Effects of Manufacturing Conditions on the Properties of Boric Acid/Melamine-Urea-Formaldehyde Microcapsules Prepared By *in situ* Polymerization: Its Inhibition Behavior on Wood Destroying Fungi

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Water-soluble boric acid (BA) was microencapsulated by *in situ* polymerization with a melamine-urea formaldehyde shell. The effects of core-shell ratio, time, and temperature on the microcapsule characteristics were investigated. The microencapsulated BA was tested for its effectiveness against wood-destroying fungi. The results showed that the core:shell ratio affected the individuality of the microcapsules (MCs), and the most individual microcapsules were those with the 1:1 core:shell ratio. The microencapsulation temperature at the 1:1 core:shell ratio affected the surface porosity and size spectrum of MCs. The surface was porous, and the size spectrum was narrow at 50 °C. The microencapsulation reaction time at the 1:1 core-shell ratio did not have a considerable effect on the MC size. Although the MC size spectrum varied in the studied parameters (core: shell ratio, temperature, time), the average MC sizes were large enough to pass through the bordered pits of the softwood cell wall. Slow boron release was obtained by optimizing the MC preparation parameters. The optimum microencapsulation parameters for slow release of BA were the 1:1 core:shell ratio, 50 °C, and time of 120 min. The capsules produced at optimum microencapsulation parameters were biologically active against the fungus *Coniophora puteana* and leaching resistance was improved.

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INTRODUCTION

Wood is an excellent material that can contribute to environmental sustainability. To ensure its longevity, wood must be treated with various methods and chemicals to protect it against abiotic and biotic factors. Borates, which provide a very broad and effective protection against wood-decay fungi and harmful insects, cannot be used in areas where it can meet soil and water because it leaches away from the wood (Lloyd *et al*. 2001). The easy leaching of boron from the wood is due to its inability to diffuse well into the wood. Boron is not fixed to the wood cell walls and does not react with it. Boron compounds form Van der Waals and hydrogen bonds in wood. These weak bonds explain the easy leaching of boron in outdoor conditions (Can 2018).

There are many studies conducted to prevent the leaching of borates. In these studies, borates were fixed to the wood to prevent their leaching, but their activity against fungi and insects was reduced or completely lost (Lloyd *et al*. 1990; Lloyd 1998). Partial fixation systems that do not hinder the mobility mechanism of borates have been developed (Liu *et al*. 1994; Lin *et al*. 2001; Kartal and Green 2003; Kartal and Imamura 2003; Baysal *et al*. 2004). The Envelope system, in which creosote and boric acid are used together, has been commercialized and currently used in sleepers (Gauntt and Amburgey 2005). However, this system is both expensive and causes undesirable surface properties in wood.

Microencapsulation is a technique in which active substances are surrounded by very small capsules. Microencapsulation is suitable for many target materials, both hydrophobic and hydrophilic, and can be an alternative method to reduce leaching of boron-based wood preservatives. Many active substances can be microencapsulated, including biocides. With the microencapsulation system, the removal of the active substance used as the core material can be significantly reduced, and the release time can be extended (Hack *et al*. 2012; Shim *et al*. 2013). The use of MCs in the forest industry is fairly new, but they have been used in pharmaceuticals, cosmetics, agrochemicals, textiles, and food (Li *et al*. 2011; Scott *et al*. 2011) in products such as fragrance, phase change agent, insect-fly repellant, antibacterial agent, wound healer, and moisturizer. They have been tested for energy saving, heat storage, and wood preservation applications (Yuan *et al.* 2006; Wu *et al.* 2008; Hayward *et al*. 2011; Mathis *et al*. 2018; Wang *et al.* 2020; Can *et al*. 2021; Yan *et al.* 2021).

It is important to determine the solubility, mobility, and fixation of preservatives for effective wood impregnation. The production parameters should be optimized by considering these factors in the microencapsulation process. There are various chemical and physical methods used in microencapsulation. Simple and complex coacervation, interface polymerization, supercritical fluid method, and *in situ* polymerization are chemical methods, whereas spray drying, centrifugation, rotational suspension separation, fluidized bed, electrostatic method, cooling drying, and hot melt are physical methods (Ghosh 2006). *In situ* polymerization is one of the most common technologies used for commercial MC production because of its easy operation (low temperature and simple equipment), clear size distribution, and stability (Brown *et al*. 2003).

The shell material used in microencapsulation determines many features (morphology, size, structure, oscillation, mechanical properties, *etc*.) of the MC (Keller and Sottos 2006; Su *et al*. 2007). Amino polymers such as melamine formaldehyde (MF), urea formaldehyde (UF), and melamine-urea formaldehyde (MUF) resins have a wide range of uses as shell material because of their manageable preparation forms, low cost, and compatibility (Gao *et al*. 2002; Keller and Sottos 2006; Wu *et al*. 2008; Wang *et al*. 2016a; Yaman 2017; Liu and Xu 2019). MF resins are harder and more water and weather resistant than UF resins due to the ring structure of melamine, but MF resins are expensive (Likozar *et al*. 2011; Zhou *et al*. 2013). To reduce the cost of MF resins, melamine and urea can be used together, up to half at most, without sacrificing performance (Likozar *et al*. 2011). Because melamine has higher reactivity than urea, it can react with more formaldehyde and subsequently reduce formaldehyde emission, so MUF resins are often used as shell materials in microencapsulation.

