Microencapsulation of pendimethalin with polyurethane-urea and determination of its stability

Hatice Yılmaz a, Hüseyin Enginar a and Cemal Çifci b

aDepartment of Chemistry, Art and Science Faculty, Afyon Kocatepe University, Afyonkarahisar, Turkey; bDepartment of Chemical Engineering, Afyon Kocatepe University, Afyonkarahisar, Turkey

ABSTRACT
In this study, pendimethalin (PM) used as an herbicide was encapsulated using interfacial polymerization method. The size, shell thickness, microencapsulation efficiency, the effect of mixing speed on capsule size and active substance release times of the produced microcapsules were investigated. Polyurethane-urea resin, which is the main component of the capsule shell, was synthesized using isocyanate/glycol/amine at different molar ratio at 55°C for 180 min. It was measured that the microencapsulation efficiency was 53.2–89.1% and the microcapsule shell thickness was 399.7–1479.0 nm. The lowest and highest release percentages of microcapsules under alcohol-water and ultraviolet (UV) light for 4 h at 20°C were found to be 30.79% and 40.12%, respectively. It has been found that the microcapsules containing ethyl glycol in the capsule wall composition had the highest stability, and the capsules containing PEG-400 in the capsule wall structure had the highest capsulation efficiency.

1. Introduction
In order to meet the food demands of this rapidly growing population, more efficient farming practices are needed [1]. Unless insecticides or herbicides are used for agricultural pest control, the yield rate drops down to 60%. Therefore, the use of pesticides has become a necessity to increase crop yield and to eliminate harmful microorganisms that cause crop loss [2].

Traditional pesticides are applied by spraying or spreading chemicals to the target areas [3]. Unfortunately, lower impact on target areas is seen due to evaporation loss, running off without adsorbing on the surface, leakage, photolysis, hydrolysis and active component decomposition in spraying and spreading methods. In order to achieve the optimum effect, the pesticides must be applied repeatedly by spraying high amounts on the agricultural land. High concentrations of harmful chemicals in the soil cause pollution of the environment, damaging of ecological systems and also losing of biodiversity [4]. One of the ways to decrease the loss of active ingredients and reduce environmental pollution is the application of the active substances in agriculture after encapsulation.

Microencapsulation is the process of the coating of core substances with a solid or liquid polymer shell, without a chemical interaction between the core and the shell material [3,5,6]. The purposes of microencapsulation application include carrying highly toxic substances safely, providing biological availability, controlling the release of the core component, and protecting the core substances from environmental conditions (microorganisms, humidity, temperature, and harmful UV rays). Thanks to these properties, microcapsules are used in cosmetics, medical, textile, construction, dyeing, fire retardant, detergent, soap, and agriculture.

There are various methods for the production of microcapsules [4]. Interfacial polymerization is suitable for microencapsulation of pesticides, and high encapsulation efficiency can be achieved with polyurethane-urea. Due to the excellent physical properties and good compatibility of polyurethane materials, they are used in industrial applications, adhesives, thermal insulation, coatings in automotive industry and drug release systems [7].

For different purposes, microencapsulation with polyurethane-urea have been performed for numerous core materials which include cellulose [8], butyl stearate [9], ammonium phosphate [10], octadecane [11,12], PolyHIPE [13], PCM [14], lemon oil [15], lavender oil [16], galingal essential oil [17], OCA (tissue adhesive) [18], sweeteners [19], softener fragrance [20], maltogenic α-amylase (MG) [21], and insecticide (pirimiphos-methyl) [22].

Pendimethalin is a dinitroaniline class herbicide that is used to control grasses and weeds in dry direct-seeded rice [23], in sugarcane [24], in leguminous and other field crops [25,26] and also for economical production of cotton, tomatoes, and onions [27].

CONTACT Cemal Çifci cifcicemal@aku.edu.tr

© 2021 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group. This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.
Pendimethalin microencapsulation was achieved using cross-linked phenol formaldehyde shell materials based on polyurethane-urea and resorcinol. Pendimethalin release from microcapsules in acid, base, and neutral environments [28], the effect of organic substances and moisture on microcapsules [29], and pendimethalin release in normal and UV-light environments [30] were all studied.

