Microencapsulation of Ethion by Interfacial Polymerization Utilizing Potassium Phthalimide-*N-oxyl* (PPINO) as a Promoter

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Abstract
Polyurea microcapsules containing an active agent, i.e. ethion as pesticide, have been prepared by interfacial polymerization between 2, 4-toluene diisocyanate (TDI) and diethylenetriamine (DETA) in an oil-in-water (O/W) emulsion system. The effects of the nature of the emulsifier, the monomer weight ratio, and a novel promoter, i.e. potassium phthalimide-N-oxyl (PPINO), on the morphology, microstructure, and thermal stability of the microcapsules have been investigated. PPINO was used as a water-soluble promoter capable of dimerizing and trimerizing the isocyanate reactant in the interfacial polymerization. The transmission electron microscopy (TEM) micrographs showed that the addition of the promoter had no significant effect on the microcapsule shell thickness. Increasing the amount of PPINO caused the degree of crystallinity of the polymer shell to decrease considerably. In addition, increasing the amount of promoter up to 2 wt% caused the thermal stability of the microcapsules to decrease, while using promoter beyond this level resulted in higher thermal stability.

Keywords: *Microcapsule, Interfacial Polymerization, Potassium Phthalimide-N-oxyl (PPINO) Promoter, Morphology*

1. Introduction

Microencapsulation of active ingredients with a polymeric shell has been widely used in various applications for many years [1]. This trapping technology mainly controls the release rate of active agents, protects sensitive materials from undesirable environmental conditions, reduces mammalian toxicity, and sustains the performance of the active ingredients [2–7]. Encapsulation of active chemical agents such as pesticides and herbicides by polyurea coating materials has been extensively investigated through interfacial polycondensation reactions between a variety of diamines and diisocyanate monomers [6, 8–11]. The functional performances of such microcapsules are highly dependent on the particle morphology and microstructure characteristics of the polymeric shell, such as thickness, composition, crosslinking density, crystallinity, and porosity of the shell. These

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characteristics can be controlled both by the polymerization process conditions and material parameters, including the nature of the emulsifier, monomer weight ratio, monomer structure, core-to-monomer shell ratio, dispersed phase to continuous phase ratio, and core material composition [9, 12–15].

Polyfunctional isocyanate systems consisting of polymethylene-polyphenylisocyanate (PMPPI)/ toluene diisocyanate (TDI) mixtures with various isocyanate functionalities have been used to prepare microcapsules containing pesticides [16–17]. Recently, polyurea microcapsules containing pyrethroid chemical agents have been prepared by reaction between a mixture of dimers and trimers of hexamethylene diisocyanate (HMDI), HMDI uretidione/isocyanurate mixture, and aliphatic ethylene diamine (EDA) as a water-soluble monomer [11, 18]. The results showed that increasing the concentration of the HMDI uretidione/isocyanurate mixture increased the thickness and mechanical strength of the microcapsule shell. Although the use of the trifunctional HMDI isocyanurate leads to the fabrication of microcapsules with superior mechanical properties, the viscosity of isocyanurate compounds is too high to permit their fine dispersal as oil droplets in a continuous phase. Thus, the in situ di- and trimerization of low viscosity isocyanate monomers at the interface of two incompatible phases by using an appropriate water-soluble promoter, thereby circumventing the above limitation, offers a new alternative approach for producing microcapsules with the required physical and mechanical properties.