In addition to the production methods and shell material type, other preparation parameters (reaction temperature and time, core/shell incorporation ratio, pH, mixing speed, type of shell/core material used, production method, added auxiliary chemicals) affect the morphological characterization and properties of the MC. These parameters

should be optimized for their target usage. For example, the sizes and diameters of MCs effect their mobility and fixation. If the size and diameter of MC becomes smaller, the penetration of MCs through the wood cell lumen and pits is improved (Hayward *et al*. 2011). Increasing the reaction temperature during MC preparation expands their size, and many different sizes can be produced (Han *et al*. 2020; Huang *et al*. 2020). In addition to the temperature, the long reaction time causes the MC sizes to increase, and the wall thickness also increases (Huang *et al*. 2020). The incorporation rates of the core/shell material also have effects on the morphology of the MC. As the amount of shell material incorporation increases, a harder shell is formed and larger MCs are obtained. However, if this ratio is equalized, a relatively thin shell and a more porous structure has been observed (Li *et al*. 2016; Zhong-qing *et al*. 2020).

In this study, microencapsulation was tested for the slow release of boric acid (BA) into wood. If an appropriate microencapsulation technology is not used, boron will be trapped in the microcapsule and leaching can be prevented, which may lead to loss of biological efficacy. The preservative properties of borates are primarily due to the tetrahydroxyborate ion $[BH_4]^-$, which is formed upon exposure to water. The ion mobility is necessary for enzyme inhibition and change in membrane function, which is vital for wood destroying fungi. When the borate is immobilized, it has no effect on biological efficacy (Lloyd *et al*. 1990; Lloyd 1998). Therefore, the slow release of boron was accomplished by optimizing the MC preparation parameters. For the first step, the optimum MC production parameters were determined by using different reaction temperature, reaction time, and core/shell ratio for slow release of BA from MC. The anti-fungal effect of microencapsulated boric acid against *C. puteana* was examined.

EXPERIMENTAL

Materials and Chemicals

Melamine-urea formaldehyde resin was used as the shell material, and BA (density: 1.44 g/cm^3, pH: 3.5 to 5, solvent: water/alcohol/glycerin; color: white and odorless) was used as the core material. BA was procured from TEKKİM Chemical Industry and Trade Limited Company (Bursa, Turkey). The melamine (color: white, purity: 99.8%, humidity: 0.02% max, pH: 8.1, melting point: 350 to 355 ºC, density: 800 kg/m^3) and urea (total nitrogen: 46% by mass, pH: 9.1, biurea: 0.92%) were used in the preparation of melamine urea formaldehyde resin, and they were provided by AGT Forest Products Industry Trade Inc. (Antalya, Turkey). Formaldehyde (purity: 37%, stabilization min: 10% methanol, melting: <-15 ºC, boiling: 93 to 96 ºC), triethanolamine (M: 149.19 g/mol, melting: 21 ºC, boiling: 360 ºC, density: 1.12 to 1.16 g/cm^3, diethanolamine: <=10.8%, water: <=0.2%), and acetic acid were procured from TEKKİM Chemical Industry and Trade Limited Company (Bursa, Turkey). Sodium hydroxide was supplied by Merck (Darmstadt, Germany). Black pine wood was obtained from the Cemaller warehouse of Karabük Forest Management as a 2 m long, 24 cm diameter log with an average of 10 cm heartwood. It was then cut into 19x19x19 mm^3 pieces. 32 samples were prepared for each of the impregnation chemicals and 16 of them were exposed to the leaching test. The other 16 were used as references.

Preparation of Microcapsules

MUF prepolymer solution was synthesized according to Han *et al*. (2020). First, 14.8 g of urea, 15.5 g of melamine, and 60 mL of formaldehyde were mixed with 60 mL of distilled water. The mixture was adjusted to pH 8 to 9 with triethanolamine and then it was heated to 70 °C. Mixing was continued until a transparent MUF prepolymer was obtained. The mixture was cooled to 25 °C, and 375 g of distilled water was added to obtain 10% by mass MUF prepolymer.

BA/MUF microcapsules were manufactured by *in situ* polymerization using the method from Wang *et al*. (2016), with some modifications (Table 1). The MCs production scheme is given in Fig. 1. A mixture was prepared by adding a certain proportion of BA as a core material to 100 mL of water and mixing at 1000 rpm for 10 min. MUF was added to the prepared core material mixture with a BA: MUF ratio of 2:1, 1:1, or 1:2. Acetic acid was added so that the resulting mixture was at pH 3 to 4. The mixture was stirred at a 50 °C or 75 °C at 350 rpm for 80 min or 120 min (Table 1). The resulting mixture was filtered; the capsules were washed with distilled water. The filtered capsules were placed in a watch glass and dried at ambient temperature until they reached a constant weight. A total of 5 different MCs were prepared.