In previous studies, the isocyanate substance was reacted with amine and glycol at constant mole concentrations to produce polyurethane-urea shell content during microencapsulation. In our research, however, we developed microcapsules containing polyurethane urea by keeping the isocyanate mole ratio constant while changing the amine and glycol mole ratios. The encapsulation yields and sizes of the microcapsules, the release rates of the active substances, and the effects of different glycol and amine ratios on the microcapsules were all investigated.

2. Materials and methods

Dibutyltin dilaurate (DBTL), ethyl glycol, hexa methylene diamine (HMDA), propyl glycol, poly vinyl alcohol (PVA), toluene diisocyanate (TDI) and hexane were supplied from Sigma Aldrich. Polyethylene glycol-400 (PEG-400) and Sep-Pak spindle mesh filter (0.45μm) were purchased from Merck. Pendimethalin was a gift from Biokon Chemistry. Triglyceride was obtained from Lipestrol. The chemicals used in the experiment were analytical grade and were used without any purification.

2.1. Preparation of microcapsules

The formation of PUU microcapsules was done (in Figure 1) by slightly modifying the method of Yılmaz et al., [31]. 3.0 mL of triglyceride, 0.70 mL of toluene diisocyanate (TDI) and hexane were supplied from Sigma Aldrich. Polyethylene glycol-400 (PEG-400) and Sep-Pak spindle mesh filter (0.45μm) were purchased from Merck. Pendimethalin was a gift from Biokon Chemistry. Triglyceride was obtained from Lipestrol. The chemicals used in the experiment were analytical grade and were used without any purification.

Table 1. Effect of different mixing speeds on the size of pendimethalin microcapsules.

| Mixing speed (rpm) | Ethyl glycol | Propyl glycol | Butyl glycol | PEG-400 |
|-------------------|--------------|---------------|--------------|---------|
| 3000              | 26–35 μm     | 25–30 μm      | 25–31 μm     | 22–32 μm|
| 4000              | 16–23 μm     | 14–20 μm      | 18–26 μm     | 17–21 μm|
| 5000              | 10–15 μm     | 7–12 μm       | 8–17 μm      | 6–13 μm |
| 6000              | 3–8 μm       | 1–5 μm        | 3–8 μm       | 2–8 μm  |

1 min. After pouring the emulsified droplets into the reactor, a 10% solution of PEG 400 (Table 1) and 30 μL of DBTL were added dropwise, and the temperature was raised to 55°C and held there for one hour. HMDA solution in different molar ratios of 1% (Table 1) was added dropwise to the reactor for one hour and then 2.5 mL of 3% hydrazine solution was added and mixed at a constant temperature for one hour, then the temperature was increased to 80°C, kept at a constant temperature for another one hour then cooled at room temperature, and stored at room temperature for analysis. Formation steps of microcapsules and mechanism for preparing microcapsules are shown in Figure 1.

2.2. Microencapsulation yield

A calibration chart was prepared to measure encapsulation efficiency. 5 mL solutions of PM prepared at different concentrations (10 ppm-80 ppm PM in hexane) were measured in 253.7 nm UV-vis spectroscopy and a calibration graph was obtained [32]. The PUU microcapsule solution was filtered through a blue band filter paper and dried in an oven at 75°C for one day. 0.2 g of dry capsules were taken into a closed test tube and 5.0 mL of hexane was added, and the PM in the capsule was transferred to the hexane phase within 24 h. The solution containing PM was shaken in a vortex for two minutes, the test tube was centrifuged at 2500 rpm for 5.0 min, and the hexane phase was separated. The absorption values were found by making the necessary dilutions from this solution. The microencapsulation efficiency (ME) of PM in microcapsules was calculated using equation below as the ratio of the weight of PM
extracted and the weight of PM added.

\[ ME = \frac{\text{weight of PM in microcapsule}}{\text{weight of PM added}} \]

### 2.3. Pesticide release in microcapsules

In tubes containing 12 mL of alcohol/water, (10:90, v/v) 0.1 g of aqueous microcapsules were put in and taken from this solution for an hour of 2.0 mL and forced through a Sep-Pak Millipore filter of 0.45 μm. The solution was diluted to calculate UV-VIS absorption. The results were derived from the concentration versus absorbance graph.

