapsules containing IPBC biocide

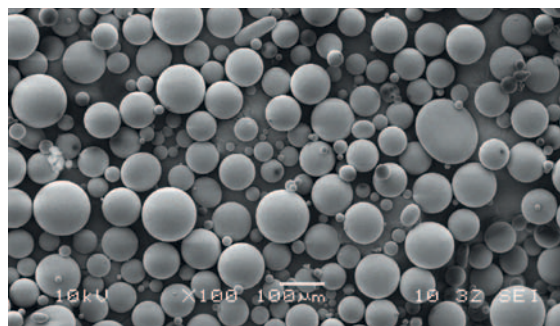


Figure 2: SEM image of synthesised PS microcapsules containing IPBC biocide

This research paper presents the synthesis and characterisation of PS microcapsules, with the objective of achieving controlled release of IPBC biocide. PS microcapsules were incorporated into paint and lacquer matrices and their anti-mould performance was demonstrated using mould tests.

How the microcapsules were synthesised

Commercially available high impact polystyrene ("Empera 622N") was supplied by Ineos Nova. The average molar mass of the polymer determined by capillary viscometer was 168.000 g/mol. Poly (vinyl alcohol) ("Mowiol 40-88", 86.7-88.7 hydrolysed, Mw ~205.000 g/mol) and 3-iodo-2-propynyl N-butyl carbamate were purchased from Sigma-Aldrich. Dichloromethane (DCM, from VWR), ethanol (Altia), methanol (Sigma-Aldrich) and acetone (Merck) were of analytical grade and used as received. All water was of "Milli-Q" purity.

The PS microcapsules were synthesised using phase separation and solvent evaporation techniques. In general, the organic phase, containing IPBC and 5 wt % PS in DCM solution, was dispersed and added to an aqueous medium containing 1 wt % poly (vinyl alcohol) under stirring. The synthesis was performed at room temperature using a Heidolph overhead stirrer. *Figure 1* presents the typical setup for the synthesis of microcapsules in laboratory scale.

The structure of the prepared PS microcapsules was characterised using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). *Figure 2* shows an SEM image of PS microcapsules containing IPBC biocide.

Table 1: Sample codes and additives in the coatings

Sample code	Additive	IPBC content in capsule / wt-%	Coating	Coating thickness/ μm
C0-1	-	-	WB acrylate paint	300
C0-2	-	-	SB PUR lacquer	150
C1-1	IPBC-suspension	20	WB acrylate paint	300
C1-2	IPBC-suspension	20	SB PUR lacquer	150
C1-3	Fungitrol 940CR	43.5	WB acrylate paint	300
C1-4	Fungitrol 940CR	43.5	SB PUR lacquer	150
C1-5	IPBC in experimental PS capsule	16.5	WB acrylate paint	300
C1-6	IPBC in experimental PS capsule	16.5	SB PUR lacquer	150

Microcapsules tested in two different coatings

IPBC biocide with and without encapsulation was incorporated into coating matrices and coated on glass plates. Two different coating types were selected: (a) one-component waterborne (WB) acrylate paint and (b) 2-component solventborne (SB) acrylic-polyurethane lacquer (PUR) with isocyanate hardener. The coatings were provided by Tikkurila Ltd.

Table 1 summarises the sample details. Three different additives were used in the experiments. 20 wt % IPBC-suspension (C1-1 and C1-2) and commercially available "Fungitrol 940CR" (Ashland Ltd.), containing microencapsulated IPBC in dispersion (C1-3 and C1-4) were used as a reference. The IPBC content was determined as 43.5 wt % for the Ashland capsules (IPBC content 40 wt % according to the MSDS). Experimental PS microcapsules (C1-5 and C1-6) containing 16.5 wt % IPBC were used in the coating experiments.

High performance liquid chromatography (HPLC) was used to determine the IPBC concentrations in the micro-

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Results at a glance

» Preventing biofouling of various surfaces conventionally requires the use of biocides, which leach out over time reducing the effectiveness of the coating as well as contaminating the environment.

» Microencapsulation has been used to retard biocide release and so extend the lifetime of coatings while reducing biocide levels. In this work, polystyrene was studied as a possible novel encapsulating polymer.

» Polystyrene microcapsules were successfully synthesised and used to encapsulate the biocide IPBC. These were compared with IPBC in free form and in a commercial microencapsulated form.

» Lower mould growth was found in samples of paint and lacquer containing IPBC biocide. The experimental microcapsules appeared to be approximately as effective as the commercial products, despite having a slower biocide release rate.