On the other hand, insecticidal seed treatment by microencapsulated formulations of organophosphates and pyrethroid has been utilized as a possible alternative to the standard seed treatment with organochlorine agents for autumn-sown wheat in soils which were heavily infested with wheat bulb fly eggs and subsequently larvae [19]. For this purpose, the proper dose of insecticides varying from 40% to 120% on the seed coat is necessary; hence it is usually proper when microencapsulated formulations have been used to seed treatment. Ethion as an insecticidal chemical agent has been effectively used against wheat bulb fly larvae in both mineral and organic soils [19]. The results showed that the seed treatment by ethion is more efficient than the chlorfenvinphos used at late-sown wheat (20 November).
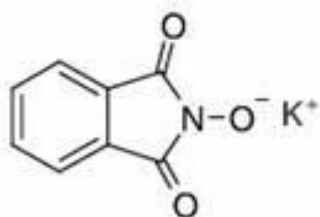
Although more research investigations have been carried out in the preparation of polyurea microcapsules using conventional chemical agents, less attention has been paid to encapsulate active agents using promoters or catalysts in order to control the shell microstructure and morphology. In the present research work, the effects of the nature of the emulsifier, the shell monomer composition, and PPINO promoter on the morphology, microstructure, and thermal properties of microcapsules containing ethion have been investigated.

2. Experimental
2-1. Materials
All reagents were purchased from Merck Co., unless otherwise stated. Diethylenetriamine (DETA) and 2, 4-toluene diisocyanate (TDI) were used as shell-

formation monomers. Polyoxyethylene (20) sorbitan monooleate (Tween80) and 88% hydrolyzed poly(vinyl alcohol) (PVA) with a weight-average molecular weight of 65,000 g mol^{-1} (Fluka) were used as emulsifying agents. Potassium phthalimide -*N*-oxyl (PPINO) as promoter, shown in Scheme 1, was prepared according to the procedure described in a publication elsewhere [20]. ***Ethion*** as an active encapsulating agent, ***technical grade,*** was a gift from the ***Agriculture*** Support Service Co. of ***Iran's Ministry of Agriculture-Jahad*** (IMAJ). Double-distilled water was prepared in the author's laboratory.

Scheme 1. Chemical structure of potassium phthalimide -*N*-oxyl (PPINO).

2-2. Preparation of microcapsules

The microencapsulation was carried out in a 100-mL three-necked glass reactor equipped with a reflux condenser, nitrogen inlet, and mechanical stirrer. The reactor was immersed in a bath kept under thermostatic control. In order to prepare the O/W emulsion, the dispersion phase containing given amounts of ethion and TDI was dispersed in a 3 wt% aqueous PVA solution by means of a two-blade impeller stirrer at 300 rpm and room temperature. The dispersion was then homogenized ultrasonically for 3 min by means of a Bandelin Sonopuls homogenizer (HD 2070, Germany) under the cooling provided by immersion in an ice-salt mixture. The emulsion was immediately transferred to the reactor and stirred at 300 rpm. Then, a given amount of DETA solution, with or without water-soluble PPINO promoter, was added to the O/W emulsion as fine droplets at 25°C, and the reaction was allowed to proceed for 1 h. The emulsion was then heated to 40 C, and the reaction was continued for a further 3 h. The starting compositions of the prepared microcapsule samples with various ratios of TDI to EDTA are shown in Table 1.

Table 1. Starting compositions for the preparation of polyurea microcapsules

Code[*]	Oil Phase		Continuous phase					
	Ethion	TDI	Water	Triton	PVA	DETA	PPINO[**]	TDI/DETA
MC1	6.65	1	59.56	1.8	-	0.77	0	1.3
MC2	6.65	1	59.56	0.9	0.9	0.77	0	1.3
MC3	6.65	1	59.56	-	1.8	0.77	0	1.3
MC4	6.65	1	59.56	-	1.8	0.50	0	2
MC5	6.65	1	59.56	-	1.8	0.40	0	2.5
MC6	6.65	1	59.56	-	1.8	0.33	0	3
MC7	6.65	1	59.56	-	1.8	0.50	1	2
MC8	6.65	1	59.56	-	1.8	0.50	2	2
MC9	6.65	1	59.56	-	1.8	0.50	5	2

*.Quantities are in weight parts.
**. The PPINO weight percent is based on total monomers used.

The dry weights of the microcapsule samples were determined by gravimetric measurements. For this purpose, 10-mL microcapsule suspension samples were centrifuged at 6000 rpm and 5 C for 2 h. The precipitated samples were washed twice with distilled water and then dried at 30°C for one week.

