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Characterization of Microcapsules Prepared by Interfacial Polycondensation of Methylene Bis(phenyl isocyanate) with Hexamethylene Diamine

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ABSTRACT

Polyurea microcapsules containing 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide as the active agent were prepared by the method of interfacial polycondensation with methylene bis(phenyl isocyanate) as the multifunctional isocyanate, hexamethylene diamine as the diamine, and anionic sodium lignin sulphonate as the emulsifying agent. Thermal stability of the microcapsules was investigated with a thermogravimetric analyzer coupled to a mass spectrometer and surface topography of the micro-capsules was investigated with atomic force microscopy. The release behaviour of the microcapsules was studied by extraction in deionized water or calcium chloride aqueous solution, drying under ambient conditions, and examining with scanning electron microscopy. Results indicate that as calcium chloride is added to the aqueous suspension of microcapsules containing anionic sodium lignin sulphonate as the surfactant, a gel phase is formed. This gel phase encompasses the microcapsules and increases the stability and modifies the release behaviour of the microcapsules.

Key Words: microencapsulation, interfacial polycondensation, methylene bis(phenyl isocyanate), hexamethylene diamine, characterization

INTRODUCTION

Microcapsules and microspheres can be prepared by a variety of physical and chemical methods. These methods include emulsion [1] and concentrated emulsion polymerization [2], suspension [3], semi-suspension [4], precipitation [5], dispersion polymerization [6], interfacial polycondensation [7–12], complex coacervation [13], autoencapsulation [14], interfacial cross-linking [15], liposomal microencapsulation [16], spray coating [17], granulation [18], sequential polymerization [19], spray drying [20], and extrusion-particularization [21]. The technique used commercially for microencapsulation of pesticides and herbicides is interfacial poly-

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condensation [21–27]. Using the method of interfacial polycondensation, pesticides and herbicides are encapsulated with different wall materials including polyurethane [28], polyurea [29], polyamide [30–32], polyester [33], and polyethyleneimine [34].

Characterization of the structure and properties of microencapsulated pesticides prepared by the method of interfacial polycondensation has been the subject of extensive research in the past two decades.

For example, Sibely and Fortin [35] attempted to visually detect mircoencapsulated pesticides in the digestive content of aquatic invertebrates and contaminated pollen samples with selective staining with Sudan IV and methylene blue for light microscopy and scanning electron microscopy (SEM). They were able to stain microencapsulated methyl parathion, permethrin, and fonofos with Sudan IV but selective staining was not possible for microencapsulated methoprene with either stain. They found the most suitable method to investigate microencapsulated formulations was SEM with the smear method for sample preparation.

Chao [36] investigated the role of surfactant in synthesizing polyurea microcapsules by the method of interfacial polycondensation. He observed that, in the presence of a fixed amount of emulsifier, sodium carboxy methyl cellulose (CMC) was better than methyl cellulose for synthesizing polyurea microcapsules in terms of average particle size and particle size distribution. He also concluded that, in a toluene diisocyanate system, ethylene diamine is required for the formation of unique microcapsules.

Zhang and collaborators [31] studied the effect of operation variables and monomers on the properties of polyamide microcapsules prepared by the method of interfacial polycondensation using phthaloyl dichloride as the oil soluble monomer and diethylene triamine (DETA) as the water soluble monomer. They observed that the microcapule diameter did not change appreciably beyond 45 s of mixing time. More importantly, they observed the initial membrane was not strong enough to prevent the microcapsules from coalescing.

Pearson and Williams [37] investigated the interfacial polycondensation of a liquid polyfunctional aromatic isocyanate and a diol to form polyurethane microcapsules. They observed that a gel layer was formed around the isocyanate droplets such that this gel layer was swollen by the diol but not by the polyfunctional isocyanate. They proposed a core-shell model for the interfacial polymerization reaction in which the liquid active agent is surrounded by a polymeric wall made of polyurethane. Microcapsules were treated with gaseous ammonia to convert the liquid droplets to solid particles and their radius was assessed with transmission electron microscopy (TEM). However, no comparison was made between the experimental and theoretical results.