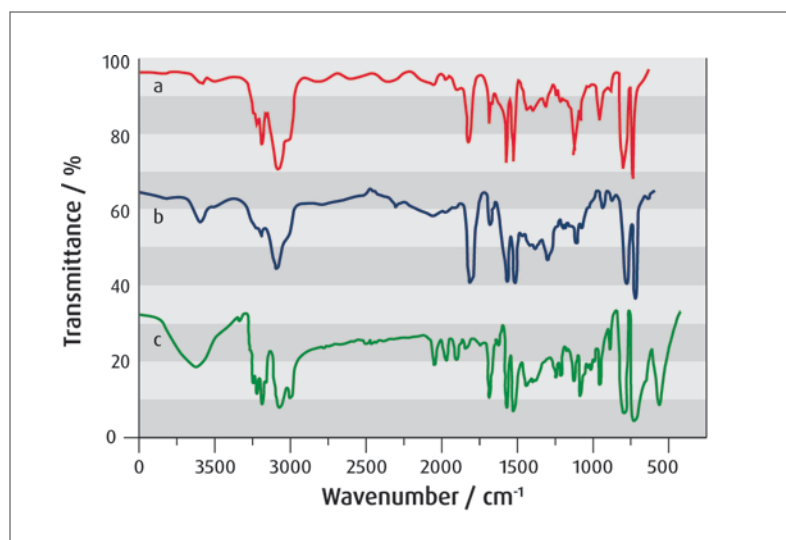


Figure 3: FTIR spectra of (a) empty PS microcapsules and PS microcapsules with increased initial IPBC content of (b) 7.5 wt %, and (c) 37.5 wt %, respectively. FTIR spectra were collected using a Perkin-Elmer "BX II" FTIR spectrometer

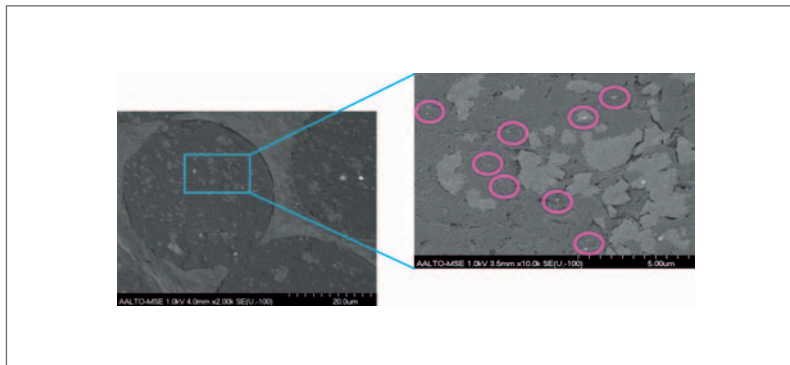


Figure 4: SEM images from a cross-section of PS-IPBC microcapsules, indicating the morphology of the capsule and the distribution of IPBC, circled in red (studied with a Hitachi "S-4700 FE-SEM" scanning electron microscope with no coating applied prior to imaging)

capsules. This was quantified at 200 nm using a seven-point calibration curve of IPBC in the range 1–100 $\mu\text{g}/\text{ml}$ ($R^2 > 0.99$).

The amount of capsules or suspended IPBC powder was adjusted to give a total concentration of IPBC in the paint matrix of 1 wt % (wet weight of the coating). The IPBC content in the wet coating matrices measured by HPLC ranged between 0.9 and 1.1 wt %.

All samples were mixed with a "Dispermat" at 2000 rpm (4 m/s tip speed) for five minutes. The coatings were applied by rod applicators to optical glass plates, size 76 x 26 mm. The wet film thickness was 300 μm for the paint and 150 μm for the lacquer.

Structural characterisation of PS microcapsules

Figure 3 shows the FTIR spectra of the empty PS capsules (a) and PS capsules containing different amounts of IPBC (b, c). The FTIR spectrum of pure PS capsules shows the characteristic absorption bands of PS due to the stretching vibration of $-\text{CH}$ (3100–2850 cm^{-1}), $\text{C}=\text{C}$ stretching vibrations (1602 cm^{-1} and 1493 cm^{-1}), CH_2 bending vibrations (1453 cm^{-1} and 1369 cm^{-1}) and $\gamma(\text{C}-\text{H})$ in the aromatic ring (756 cm^{-1} and 690 cm^{-1}).