2-3. Microcapsule characterization

The chemical structures of the microcapsule samples were analyzed by Fourier transform infrared (FTIR) spectroscopy (8400S, Shimadzu, Japan) in the wave number range 500–4000 cm^{-1}. X-ray diffraction patterns of the microcapsules without any liquid pesticide were obtained on an XRD analyzer (D5000, Siemens, Germany). Prior to the XRD experiments, the shells of frozen microcapsule particles were slowly broken with a ceramic hammer, washed three times with *n*-hexane and water, and dried under vacuum to remove impurities. Thermogravimetric analysis (TGA) experiments were carried out on a thermogravimetric analyzer (PL1500, Polymer Laboratories Co.) at a heating rate of 10°C/min to investigate the thermal stabilities of the microcapsules. The tests were performed in the temperature range 25–750 C, under a nitrogen atmosphere to inhibit oxidation.

Transmission electron microscopy, TEM (Zeiss CEM 902A), was used to observe the morphologies of the microcapsules. Suspension samples were further diluted with distilled water, and then a dilute droplet was transferred onto a copper grid, mesh 200, and dried in the open air prior to microscopy.

3. Results and discussion

Interfacial polymerization between bifunctional TDI as an oil-soluble monomer and trifunctional DETA as a water-soluble monomer yields polyurea shells with a crosslinked structure. Fig. 1 shows the FTIR spectra of ethion and a microcapsule sample of MC4 (Table 1). The disappearance of the N=C=O absorption band at 2278 cm^{-1}, and the appearance of N–H absorption bands at 3358 and 1557 cm^{-1} and a C=O band at 1646 cm^{-1}, both of which are characteristic chemical bonds of a urea linkage, showed that a microcapsule with a polyurea shell accommodated the core active material. An observed weak band at 1709 cm^{-1} corresponds to the C=O of a urethane linkage, which was formed as a result of the reaction between the hydroxyl group of the PVA emulsifier and the isocyanate group of TDI.
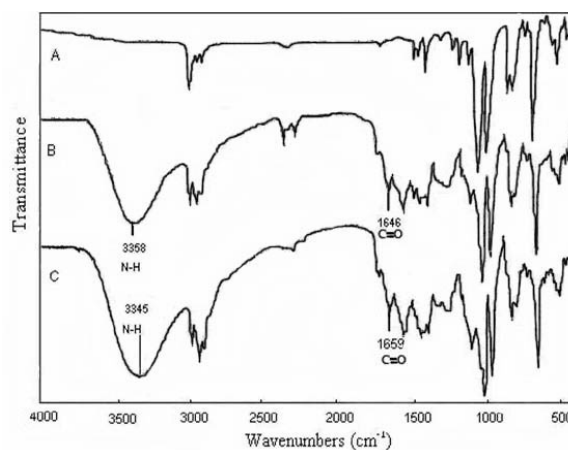

Figure 1. FTIR spectra of: (a) the ethion pesticide, (b) the polyurea microcapsule sample of MC4 prepared without promoter, and (c) MC9 sample prepared with 5 wt% promoter.

3-1. Effect of surfactant type

The effect of different kinds of non-ionic surfactants, namely Tween80, PVA, and

PVA/Tween80 mixture (50:50, w/w), on the morphology of small microcapsules was investigated by means of transmission electron microscopy (TEM). As shown in Fig. 2, a core−shell structure with a dark liquid core phase and a bright polymer shell was observed only for the microcapsule samples prepared using PVA emulsifier. Nevertheless, the inner surface of the membrane shell was coarse; hence the microcapsules had a non-uniform shell thickness (Fig. 2b, d). Neither Tween80 nor PVA/Tween80 mixture as emulsifying agents yielded microcapsules with a core−shell or micro-reservoir structure (Fig. 2a). These different morphologies that appear to have arisen from using different surfactant types can be ascribed to the thermodynamic/kinetic control limitations that determine the final morphology based on getting the minimum possible Gibbs free energy of the system. In fact, one of the most direct approaches to obtain the proper morphology is to use various surfactants to alter the interfacial tension between phases [21–22].