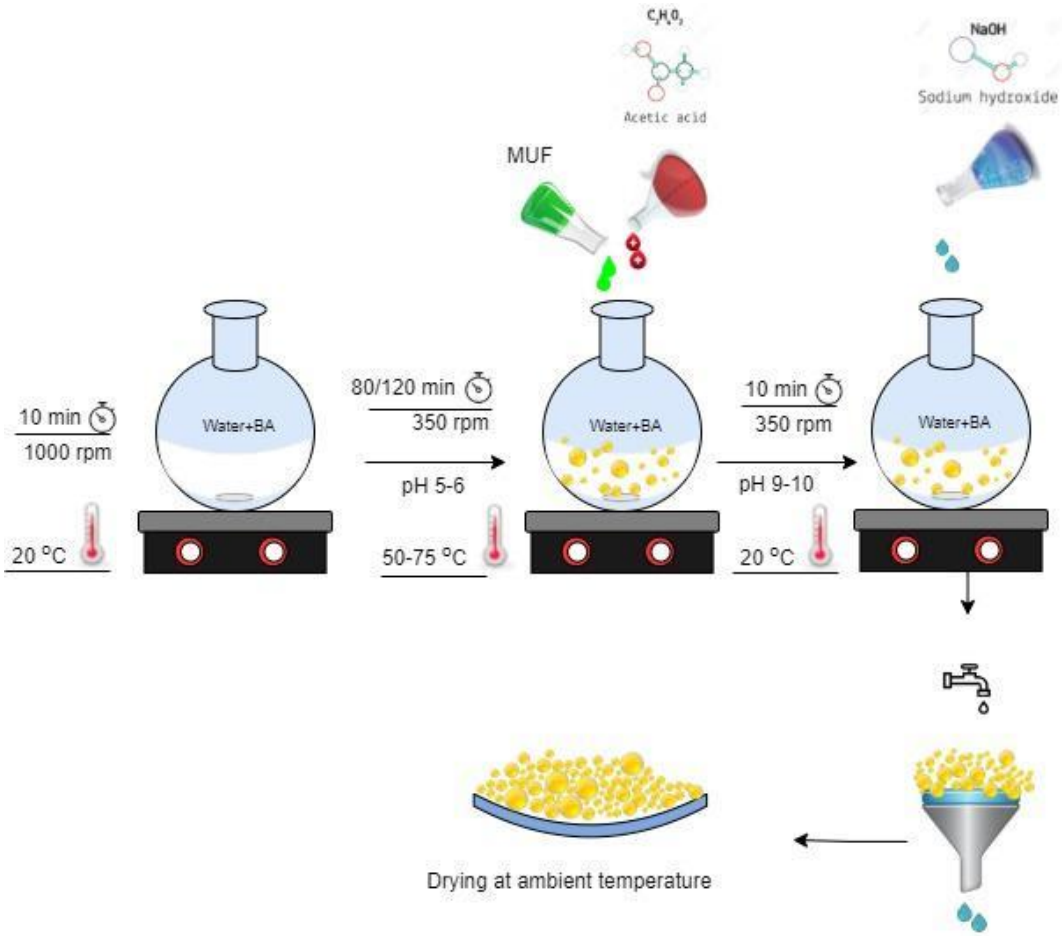

Fig. 1. Microcapsule production stages

Table 1. Experimental Design

Samples	Core / Shell Ratio	Reaction Temperature (°C)	Reaction Time (Min)	Final Reaction pH	Reaction Rate (rpm)
1-1	2:1	50	120	5-6	350
1-2	1:1	50	120	5-6	350
1-3	1:2	50	120	5-6	350
1-2	1:1	50	120	5-6	350
2-1	1:1	75	120	5-6	350
3-1	1:1	50	80	5-6	350
1-2	1:1	50	120	5-6	350

Characterization of Microcapsules

The surface morphology, size, and distribution of MCs was analyzed by scanning electron microscope (SEM; Carl Zeiss Ultra Plus Gemini, Karabuk, Turkey). The microcapsule powder samples were sprinkled on conductive adhesive and sprayed with a thin layer of platin.

The inner structure and thickness of the MC shell were studied by transmission electron microscope (TEM; JEOL JEM-1220, Eskisehir, Turkey). The microcapsule powder was dispersed into distilled water by ultrasonication. The dispersion was dropped into the 300-mesh Formwar/carbon grids and dried for observation.

The encapsulation efficiency of MCs was analyzed by differential scanning calorimetry (DSC; Perkin Elmer Diamond, Eskisehir, Turkey). DSC studies were carried out under nitrogen gas at -50 °C to +80 °C, with a heating rate of 10 °C/min. The boric acid contents in different boric acid/MUF microcapsules were calculated by Eq. 1,

$$\eta = \frac{\Delta H_{m,MC} + \Delta H_{c,MC}}{\Delta H_m + \Delta H_c} \times 100 \quad (1)$$

where η is encapsulation ratio of boric acid, $\Delta H_{m,MC}$ and $\Delta H_{c,MC}$ are the crystallization enthalpies and melting enthalpies of boric acid/MUF microcapsules, respectively, and ΔH_m and ΔH_c crystallization enthalpies and melting enthalpies of boric acid, respectively (Han *et al*. 2020).

Inhibition of Fungal Growth Assessment of Microcapsules

The activity of the microcapsules was tested against the brown rot fungus *C. puteana*, which attacks softwoods. All anti-fungal assays and controls were replicated three times. The optimized microcapsule and control samples (only boric acid) were added to sterilized potato dextrose agar (PDA) to give 1% concentration of biocides (both MCs and boric acid). The fungal mycelia reached the edge of control plates (without adding biocides) by incubating at 26 ± 1 °C for 7 to 8 days. The colony diameter was measured at the end of the test, and the percentage mycelia inhibition was calculated with Eq. 2,

$$I = \frac{C - T}{C} \times 100 \quad (2)$$

where I is the inhibition, C is the colony diameter of mycelium from control dishes, and T is the colony diameter of mycelium from dishes containing the biocide (both encapsulated and unencapsulated). At an inhibitory ratio greater than 20%, the test fungus was considered to be inhibited (Terzi *et al*. 2016).