Apparently the FTIR spectra of PS-IPBC capsules shows the combination of polystyrene and IPBC. IPBC exhibits

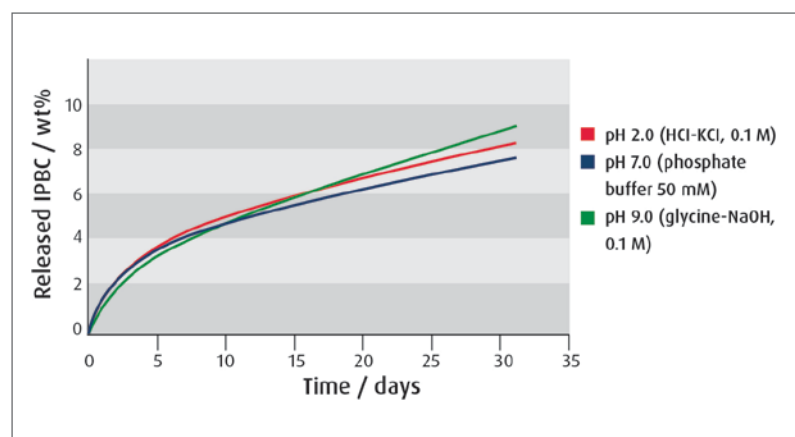


Figure 5: IPBC release from PS microcapsules into water at different pH values

intense absorption bands at 1733 cm^{-1} and 3410 cm^{-1} attributed to the $\text{C}=\text{O}$ and $\text{N}-\text{H}$ stretching bonds, respectively. Figure 4 shows the morphology of the dense PS microcapsules and the distribution of IPBC, which were obtained using SEM. The diameter of the microcapsules was 30–40 μm . The IPBC distribution can be seen from the amount of iodine (derived from the IPBC), using SEM with secondary electron (SE) detector. The SE images show a purely morphological contrast of each sample. The high iodine content in IPBC showed good contrast in the energy-filtered images. The result indicates that IPBC was successfully encapsulated into the PS microcapsules.

Measuring biocide release

The release of encapsulated IPBC from isolated PS microcapsules was studied by an HPLC technique. Microspheres (ca. 17–19 mg) were added to water (14 ml) and the mixtures were vortex mixed for 0.5 min and placed in the dark. The release of IPBC from the polymer microspheres into water was evaluated, with the samples prepared in triplicate.

Figure 5 shows the IPBC release from the PS microcapsules in alternating pH (pH 2, 7 and 9) conditions. In general, IPBC was released continuously. The change in pH did not show any remarkable effect on release behaviour. The amount of IPBC released from the coatings to water was determined during a three month period. The glass wafers coated with different paint matrices were incubated in water (40 ml) in the dark. The amount of IPBC released was determined by HPLC. Figure 6 shows the release of IPBC to water from both test coatings. In general, the release rate of IPBC stabilised after the initial burst.

The results indicate that IPBC released faster from the paint matrices in comparison to the lacquer. This is most likely due to a more permeable coating structure of the acrylate paint. Moreover, the IPBC suspension (C1-1) and commercial "Fungitrol 940CR" biocide capsules (C1-3) had significantly faster release behaviour in comparison to the experimental PS capsules (C1-5). Indeed, the suspended IPBC and the commercial IPBC capsules had quite similar release rates and behaviour. An almost identical trend was observed with the lacquer, although the differences were not as remarkable.

Procedure and results from the mould tests

The efficiency of the coatings against mould was evaluated by placing the coated glass plates on a Petri dish containing malt extract agar. Before the mould tests, the coated samples were aged (without UV light) by submerging them in water for six hours following 18 days drying in air.

The mould suspension contained the following fungi: *Aspergillus niger*, *Penicillium funiculosum*, *Chaetomium globosum*, *Paecilomyces* varieties and *Trichoderma viride*. It was spread on agar and on the sample surfaces. As a reference, birch veneer was used in the same Petri dish. The samples were incubated at 23 $^{\circ}\text{C}$ and 70 % RH. The Petri dishes were inspected once a week and all experiments were performed with five replicate samples.