### 2.4. Pesticide release from microcapsules under UV light

10.0 g PUU microencapsul solution was exposed to 2 × 18 W UV light. 2.0 mL samples were taken every hour and filtered with Sep-Pak Millipore filters (0.45 μm pores). 2.0 mL of hexane was added to this solution, shaken in the vortex system for 2 min, and centrifuged at 2500 rpm for 5 min. The amount of active substance in the hexane phase was determined using UV-VIS spectrophotometer.

### 2.5. Dimensional analysis of microcapsules

Following drying and carbon coating, capsule samples were examined using SEM. The Malvern Nano-Zs unit was used to investigate the distribution of microcapsule size in the aqueous medium.

### 2.6. Optical microscopy

The Olympus CH20 optical microscope was used to observe changes in the stability of emulsified droplets, the stage of capsule-shell formation, and environmental impurities.

### 2.7. Thermo gravimetric analysis (TGA)

The TGA device was used to measure the mass change in the decomposition and evaporation of microcapsules with and without pendimethalin (empty capsule). The temperature mass changes of 2.0–5.0 mg samples in the nitrogen gas environment were measured between 20°C and 450°C by increasing the ambient temperature by 10°C per minute.

### 2.8. Fourier-transform infrared spectroscopy (FT-IR)

FT-IR was performed in 3000–400 cm\(^{-1}\) operating range, by forming KBr pellets. Empty microcapsules were completely dried, then mixed with 2.0–6.0 mg KBr, powdered in mortar to form discs under pressure in order to make measurements in the FT-IR device. FT-IR of liquid substances were measured by dropping liquid onto a solid KBr disc.

### 3. Results

When the FT-IR spectrum of PM-free empty capsules in Figure 2 was examined, it was observed that they all have peaks in the same regions. In this figure, the spectrum no 1 belongs to PEG-400, the spectrum no 2 belongs to butyl glycol, the spectrum no 3 belongs to ethyl glycol, and the spectrum no 4 belongs to propyl glycol. When all spectra were examined; N–H and O–H stretching peaks seen between 3300 and 3200 cm\(^{-1}\), C–H stretching vibrations seen at 2926 and 2856 cm\(^{-1}\), C = O (carbonyl) peak seen at 1750 cm\(^{-1}\), and C = C (alkene) peak seen at 1650 cm\(^{-1}\).

![Figure 2](image-url). FT-IR spectrum of empty microcapsules (1, green line: PEG-400; 2, red line: butyl glycol; 3, blue line: ethyl glycol 4, black line: propyl glycol).
Figure 3. FT-IR spectra of toluendiisocyanate (TDI) and empty microcapsule (1, red line: TDI; 2, black line: empty capsule).

Table 2. Release percentages of microcapsules containing pendimethalin.

| Time (hour) | Alcohol-water medium | UV rays medium |
|-------------|----------------------|----------------|
|             | PEG-400 | Propyl glycol | Butyl glycol | Ethyl glycol | PEG-400 | Propyl glycol | Butyl glycol | Ethyl glycol |
| 0           | 18.01   | 16.09        | 15.12        | 17.16        | 28.21   | 24.19        | 23.52        | 25.96        |
| 1           | 24.16   | 21.57        | 20.29        | 23.03        | 33.06   | 28.35        | 27.55        | 30.41        |
| 2           | 28.58   | 25.52        | 24.00        | 27.23        | 40.12   | 34.31        | 32.36        | 36.87        |
| 3           | 30.79   | 27.50        | 25.86        | 29.35        | 42.00   | 36.02        | 35.02        | 38.63        |

Figure 3 shows that N-H stretching peak seen around 3300 cm$^{-1}$, C–H stretching vibrations seen at 1600 and 2926 cm$^{-1}$, carbonyl peak seen between 1780 and 1600 cm$^{-1}$, and that polyurethane/urea reaction occurs at 1643 cm$^{-1}$ (urea carbonyl) and 1732 cm$^{-1}$ (urethane carbonyl) peaks where the vibration intensities were strong. The peaks at 1556 and 1244 cm$^{-1}$ belong to the amide vibration, while the vibration seen at 1106 cm$^{-1}$ belongs to the ether Group C–O–C stretching. The low strength due to this vibration also confirms the urethane character of the microcapsules formed and shows that there was a reaction of glycols and isocyanate. The fact that the isocyanate strenuous vibration at 2270 cm$^{-1}$ seen in the toluendiisocyanate spectrum was missing in the empty microcapsule shell at the same position suggests that all TDI had been completely exhausted by glycol, HMDA and HYD reactions.