Pense and collaborators [38] studied the formation of benzalkonium chloride loaded microcapsules by interfacial polycondensation with methylene bis-(phenyl isocyanate) as the isocyanate. In this work, the morphology of the microcapsules was investigated with light microscopy and SEM. The mechanical resistance of the microcapsules was determined by viewing them with an optical microscope before and after the application of shear stress in a coaxial cylinder of a couette viscometer.

The formation of polyurethane wall was monitored by measuring the viscosity of systems containing the isocyanate monomer and the surfactant in different solvents. To visualize the initial site of polycondensation reaction and subsequent growth of the interfacial layer, finely divided carbon black powder was introduced at the interface of a two-phase unstirred organic/aqueous system. Carbon black was insoluble in both phases but it was wetted by the water phase. They observed that the carbon black, which was spread on the aqueous side of the interface, was not included in the thickness of the polymeric film after recovering. Therefore, according to their results, the microcapsule wall was formed and grown in the organic phase. This result was supported by the fact that both the isocyanate and the oligomers formed at the interface by water hydrolysis of the isocyanate were oil soluble. Their results indicated that the nature of the components and the composition of the dispersed oil phase significantly affected the course of the interfacial polycondensation reaction and morphology of the microcapsules. Their results indicated that the process of microencapsulation was

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affected by many interrelated parameters such that some of these parameters affected the precipitation of the polymer film at the interface and others controlled the rate of polymer formation. The morphology or the mechanical properties of microcapsules could be altered by modifying these parameters.

In another study, Ichikawa [39] investigated the dynamic mechanical properties of polyurethane-urea microcapsules, prepared by interfacial polycondensation method, on a paper substrate. Based on his results, the glass transition temperature of microcapsules without the core material was higher than microcapsules with the core material which indicated that the core material plasticized the wall. Moreover, his X-ray diffraction results indicated that the wall material was amorphous with no melting point of the hard segments. He observed a core-shell morphology for the structure of microcapsules using SEM.

Shanta and Rao [40] prepared polyurethane microspheres using the method of suspension condensation polymerization with toluene diisocyanate (TDI) or methylene bis(phenyl isocyanate) (MDI) as the multifuntional isocyanate. According to their results, MDI containing microspheres were more porous as compared to TDI containing microspheres and the release rate of bromomethyl blue, as the active agent, was faster with MDI as compared to TDI microspheres.

Polyurethane microspheres were prepared by us [41] using the method of suspension polycondensation with MDI and polyethylene glycol 400 as the multifunctional isocyanate and diol, respectively. The microspheres were porous due to the formation of carbon dioxide by the reaction of MDI with water and the porosity was significantly affected by the concentration of chain extending agent due to the variations in the ratio of hard to soft segments of the PU chains.

According to these results, the morphology and microstructure of the microspheres was strongly affected by variations in the density of hard segments of the PU chains.

The results of previous studies clearly indicate that the process of interfacial polycondensation is very complex and the course of wall formation is affected by many interrelated parameters. In general, the process of interfacial polycondensation and wall formation is affected by the nature and composition of the two immiscible phases, the concentration of the reactants, physico-chemical properties of the encapsulating agent, the partition coefficient of each reactant between the two phases, chemical nature and concentration of the chain extending agent, type and concentration of the emulsifying and suspending agent, the swelling or solubility of the microcapsule wall, and the rate of reaction between the monomers.

The objective of this research was to investigate the morphology, microstructure, and release behaviour of polyurethane-urea microcapsules prepared by interfacial polycondensation of methylene bis(phenyl isocyanate) as the multifunctional isocyanate and hexamethylene diamine as the diamine, anionic sodium lignin sulphonate as the emulsifying agent, and the herbicide 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, as the active agent.

EXPERIMENTAL

4,4′-Methylene bis(phenyl isocyanate) (MDI) with functionality of 2.2 and equivalent weight of 113.6 and hexamethylene diamine (HMDA) with functionality of 2.0 and equivalent weight of 58 were obtained from Merck. The anionic emulsifying agent REAX-88B, a sodium lignin sulphonate (SLS), was a registered trademark of Westvaco Corp. and the herbicide alachlor, as the active encapsulating agent, with chemical name 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide, with 94.8% purity was a registered trademark of Monsanto Corp. They were provided by the Agricultural Support Services Co., a subsidiary of Iran's Ministry of Agriculture. Sodium chloride and anhydrous calcium chloride were obtained from Merck.