3-2. Effect of monomer ratio

Polyurea microcapsule samples with a constant amount of TDI and various initial ratios of TDI to DETA were prepared (Table 1). As shown in Fig. 2, the size and shell thickness of the microcapsules decreased with increasing initial weight ratio of TDI to DETA. On the other hand, the size distribution of the microcapsules seemed to increase with increasing TDI to DETA ratio.

As shown in Fig. 2c, a very smooth inner shell surface and uniform microcapsule wall thickness was only observed at TDI/DETA=2. At lower and higher ratios,

the polyurea shell had a rough inner surface and a non-uniform thickness (Fig. 2b, d). Increasing the ratio of TDI to DETA at the inner surface of the microcapsule shell, where the reactions take place, increases the polymerization rate during the initial reaction period, but as the reaction proceeds the diffusion of the DETA through the shell polymer decreases. The formation of shell polymer with non-uniform thickness may be attributed to the catalytic effect of the urea produced by the reaction between the TDI and DETA monomers. On the other hand, there is another possibility that those particles with nonuniform wall thickness can be the result of the coalescence of various small particles giving that irregular shape with different thickness.
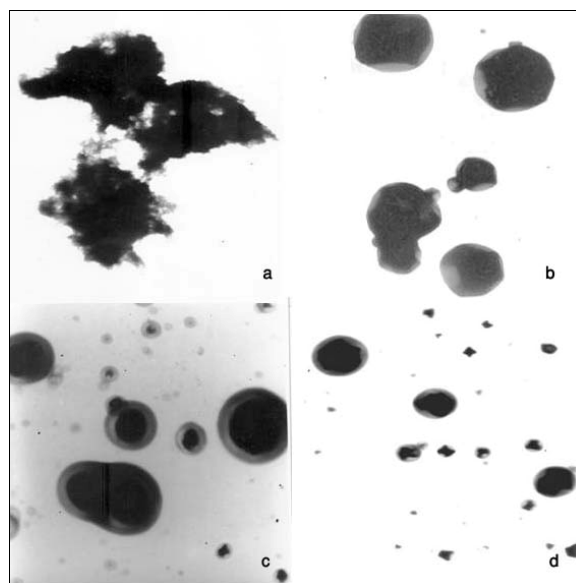

Figure 2. TEM micrographs at ×7000 magnification of the microcapsules prepared by using different non-ionic emulsifiers and with various ratios of TDI to DETA: (a) MC1 (Tween80, TDI/DETA=1.3); (b) MC3 (PVA, TDI/DETA=1.3); (c) MC4 (PVA, TDI/DETA=2); and (d) MC6 (PVA, TDI/DETA=3)

The relationship between composition and thermal stability of the microcapsules was quantitatively investigated by thermogravimetric analysis (TGA). Fig. 3 indicates the effect of membrane shell composition, prepared with various TDI to DETA ratios, on the thermal stability of the microcapsule samples. Increasing the TDI to DETA ratio decreased the thermal stability because of the reduced thickness of the shell polymer. Comparing the curves, it can be seen that the microcapsule sample having the lowest TDI to DETA ratio exhibits the highest thermal stability. The weight losses shown from 150 to 200 C are due to the release of the ethion, which has a boiling point of 150 °C, that is more or less 50% of the mass of the microcapsules. After this, the polymer decomposes and the weight deceases gradually in the temperature range 200–650°C. In contrast, for the other samples prepared at higher TDI to DETA ratios, a lower initial decomposition temperature and thermal stability were observed.
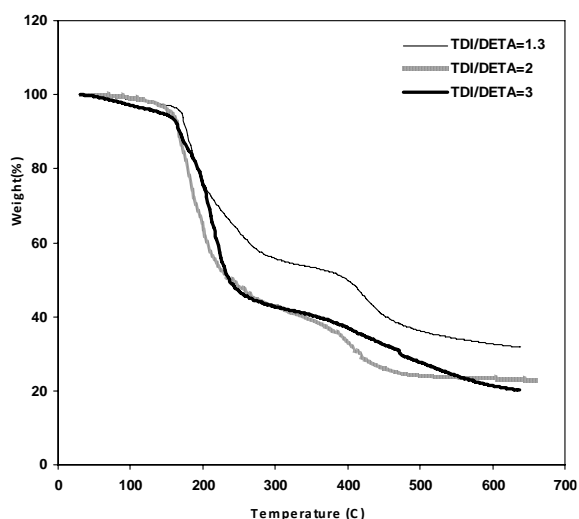