Table 1 shows the effect of different mixing speeds on capsule sizes. The capsule size was found to decrease as mixing speed increases. Microcapsules containing propyl glycol in their shell material were found to be smaller in size compared to other glycols.

As shown in Table 2, the release percentages of microcapsules containing PEG-400, propyl glycol, butyl glycol and ethyl glycol in their shell material were examined under UV ray and in the alcohol-water medium for 1, 2, 3, and 4 h. Microcapsules containing PEG-400 in their shell material were found to have the highest release percentage in both environments, compared to other glycol-containing capsules. In the alcohol-water medium and under UV light, these values were 18.01% and 28.21% after 1 h, 24.16% and 33.06% after 2 h, 28.58% and 40.12% after 3 h, and 30.79% and 42.00% after 4 h, respectively. The microcapsules containing butyl glycol in their shell material were found to have minimal release. In the alcohol-water medium and under UV light, these values were 15.12% and 23.52% after 1 h, 20.29% and 27.55% after 2 h, 24.00% and 32.36% after 3 h, and 28.86% and 35.02% after 4 h, respectively.

Figure 4 shows the colour change of the medium due to the release of the core material from the capsule over time in the alcohol-water medium and under the UV light. Since PM is a coloured compound, its release is visible. Increasing in colour caused by the release of active substance supports by Table 2. According to the results of the studies on the release under UV light in alcohol-water medium, microcapsules containing butyl glycol in the cell material have a lower release ratio compared to other microcapsules, whereas microcapsules containing PEG-400 shell material were found to have the highest release ratio. It was observed that the ambient colour darkens as the release amount in the microcapsules increases. When the release rates under UV light and in the alcohol-water medium were compared over the same periods, it was found that UV rays were more effective on microcapsules.

According to the TGA findings of microcapsules with a core material of PM and shell materials of PEG-400, propyl glycol, butyl glycol and ethyl glycol that the
Figure 4. Pendimethalin release from microcapsule (a: alcohol-water medium, b: UV rays medium).

Table 3. Table of degradation temperature values and % mass loss obtained from TGA spectra of pendimethalin-containing and non-containing microcapsules made with ethyl glycol, butyl glycol, PEG-400 and propyl glycol.

| TGA            | Degradation temperature (°C) | Percentage mass loss (%) |
|----------------|------------------------------|--------------------------|
| Pendimethalin-containing microcapsule | Ethyl glycol 150–400 | 96.44 |
|                | Butyl glycol 160–350 | 95.53 |
|                | PEG-400 160–350  | 95.01 |
|                | Propyl glycol 170–350 | 99.53 |
| Pendimethalin-free microcapsule | Ethyl glycol 230–400 | 96.44 |
|                | Butyl glycol 220–350 | 95.53 |
|                | PEG-400 200–350  | 95.01 |
|                | Propyl glycol 280–350 | 99.53 |
| Total          | Ethyl glycol 150–400 | 96.44 |
|                | Butyl glycol 160–350 | 95.53 |
|                | PEG-400 160–350  | 95.01 |
|                | Propyl glycol 170–350 | 99.53 |

First temperature decreases. This decreasing in temperature indicates the release of the core material from the capsule, and the other temperature change indicates the decomposition of the shell material. According to Table 3, decomposition of microcapsules containing PM and the shell material of ethyl glycol starts at 150°C, whereas decomposition of the ones with propyl glycol starts at 170°C. Similarly, according to this table, the lowest decomposition temperature of empty microcapsules was seen with PEG-400 at 200°C, while the highest decomposition temperature was seen with propyl glycol at 280°C.

Figure 5 shows the size distribution chart which was obtained using the Malvern Nano-Zs device of the microcapsules made with ethyl glycol, butyl glycol, PEG-400 and propyl glycol at a mixing speed of 5000 rpm. According to the graph, almost all microcapsules were similar in size but available percentages of these capsules were different. Although the mixing speeds were the same, the percentage of capsules with butyl glycol available in the medium was higher than the others.