Leaching Resistance of Microcapsules

Thirty-two pine samples that were 20x20x10 mm^3 in size were selected for the leaching test. Samples were divided into two groups that were impregnated with MC mixture and BA solution, respectively. The MC and BA solutions' boron concentrations were adjusted as 3.7% for the impregnation process. Then the samples were subjected to vacuum condition (100 mmHg) for 20 min. This was followed by a 15-h pressure treatment at 0.8 MPa. The retention levels of the samples were calculated according to Eq. 3:

$$\text{Retention (kg/m}^3\text{)} = \frac{GC}{V} \times 10 \quad (3)$$

where G is T_1-T_0 (T_1 is the impregnated sample weight, and T_0 is the sample weight before impregnation), C is the concentration of impregnation chemical, and V is volume of the sample. Then all impregnated samples were conditioned (20±2 °C; 65±5% RH) for a week before being conditioned at 40 °C to constant weight.

The leaching technique was similar to AWPA E10-12 (2012) without shaking. Wood samples were put into an 800-mL beaker of deionized water. After 6, 24, and 48 h and thereafter at 48-h intervals, the leaching water was discharged and replaced with an equal amount of fresh deionized water. Leaching tests lasted 336 h. ICP analysis was used to measure the boron contents in the leaching water and leached wood (AWPA A12, 2012).

RESULTS AND DISCUSSION

Effects of the Ratio of Boric Acid Core to MUF Shell

The weight ratios of boric acid core-MUF shell material were changed as 1:2, 1:1, and 2:1. The effects of different weight ratios of boric acid core-MUF shell material (samples 1-1 to 1-3) on the diameter and morphology of MCs were examined. The FE-SEM images of MCs are shown in Fig. 2. The encapsulation efficiencies of the samples 1-1, 1-2, and 1-3 were 98.01%, 92.84%, and 99.77%, respectively. When the encapsulation efficiencies were evaluated together with the SEM micrographs, the agglomeration in some capsule micrographs (Fig. 2-a and Fig. 2-c) may affect the encapsulation efficiency results, and the high encapsulation efficiencies may be misleading. MCs with a 1:2 core-shell ratio were spherical but agglomerated; agglomeration may result in high encapsulation efficiency (99.77%). The wall structure was porous. The size spectrum was wide (0.49 to 3.82 µm), and the average capsule size was 1.93 µm (Fig. 2-a). MCs with a 1:1 core to shell ratio were generally spherical and had a porous wall structure. They had a homogeneous size distribution, mostly narrow (0.53 to 1.90 µm), and the average capsule size was 1.22 µm (Fig. 2-b). Capsules with a 2:1 core-shell ratio had spherical, porous shells. They were more individual than the sample that had a 1:2 core-shell ratio and less individual than the samples that had a 1:1 core-shell ratio. The differences in this agglomeration degree also affected the encapsulation efficiency. There were some droplet forms of MUF accumulation on the capsule surface. The size spectrum was broad (0.25 to 3.40 µm), and the average microcapsule size was 1.55 µm (Fig. 2-c). With the reduction of the core ratio, excess MUF crust was collected on the surface of the core material, resulting in a thick and smooth shell structure. Conversely, the higher weight ratio of core to shell resulted in the fracture of microcapsules because of the thinner shell. MCs 1-2 (Table 1) were considered optimum due to their narrow size spectrum, porous surface, and individual structure.