Figure 3. TGA diagrams of microcapsule samples of MC3, MC4, and MC6 prepared, by using various weight ratios of TDI to DETA.

3-3. Effect of PPINO promoter

Potassium phthalimide -*N*-oxyl (PPINO) was used as a water-soluble promoter capable of dimerizing and trimerizing the isocyanate monomers[20]. In this case, an aqueous solution of DETA containing PPINO was added as droplets into the O/W emulsion at room temperature. It was expected that the promoter molecules, being similar to DETA monomers, would transfer to the polymer surface in the aqueous phase, diffuse through the shell polymer, and probably trimerize TDI molecules to TDI isocyanurate at the interface of the polymer and oil droplets. For the microcapsule sample prepared by adding 5 wt% promoter to the continuous phase, a change in the absorption frequency of the C=O band from 1646 to 1659 cm^{-1} and in that of the N–H band from 3358 to 3345 cm^{-1} were observed (Fig. 1). In addition, no significant amount of unreacted isocyanate groups remained because of the fast reaction between the reactants, especially in the presence of the promoter.

3-3-1. Effect on morphology

The addition of the promoter had no significant effect on the microcapsule shell thickness for samples prepared from the same starting composition under the same polymerization conditions. Nevertheless, the inner surface of the polymer shell prepared with the promoter was slightly coarser than that of the membrane shell formed without the promoter (Figs. 2c, 4).

3-3-2. Effect on crystallinity

Increasing the initial promoter level in the continuous phase caused the crystallinity of the polymer shell to decrease considerably.

Fig. 5 shows the XRD patterns of three polyurea samples prepared by using 0, 2, and 5 wt% promoter, respectively. It can be seen that there was a considerable decrease in the degree of crystallinity of the polyurea shell as the promoter level was increased. Thus, the shell polymer of the microcapsule sample with 5 wt% promoter seems to be the most amorphous, with the highest crosslink density.
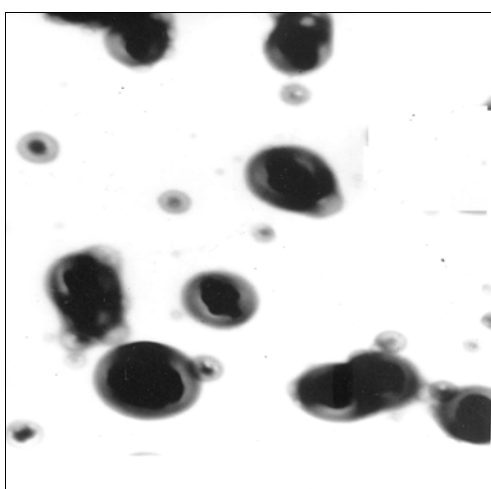