Figure 6 shows the percent yields of PM microcapsules made with PEG-400 in shell, propyl glycol, butyl glycol and ethyl glycol. In the microcapsules containing PEG-400, the highest yield was obtained with microcapsules having a ratio of glycol/amine (mol/mol) 0.004/0.0029; whereas this ratio was 0.0045/0.0025 for propyl glycol, 0.004/0.0029 for butyl glycol, and 0.0045/0.0025 for ethyl glycol.

Figure 7 shows the SEM and optical microscope images of microcapsules encapsulated with the highest yield at a mixing speed of 5000 rpm according to the graph in Figure 6.
4. Discussion and conclusions

Emulsified droplets need to be formed at room temperature (about 20°C) to make them stronger. The capsules were found to be stable when the temperature was gradually increased from 20°C to 55°C, but as the temperature was quickly increased from 20°C to 55°C, the environment became less stable and more contaminants were produced.

The particle size distribution of the microcapsules produced was determined using the laser dispersion technique and SEM. The sizes of the resulting capsules decreased from 23–35 to 1–8 μm as the rotation was increased from 3000 to 6000 rpm. In Table 1, it was seen that by increasing the mixing speed, microcapsule diameters decreased. This is because, when the mixing speed is increased, the micro droplets hit the walls of the homogenizer, causing their diameter to become smaller. The shapes of the microcapsules produced were in spherical form, as seen in optical microscope and SEM images. In a study, softener fragrance was encapsulated with polyurethane-urea, and an inverse ratio was found between the capsule size and the mixing speed, with a decrease in capsule sizes as the mixing speed increased [29]. In another study, the capsule size was found to decrease as the mixing speed increases during the encapsulation of the essential oil with polyurethane-urea [17]. In our study, mixing speed was found to be inversely proportional to capsule size when performing encapsulation with the polyurethane-urea, similar to the above-mentioned studies. It was observed that microcapsules with propylene glycol in the wall shell had a smaller diameter than the others at the same speed/min. mixing speeds. Although the initial sizes of the emulsified droplets at the same mixing speed were the same, the capsule wall diameters changed as the shell materials were added to the medium. The basis for this is that the emulsifier (PVA) can not hold the emulsified droplets sufficiently stable.

It has been observed that the shell materials introduced into the environment during the formation of the microcapsule shells have affected the stability of the emulsion and, especially the propyl glycol, have a negative effect on the stability of the droplets. By looking at the FT-IR spectra of the empty capsules of different glycols in Figure 2, and the FT-IR spectra of the TDI and sample empty capsules in Figure 3, the reaction of the TDI, given to the medium for microcapsule shell formation, with glycols and amine in the medium was monitored by FT-IR spectroscopy. While the TDI isocyanate group had a high sharp peak of 2270 cm⁻¹, it was observed that this peak had disappeared after the formation of the capsule shell and that the TDI isocyanate group had been completely consumed in the reaction. Capsule shells must be of a certain thickness to have microcapsules resistant to environmental conditions, have a long shelf life, and carry the core material easily. We obtained a range of 399.7–1479 nm thickness of the microcapsules and indicated that the produced microcapsules are sufficiently stable.

TGA analysis, SEM and release studies were carried out by taking samples from microcapsules with the highest yield rates. When the results of the TGA analysis were examined, the glycols (PEG-400, butyl glycol, propyl glycol, and ethyl glycol) used to form the capsule shell were found to have closer stability. It has been observed that the release of active ingredients of microcapsules containing PM varied between 150°C and 450°C. It was observed that the loss of active substance in the core was firstly in microcapsules with ethyl glycol in the wall structure (150°C) and then in microcapsules with propyl glycol in the core were the latest release (170°C). With the increase in temperature in the TGA, bond breaks occur as a result of the active substance molecules in the core moving into the gas phase and exerting pressure on the walls or increasing the intermolecular bond vibrations forming the wall shell.
Figure 7. SEM and light microscopy (LM) image of highest yield microcapsules at 5000 rpm mixing speed microcapsules propyl glycol (A1: SEM; A2: LM), butyl glycol (B1: SEM; B2: LM), PEG-400 (C1: SEM; C2: LM), and ethyl glycol (D1: SEM; D2: LM).
Active ingredient losses in the microcapsule are usually caused by the nano-sized pores in the microcapsule wall or by breaking the weak parts of the microcapsule wall. When microcapsule wall structures without PM were examined, it was observed that the first degradation was PEG-400 at 200°C and the highest degradation occurred in propyl glycol at 280°C. In addition, the deterioration of all wall materials except ethyl glycol was completed at 350°C, while that of ethyl glycol ended at 400°C. This result showed that the wall shell containing ethyl glycol was more stable than the others. The fact that microcapsules with strong wall structures lose substance at lower temperatures reveals that there are micro pores in their walls.