All chemicals and reagents were used as received without further purification.

The following procedure was used for the preparation of microcapsules. To prepare the oil phase, 12.6 g (5×10^{-2} mol) of MDI was added to a beaker containing 200 g of herbicide alachlor, as the active agent, to provide a 6.3 w/w (%) solution of the isocyanate monomer in the oil phase. To prepare the

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aqueous phase, 12 g of SLS, as the emulsifying agent, was added to a beaker containing 300 g of distilled water to provide a 4 w/w(%) aqueous solution. To prepare the aqueous HMDA solution, 5.8 g (5×10^{-2} mol) of HMDA was added to a beaker containing 23.2 g of distilled water to provide a 20 w/w (%) HMDA in water. The aqueous and the oil phase were preheated to 55 °C in an oven before the encapsulation.

For microencapsulation, the preheated aqueous phase was poured into a 1 L stainless steel vessel and it was allowed to mix for 30 s at an agitation rate of 5000 rpm. Next, the preheated oil phase was added slowly to the aqueous phase over a 60 s time interval while the agitation rate was kept at 5000 rpm. After the addition of the oil phase, the mixing was continued for an additional 30 s. Then, the 20 % HMDA solution was added dropwise to the emulsion over a 60 s time interval. After the addition of HMDA, the agitation rate was reduced to 2000 rpm to reduce the shear rate and avoid break up of microcapsules.

Formation of the polymeric wall around the droplets was allowed to proceed for 45 min while the temperature of the reaction was kept constant at 60 °C by cooling or heating the reaction vessel. After the completion of the microencapsulation reaction, the agitation rate was reduced to 500 rpm and 14 g of calcium chloride, equal to 4% w/w of the aqueous phase, was added to the microcapsule suspension to stabilize the microcapsules. After the addition of calcium chloride, the suspension was mixed for 10 min at 500 rpm, bottled, and stored at ambient conditions. The percent of the active agent in the formulation was 35% w/w and the percent of the polymeric shell wall, for 100% conversion of the monomers, was 3.2%.

The microcapsules were examined visually with an optical microscope (Euromex). A drop of the microcapsule suspension was placed on a microscope slide, diluted with distilled water, and examined at a magnification of 100 or 400. The average diameter and size distribution of the microcapsules were measured with a Coulter particle size analyzer (Coulter LS130) by injecting approximately 1 mL of the microcapsule suspension in the holding reservoir of the analyzer.

Dynamic viscosity measurements were carried out with a Haake VT500 viscometer (Fisons Instruments) at a shearing rate of 20 Hz. Initially, in order to measure the viscosity, the shear rate was raised to 45 Hz and the sample was sheared for 10 min to reduce the formation of thixotropic structure related to sample history. Then, the shear rate was reduced from 45 Hz to 20 Hz and the viscosity was measured over a 2 min time period after the reduction of shear rate.

For scanning electron microscopy examination, the microcapsule suspension was spray-dried to obtain dry powder using a Buchi 190 mini spray dryer. The inlet and outlet temperature of the dryer was 120 °C and 70 °C, respectively. The compressed air pressure was 2.1 bar and the air flow rate was 12 L/min. Before spray drying, the microcapsule suspension was diluted with distilled water in a 3:1 ratio to reduce the viscosity. The volumetric flow rate of the liquid in the dryer was 22 mL/min. The moisture content of the dried microcapsules after drying was 8% which was measured by weighing the microcapsules before and after complete drying in an oven at 120 °C for 10 min.

The size distribution and surface morphology of the spray-dried microcapsules were examined with SEM. The sample was sprinkled on a double stick tape which was attached to an SEM mount. Then, the sample was sputter coated with a combination of gold and palladium and examined with a JEOL 840 SEM at an accelerating voltage of 10 KeV.

To examine the morphology, porosity, and roughness of the surface of microcapsules, atomic force microscopy (AFM) was used. The experiments were performed with a Nanoscope III atomic microscope (Digital Instruments) equipped with an intermediate range atomic force scan head. For sample preparation, the spray-dried microcapsules were fixed to a SEM sample stub with a double-sided adhesive tape. The scan ranges of the images were 150 nm by 10 μm. The microcapsule surface was examined in the height mode with a 100 μm long SiN cantilever (Park Scientific) with a spring constant of 0.1 N/m. The force applied to the microparticle surface was 7 nN with a scan rate ranging from 1 to 5 Hz.