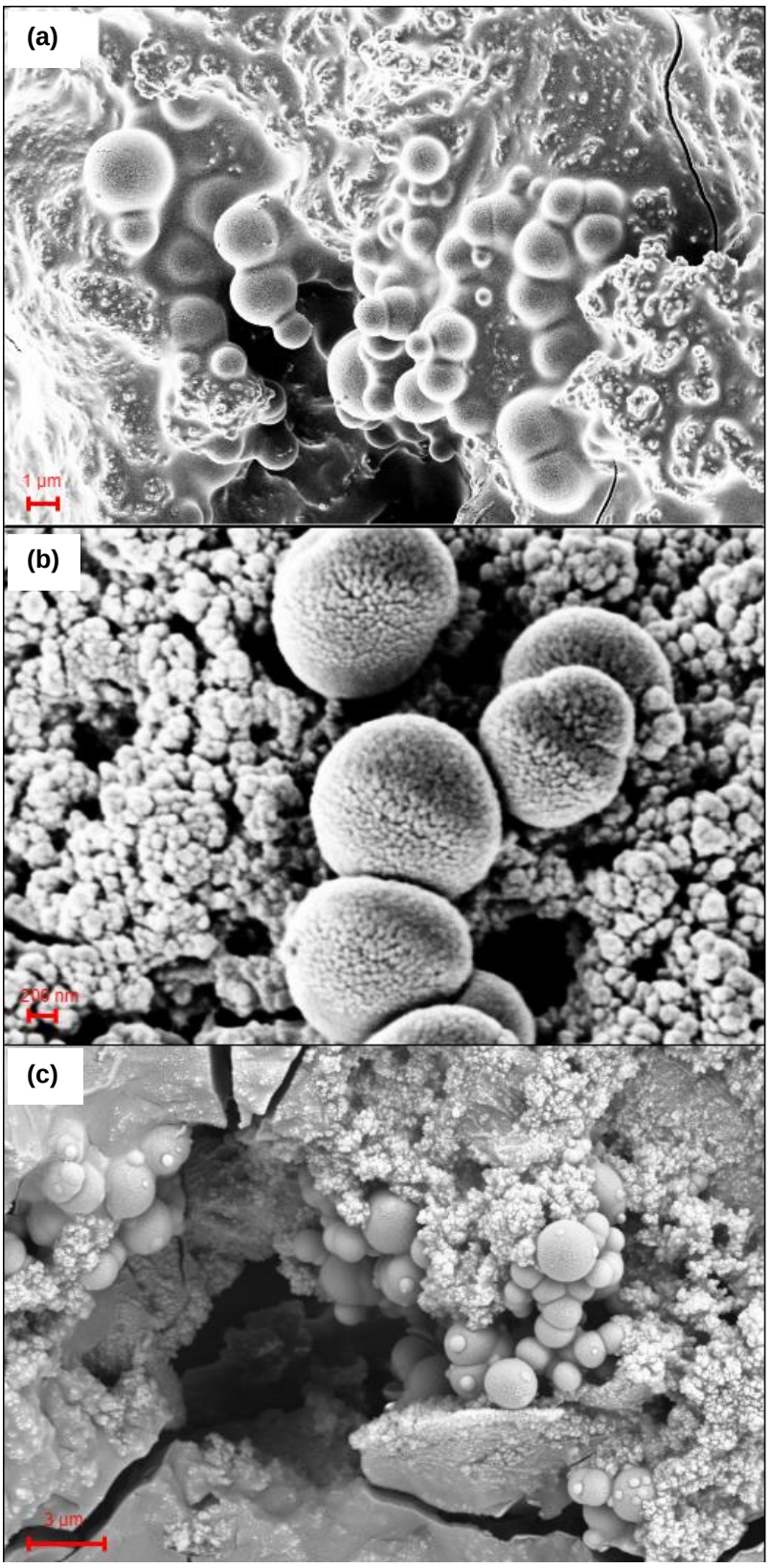

Fig. 2. Effect of core/shell ratio on morphology of microcapsules (a): 1-3, (b): 1-2, (c): 1-1

The surface properties of microcapsules vary considerably according to the core-shell ratio. The morphology and micropore structure of the capsule surface can be controlled by adjusting this ratio (Qian *et al*. 2017; Zhong-qing *et al*. 2020).

Effects of the Reaction Temperature

While the MUF shell can be formed at a reaction temperature of less than 75 °C, it is thin and incomplete. Thus, temperatures below 75 °C may be more suitable for the formation of porous structures. With increased temperature, the polymerization reaction of MUF is accelerated, resulting in increased shell thickness and greater density (Kage *et al*. 2002; Han *et al*. 2020). In this study, the reaction temperature was 50 °C or 75 °C. Figure 3 shows FE-SEM images of MCs obtained at different temperatures. The acceleration of the polymerization reaction of MUF with the increase in temperature caused the microcapsules to stick together (Fig. 3-b). This situation may cause misleading rates by increasing the encapsulation efficiency (92.84% at 50 °C, 98.55% at 75 °C). The outer surfaces of the microcapsules produced at 75 °C were smoother. MCs 1-2, which were produced at 50 °C, were considered optimum due to their porous surface and individual structure (Fig. 3-a). The temperature affected the size spectrum of MCs. The size spectrum ranged from 0.84 to 3.51 µm at 75 °C, and between 0.53 and 1.90 µm at 50 °C. At the higher temperature, the size spectrum of MCs became broader.

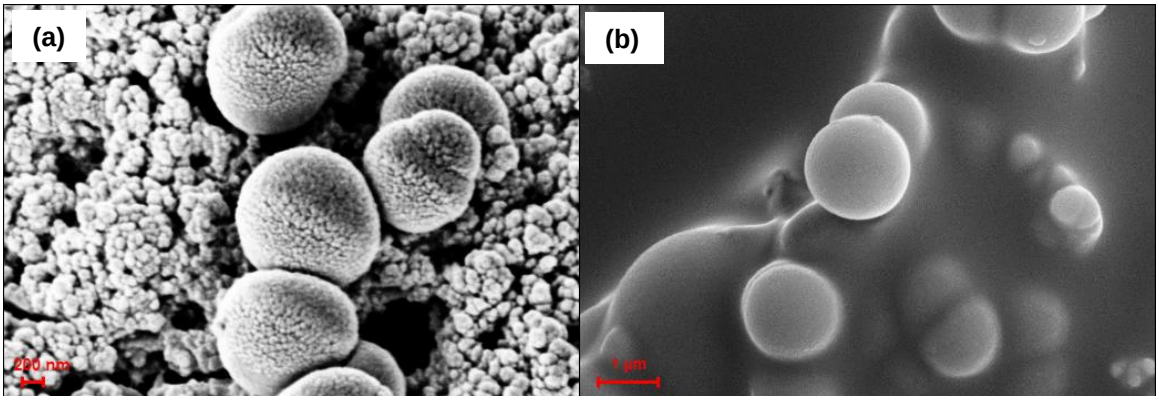

Fig. 3. Effect of reaction temperature on morphology of microcapsules (a): 1-2, (b): 2-1