Some of the emulsifying agents may have both emulsifying and stabilizing properties. It is seen that the sizes of the micro droplets obtained with materials having these two properties are very close to each other and the droplet sizes do not change much in the microencapsulation process (source). While micro emulsion droplets were formed, the stability of the emulsifier and micro droplets was provided by PVA. If the stability of the initially obtained droplets is not well maintained, these droplets deteriorate over time and the particle size distribution also changes. Glycols and amines introduced as shell wall materials have effects on emulsion stability. When the microcapsule size distributions given in Figure 5 are examined, it is seen that the capsule size distributions of PEG-400 are closer to each other, and the PEG-400 material contributes more to the emulsion stability than other glycols (Figure 5). This is because it has long-chain methoxylated groups.

In order to preserve the stability of the microdroplets obtained during the emulsion, stabilizers are given to the environment and restrict the movement of the microdroplets towards each other. If the stability of the microdroplets is not maintained, they burst with the effect of temperature increase or by the effect of mixing and release the active substance from the inside of the micelles. There are two factors affecting the stability of micro droplets, one of which is van der Waals attraction forces and the other is electrostatic repulsive forces. While the first one reduces the stability of microemulsions, the second one increases the stability. According to the values in Figure 6, due to the long chain structure of PEG-400 compared to other glycols, it bound to the microdroplets surface and reduced the van der Waals attraction force of the microdroplets due to its steric effect. It has been observed that the amino groups given to the environment to form the capsule shell have an effect on the emulsion stability. In cases where amine groups exceed a certain amount, it was thought that van der Waals increased the attraction forces and reduced the capsule yield by causing the microdroplets to decompose.

The pictures given in Figure 7, were microcapsules created in a homogenizer at 5000 rpm. A1, B1, C1 and D1 pictures are SEM images at different magnifications, and A2, B2, C2 and D2 pictures are light microscope images. Before the SEM images were taken, the process was carried out after they were covered with carbon. According to the SEM image results, all microcapsules were spherical and slightly flattened on their surfaces, and the surfaces of the microcapsules with butyl glycol in the shell were smoother than the other microcapsules. The reason why the images were taken at the same magnification was that, due to the low weight of the microcapsules, the electrons sent to the surface caused charge on the surface and caused the microcapsules to move away from the surface. Pictures taken with a light microscope are photographs obtained by dropping microcapsules onto a slide in an aqueous environment. The light microscope had low resolution and when the microscope was focused on a specific point, the microcapsules of other depths showed blurred or contamination.

Since the spraying of the plants is done in open environments, they are exposed to sunlight with UV rays. In addition, mega-galactic rays come from the stars of our world, and some of them reach the earth’s crust by passing through the atmosphere. Since the energies of these rays are at the level of eV-MeV, they break the bond between atoms, ionize the atoms and stimulate their electrons. Ultraviolet A rays reach the earth’s crust by passing through the earth’s atmosphere and their energies range from 3.1 to 3.94 (315–400 nm) eV. The energies required for breaking the chemical bonds between C–C and C–N are 3.52 and 3.00 eV, respectively. UV rays from the sun and mega-galactic rays break the bonds between molecules and cause the compounds to decay. When the microcapsules produced are applied to the plants, they will be exposed to external rays since they will remain in the leaves for a long time. The effect of these rays on the microcapsule structure was examined by exposure to UV rays at 2 × 18 W power. Since the PM is a yellow colour, it gives yellow to the medium where it dissolves. Although the colours of the initial solutions are colourless, the colour of the medium changes to dark yellow over time. The colouration of the environment is when the capsule shells break and release the active substance into the environment.