Figure 4. TEM micrograph at ×7000 magnification of the microcapsule sample of MC9 prepared using 5 wt% promoter and with TDI/DETA=2.
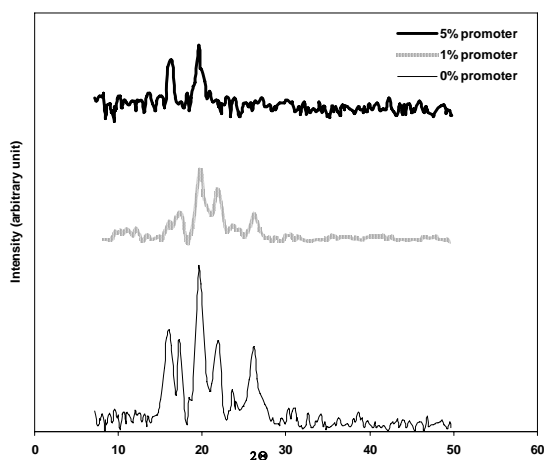

Figure 5. XRD patterns for polyurea shells prepared by various amounts of promoter. (The ratio of TDI to DETA in all the samples was 2)

3-3-3. Effect on thermal stability

Addition of up to 2 wt% promoter decreased the thermal stability of the microcapsule samples, but beyond this level the thermal stability increased considerably (Fig. 6). This behavior can be attributed to the decrease in crystallinity and the increase in crosslink density of the shell polymer as the promoter level is increased. The decrease in the amount of crystalline phase at up to 2 wt% promoter lowered the strength and thermal stability of the microcapsules, while the addition of more promoter improved the thermal stability. Although the use of a large amount of the promoter considerably decreased the degree of crystallinity, the higher crosslink density and isocyanurate concentration generated enhanced the mechanical and thermal properties of the shell polymer.
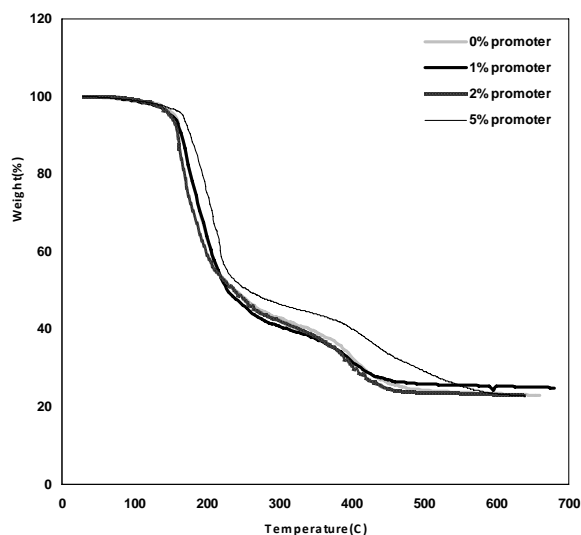

Figure 6. TGA diagrams of polyurea microcapsules prepared with 0, 1, 2, 5 wt% promoter. (The ratio of TDI to DETA in all the samples was 2)

4. Conclusions

Polyurea microcapsule samples with a constant amount of TDI and various initial

ratios of TDI to DETA have been prepared by interfacial polycondensation polymerization. The FTIR results showed that the interfacial polymerization between TDI as an oil-soluble monomer and DETA as a water-soluble monomer yields polyurea shells with a crosslinked structure. TEM micrographs indicated a core−shell structure only for the microcapsule samples prepared using PVA emulsifier as compared to other nonionic surfactants used. In this case, increasing the ratio of TDI to DETA led to a decrease in the shell thickness and average particle size of the resulting microcapsules. Interestingly, a very smooth inner shell surface and uniform microcapsule wall thickness was only observed at TDI/DETA=2. The increase of TDI to DETA ratio decreased the microcapsule thermal stability because of reduced thickness of the shell polymer.

Potassium phthalimide-*N*-oxyl (PPINO), having the ability to dimerize and trimerize the isocyanate monomers was used as water-soluble promoter. The incorporation of the promoter had no significant effect on the shell thickness of the microcapsule samples prepared. On the contrary, the introduction of PPINO considerably decreased the degree of crystallinity of the shell polymer as a result of increasing the polymerization rate and the shell crosslink density. Addition of up to 2 wt% promoter decreased the thermal stability of the microcapsule samples, while using higher promoter levels increased the thermal stability considerably.

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