Effects of the Reaction Time

The MCs after 80 min were spherical, but the outer surface was smooth, not porous. The size spectrum was narrow (0.39 to 17.2 µm), and the average microcapsule size was 0.90 µm (Fig. 4-a). MCs after 120 min were generally spherical and had a porous walls. They had a broad size spectrum (0.84 to 3.51 µm), with an average capsule size of 1.21 µm (Fig. 4-b). The encapsulation efficiency of capsules produced in 80 min was 98.89%, while that of capsules produced in 120 min was 92.84%. This high encapsulation efficiency may be due to the excess of boric acid (Fig. 4-a), which is not realistic in most applications. The MCs 1-2 produced at 120 min were considered optimum due to their porous surface and individual structure (Fig. 4-b). There was a slight increase in microcapsule sizes with increasing reaction time, but the MCs obtained with a reaction time of 120 min were more individual and still convenient to pass through bordered pits of wood cells (porous diameter of wood cell is between 5 µm and 20 µm). The reaction time did not have a considerable effect on microcapsule size. Similar results were presented by Leskovšek *et al*. (2022), where the mean size of MF microcapsules did not change significantly with reaction time.

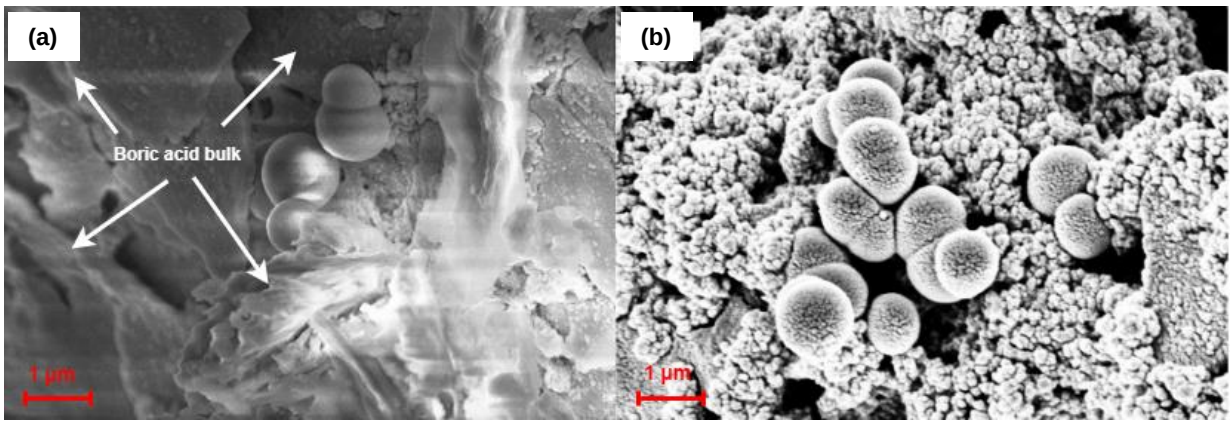

Fig. 4. Effect of reaction time on morphology of microcapsules (a): 3-1, (b): 1-2

Characterization of Optimal Microcapsule

Considering the microcapsule formation characteristics (individuality, size, and porosity) produced under different conditions, the capsules obtained at 1:1 core-shell ratio at 50 °C and 120 min conditions had the targeted slow-release properties. The encapsulation efficiency of the microcapsule was 92.84%. TEM analysis was performed on these capsules to examine the internal structure and shell formation in more detail (Fig. 5).

In Fig. 5-c, the microcapsule shell and the core material are clearly distinguishable. The porous structure in the shell was quite prominent, and the shell thickness was on average 40 nm. Boric acid will be slowly released out of the capsule through the micropores on the capsule surface, and there will be no change in its mechanism of action against wood-destroying fungi (Fig. 5-f).

In this study the sizes of optimal MCs ranged from 530 to 1900 nm. Complete penetration and even dispersion of chemicals in wood would be anticipated if the size of chemicals is smaller than the diameter of wood pores such as pits in the cross-field of parenchyma cell (10 µm), in the margo region of bordered pits (400 to 600 nm) and aperture of the bordered pit (5 to 10 µm) (Freeman and Mclntyre 2008). In light of all of this, it can be concluded that the majority of MCs produced under optimal conditions can pass through pine wood window pits, and the smaller ones can pass via the margo region of the bordered pits passageways between the tracheids. Alternatively, before being impregnated with MCs, the porosity of wood can be improved using novel methods such microwave-induced steam explosion.

The effectiveness of the optimal microcapsule in inhibiting the growth of *C. puteana*, a brown rot fungus, was investigated. At a concentration of 1%, microencapsulated boric acid had an excellent inhibition activity against wood decaying fungus. The inhibition of MCs at 1% concentration was also indistinguishable from boric acid alone at 1% concentration (Fig. 5-a and c). An inhibition of 100% was obtained. The preservative properties of borates are primarily due to the tetrahydroxyborate $[B(OH)]_4$ ion formed upon exposure to water. The ion mobility is necessary for enzyme inhibition (Lloyd *et al*. 1990; Lloyd 1998). The inhibition of fungal growth as a result of the test shows that boric acid is slowly released, and ion mobility is realized through the porous wall structure of the microcapsule (Fig. 5-a).