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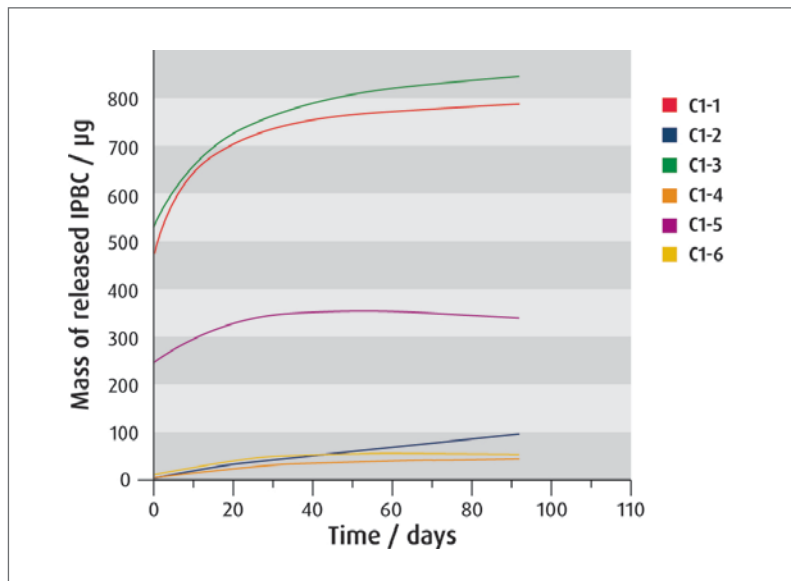


Figure 6: Release of IPBC to water from waterbased acrylate paint (C1-1, C1-3 and C1-5) and solventbased acrylic-polyurethane lacquer (C1-2, C1-4 and C1-6)

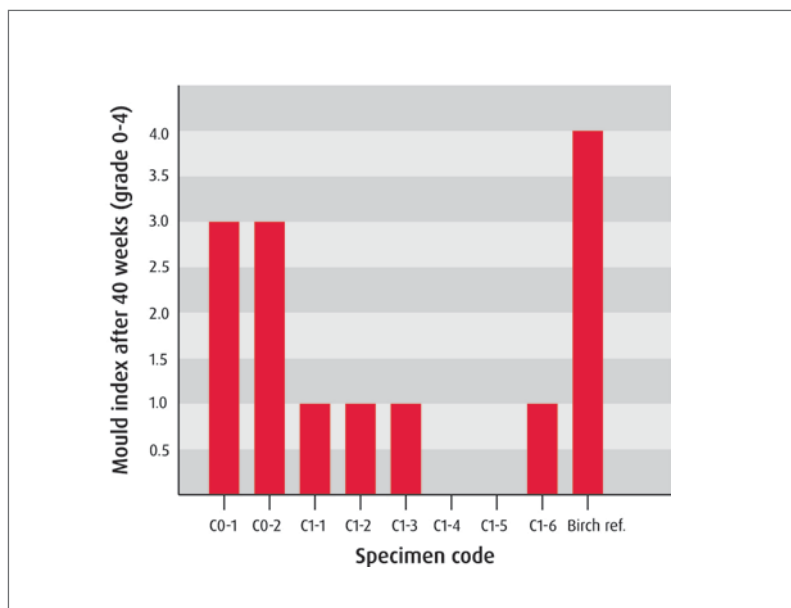


Figure 7: Mould indexes for waterbased acrylate paint (C1-1, C1-3 and C1-5) and solventbased acrylic-polyurethane lacquer (C1-2, C1-4 and C1-6) after 40 weeks incubation

The mould growth was evaluated using the mould index shown below:

- » 0 = no growth
- » 1 = visual growth ~1-10 % of the surface covered
- » 2 = visual growth ~10-30 % of the surface covered
- » 3 = visual growth ~30-50 % of the surface covered
- » 4 = visual growth ~50-100 % of the surface covered

Figure 7 presents the test results after 40 weeks' incubation time in the mould suspension. The surface of the reference birch veneer was fully covered with the mould after only six weeks of exposure. The mould growth on unmodified paint and lacquer specimens increased up to

mould index 3. As expected, lower mould growth was found in the samples containing IPBC (mould index from 0 to 1).

Indeed, the mould growth on the paint surfaces was slower than on the lacquer surfaces, which is in good agreement with the IPBC release behaviour determined by HPLC. However, no differences were noticed between the unmodified coatings after the 40 weeks' exposure.

The mould growth was low (mould index 1) in the samples containing IPBC suspension (C1-1) or commercial biocide (C1-3). Moreover, no growth was seen on the surfaces of paints containing PS-IPBC microcapsules (C1-5). The results indicate that the anti-mould performance with PS microcapsules was somewhat greater, although the IPBC release was significantly slower from the PS microcapsules. The hindered release of IPBC could be expected to provide longer protection for the paint.

In addition the mould growth was low on the lacquer surfaces. Among the coated lacquer specimens, the lowest mould growth was detected in the lacquer containing commercial encapsulated IPBC (C1-4). In addition, the specimens containing IPBC-suspension (C1-2) or experimental PS-IPBC microcapsule (C1-6) showed low mould growth (mould index 1). ◀

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