In conclusion, the purpose of this study was to microencapsulate PM, a commonly used herbicide in agriculture, with polyurethane urea. For this reason, PM was successfully encapsulated with polyurethane urea resin using an interfacial polymerization method. The microcapsule forming phases were analyzed by optical microscopy and the surface morphology of the microcapsules was investigated by SEM. The scale of the microcapsules ranged from 1 to 50 μm and the thickness of the capsule shells ranged from 399.7 to 1479 nm. The microcapsules with butyl glycol in their shell material had the highest encapsulation yield, with an 89.1% yield. The microcapsules with a shell material of PEG-400 were found to have the highest release
rate, which reached 30.79% in alcohol-water medium, and 42% under UV rays for 4 h. The shell diameter of the PM microcapsules we encapsulated at different mixing rates was also found to decrease as the mixing speed increased. This indicates that there is an inverse correlation between capsule size and mixing speed. According to the results obtained in TGA analysis, microcapsules with shell material of propyl glycol were found to decompose slowly, whereas the microcapsules that decompose quickly were found to be the ones with PEG-400 shell material. The highest encapsulation yield, microcapsules with a round shape and a clean environment, and the lowest emission percentage of microcapsules in alcohol-water and UV medium have been butyl glycol containing in the shell microcapsules.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This study was funded by Afyon Kocatepe Üniversitesi, Experimental Research Projects (BAP) [grant number 18.FEN.BİL.60]. The writers would like to thank Biokon Chemistry for providing PM.