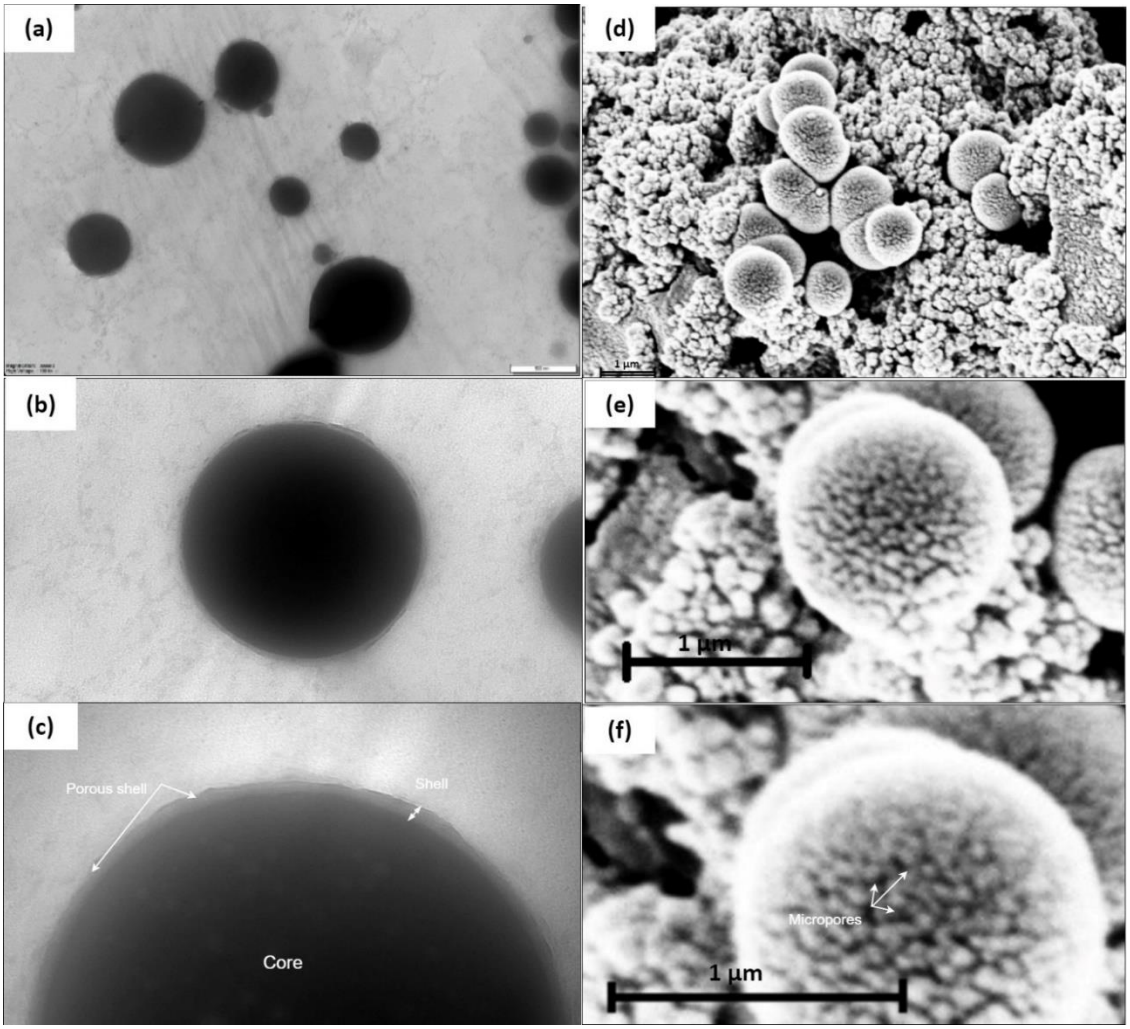

Fig. 5. TEM and SEM images of the optimal MCs (core:shell ratio is 1:1; reaction temperature is 50 °C and the reaction time is 120 min)

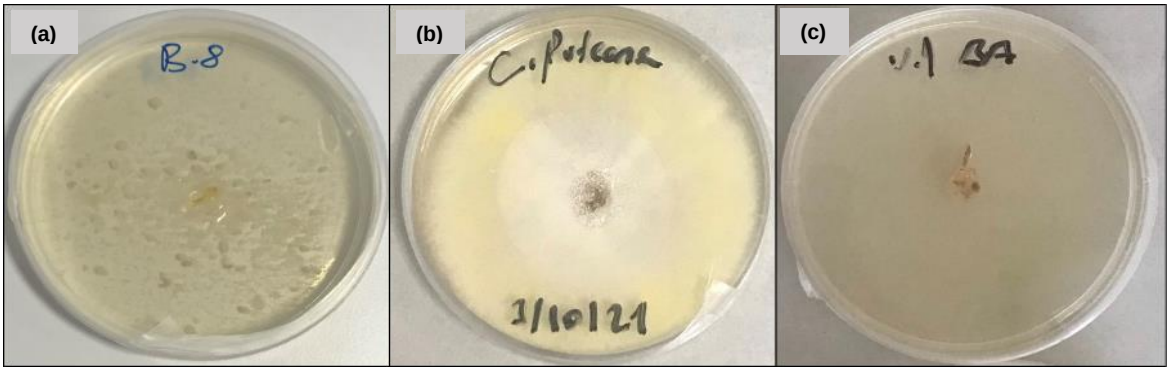

Fig. 6. Growth of *C. puteana* (1-2). (a): Microencapsulated BA at a concentration of 1%, (b): control, (c): boric acid at a concentration of 1%.

Leaching Behavior of Microcapsules

Preservative retention in wood is an indicator of how resistant it will be to deterioration (Shukla *et al.* 2019). MC impregnated wood had a retention amount of 13.05

kg.m^{-3}, whereas BA impregnated wood had a retention amount of 12,000 kg.m^{-3}. So, with microencapsulation, the retention was enhanced. Scanning electron microscopy shows the penetration of MC into the cross section of wood (Fig. 7). The MCs were gathered within the inner surface of the cell wall in a spherical shape (Fig. 7-a). MC with MUF shells contain nitrogen, thus the distribution of MC could be observed with nitrogen mapping using EDX (Fig. 7-b and c). SEM-EDX mapping showed that MCs can effectively enter inherent pores of wood and adhere to the cell wall.

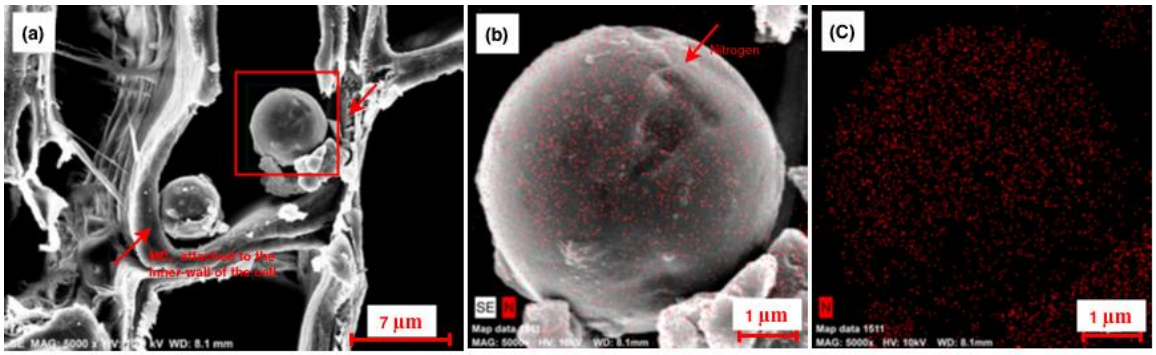

Fig. 7. SEM and SEM-EDX maps of wood impregnated with MCs. (a: Some wood tracheids are filled with a few microcapsules, b and c: The corresponding EDX mapping showing the elemental distribution of nitrogen)

The leaching test showed that MC-treated samples gave lesser boron release as compared to BA-only treated samples. At the end of leaching test running 6, 12, 24, and 48 h, the amounts of released boron from MC-treated wood and BA-treated wood are shown in Fig. 8. In BA-only treated samples, 45 ppm boron was released in total, and only 164 ppm boron was released during the first 6 h of leaching. In MC-treated samples, 31 ppm boron was released in total, and only 141 ppm boron was released during the first 6 h of leaching. This indicated that the MC structure retained the preservative longer and slowly released boron.

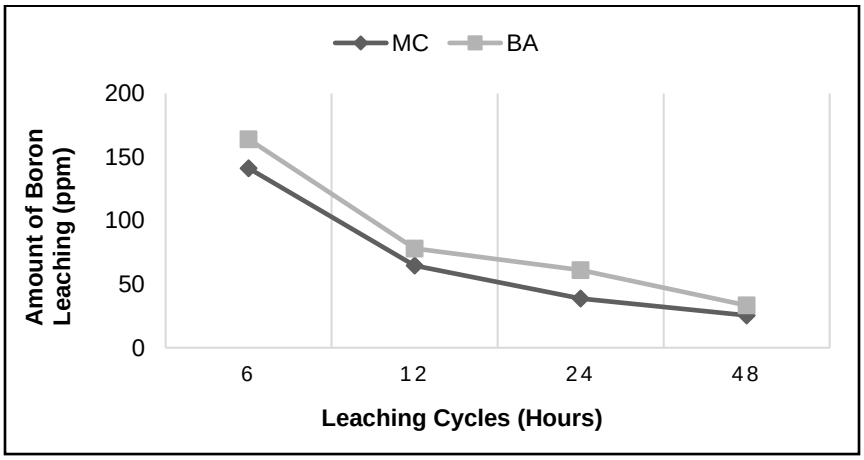

Fig. 8. Leach rate of boron from vacuum-treated black pine (Data points represent results for leachates collected after 6, 12, 24, and 48 h)

CONCLUSIONS

1. The core/shell ratio particularly affected the individuality of the microcapsules. It was determined that the most individual microcapsules were those with 1:1 core-shell ratio.
2. The microencapsulation reaction temperature at 1:1 core:shell ratio especially affected the surface porosity and size spectrum of the microcapsules. The surface was porous, and the size spectrum was narrow at 50 °C.
3. The microencapsulation reaction time at 1:1 core:shell ratio did not have a considerable effect on microcapsule size.
4. Although the microcapsule size spectrum varied in the studied parameters (core: shell ratio, temperature, time), it was determined that the average microcapsule sizes were small enough to pass through the bordered pits of the softwood cell wall.
5. The slow release of boron was obtained with optimization of microcapsule (MC) preparation parameters. Optimum microencapsulation parameters determined for slow release of boric acid (BA) from MC are 1:1 core: shell ratio, reaction temperature of 50 °C, and reaction time of 120 min.
6. The capsules produced at optimum microencapsulation parameters were still biologically active against the fungus *C. puteana* when compared with only boric acid.
7. Wood species with large macropores (>500 nm) could be easiest to impregnate with MC.
8. MC-treated wood had a lower leaching compared to BA-treated wood. The MC can little increase the retention and prevent the leaching of boron in the treated wood.

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