ORCID

Cemal Çifci http://orcid.org/0000-0001-9410-211X

References

[1] Yearla SR, Padmasree K. Research, exploitation of sub- abdominal stem lignin as a matrix in controlled release agrochemical nanoformulations: a case study with herbicide diuron. J Environ Sci Pollut Res. 2016;23:18085–18098.
[2] Tiryaki O, Canhilal R, Horuz S. Tarım ilçeleri ve riskleri. J Erciyes Üniversitesi Fen Bilimleri Enstitüsü Fen Bilimleri Dergisi. 2007;26:154–169.
[3] Akelah A. Novel utilization of conventional agrochemicals by controlled release formulations. J Mater Sci Eng C. 1996;4:83–98.
[4] Patil DK, Agrawal DS, Mahire RR, et al. Synthesis, characterization, and controlled release study of polyurea microcapsules containing metribuzin herbicide. J Russian Appl Chem. 2015;88:692–1700.
[5] Erkan G. Bazi antifungal ajanlarının mikrokapsülasyonu ve tekstil materyallerine uygulanması. İzmir: DEÜ Fen Bilimleri Enstitüsü. 2008.
[6] Benita S. Microencapsulation: methods and industrial applications. New York: CRC Press; 2005.
[7] Rodrigues S, Martins I, Fernandes I, et al. Scentfashion*: microencapsulated perfumes for textile application. J Chem Eng. 2009;149:463–472.
[8] Yoo Y, Martinez C, Youngblood P, et al. Synthesis and characterization of microencapsulated phase change materials with poly (urea–urethane) shells containing cellulose nanocrystals. J ACS Appl Mater Inter. 2017;9:31763–31776.
[9] Liang C, Lingling X, Hongbo S, et al. Microencapsulation of butyl stearate as a phase change material by interfacial polycondensation in a polyurea system. J Energy Conver Manage. 2009;50:723–729.
[10] Saihi D, Vroman I, Giraud S, et al. Microencapsulation of ammonium phosphate with a polyurethane shell. part II. interfacial polymerization technique. J React Func Polym. 2006;66:1118–1125.
[11] Zhang H, Wang X. Synthesis and properties of microencapsulated n-octadecane with polyurea shells containing different soft segments for heat energy storage and thermal regulation. J Solar Energy Mate Solar Cell. 2009;93:1366–1376.
[12] Kim EY, Kim HD. Preparation and properties of microencapsulated octadecane with waterborne polyurethane. J Appl Polym Sci. 2005;96:1596–1604.
[13] David D, Silverstein MS. Porous polyurethanes synthesized within high internal phase emulsions. J Polym Sci Part A Polym Chem. 2009;47:5806–5814.
[14] Aydin AA. In situ preparation and characterization of encapsulated high-chain fatty acid ester-based phase change material (PCM) in poly (urethane-urea) by using amino alcohol. Chem Eng. 2013;231:477–483.
[15] Silva M, Martins IM, Barreiro MF, et al. Functionalized textiles with PUU/limonene microcapsules: effect of finishing methods on fragrance release. J Text Inst. 2017;108:361–367.
[16] Cui G, Wang J, Wang X, et al. Preparation and properties of narrowly dispersed polyurethane nanoencapsulates containing essential oil via phase inversion emulsification. J Agr Food Chem. 2018;66:10799–10807.
[17] Podshivalov AV, Bronnikov S, Zuev VV, et al. Synthesis and characterization of polyurethane–urea microcapsules containing galangal essential oil: statistical analysis of encapsulation. J Microencapsul. 2013;30:198–203.
[18] Gandham VD, Brochu A, Reichert W. Microencapsulation of liquid cyanoacrylate via In situ polymerization for self-healing. MRS Proc. 2011;14:1711–1417.
[19] Salaiń F, Bedek G, Devaux E, et al. Microencapsulation of a cooling agent by interfacial polymerization: influence of the parameters of encapsulation on poly (urethane–urea) microparticles characteristics. J Memb Sci. 2011;370:23–33.
[20] Tencin R, Bac N, Erdogmus H. Microencapsulation of fragrance and natural volatile oils for application in cosmetics, and household cleaning products, macromolecular symposia. Wiley Online Library. 2013;333(1):35–40.
[21] Mačiulytė S, Gutauskiene G, Niedritis J, et al. PVA and aminoglucosides and natural volatile oils for application in cosmetics, and household cleaning products, macromolecular symposia. Wiley Online Library. 2013;333(1):35–40.
[22] He R, Wang J, Wang X, et al. Fabrication and characterization of core–shell novel PU microcapsule using TDI trimer for release system, colloids surfaces A: physicochemical. Eng Aspects. 2018;550:38–144.
[23] Talcott PA. Miscellaneous herbicides, fungicides, and nematocides. In: Peterson ME, Talcott PA, editor. Small animal toxicology, 3rd ed. St. Louis: Saunders/Elsevier; 2013; p. 401–408.
[24] Finch S, Samuel A, Lane GP. Fertilisers and manures. In: Finch S, Samuel A, Lane GP, editors. Lockhart and Wise- man’s crop husbandry including grassland. Woodhead, Publishing/Elsevier; 2014. p. 608.
[25] Smith DT, Richard EP, Santo LT, et al. Weed control in sugarcane and the role of triazine herbicides. In: LeBaron HM, editor. The triazine herbicides. New York, NY: Elsevier; 2008. p. 185–198.
[26] Lin HT, Chen SW, Shen CJ, et al. Dissipation of pendimethalin in the garlic (Allium sativum L.). Bull Environ Contam Toxicol. 2007;79:84–86.
[27] Mattas K, Tsakiridou E, Michailidis A, et al. Economic assessment of Pendimethalin herbicide use in selective crops (cotton, processing tomato & onion). Thessaloniki, Working Papers 166116, Aristotle University of Thessaloniki, Department of Agricultural Economics; 2014. p. 58.

[28] Hedaoo RK, Tatiya PD, Mahulikar PP, et al. Fabrication of dendritic 0 G PAMAM-based novel polyurea microcapsules for encapsulation of herbicide and release rate from polymer shell in different environment. J Design Mono Polym. 2014;17:111–125.

[29] Zhang D-x, Zhang X-p, Luo J, et al. Causation analysis and improvement strategy for reduced pendimethalin herbicidal activity in the field after encapsulation in polyurea. J ACS Omega. 2018;3:706–716.

[30] Hedaoo R, Mahulikar P, Gite T, et al. Engineering, Synthesis and characterization of resorcinol-based cross linked phenol formaldehyde microcapsules for encapsulation of pendimethalin. J Design Mono Polym. 2013;52:243–249.

[31] Yılmaz H, Enginar H, Çifci C. Microencapsulation of lambda-cyhalothrin with polyurethane-urea and application on peppermint plant leaves containing a two-spotted red spider mite (tetranychus urticae). J Taibah Univ Sci. 2021;15(1):63–70.

[32] Perez ER, Calve SL, Mirabel P. Near-UV molar absorptivities of alachlor, mecroprop-p, pendimethalin, propanil and trifluralin in methanol. J Photochem Photobiol A. 2008;193:237–244.