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Thermal behaviour of the spray-dried micro-

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capsules was examined with a thermogravimetric analyzer (TGA) coupled to a mass spectrometer (MS). The temperature was increased from ambient to 400 °C at a rate of 10 °C/min. The TGA experiments were carried out with a Mettler TA-1 analyzer. The species evolved on heating the sample were transferred to a HP-5992A mass spectrometer via heated stainless steel tubing and they were analyzed with a quadrupole mass spectrometer. The TGA/MS experiments were carried out under 20% oxygen in helium atmosphere.

RESULTS AND DISCUSSION

The addition of the aqueous HMDA solution changed the pH of the microencapsulation reaction mixture from 7.5 to 11.8. As the HMDA reacts with the isocyanate, the pH of the reaction mixture drops. The changes in the pH as the HMDA is consumed can be used to follow the conversion or the extent of the reaction. Figure 1 shows the change in pH and the percent conversion, based on the HMDA monomer, as a function of the reaction time. As the microencapsulation reaction proceeds, the pH changes from 11.8 to 7.7 and the conversion reaches 96% after 60 min.

The optical micrograph of the microcapsules at a magnification of 400 is shown in Figure 2. The microcapsules are spherical and have a narrow size distribution with a smooth surface structure, which clearly indicates that the microcapsules are formed by interfacial polycondensation. The size distribution of the microcapsules, as measured by Coulter particle

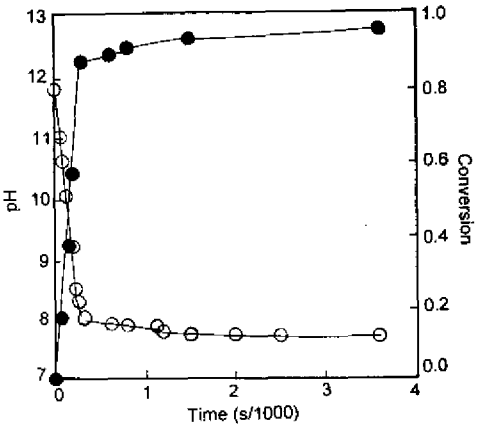

Figure 1. Changes in the pH of microencapsulation mixture as a function of reaction time.

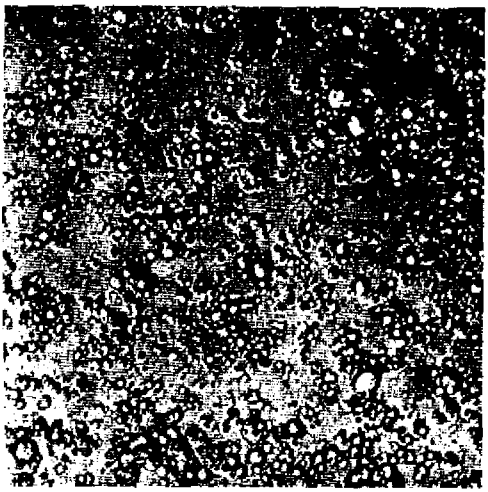

Figure 2. Optical micrograph of the synthesized polyurea microcapsules at a magnification of 400.

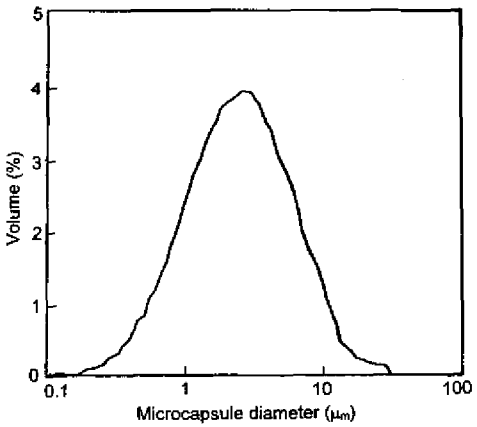

Figure 3. Size distribution of the synthesized polyurea microcapsules.

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size analyzer, is shown in Figure 3. The mean and mode of the distribution was 3.4 and 2.5 μm, respectively, with a mean to median ratio of 1.4. Therefore, the distribution was slightly right skewed. The mean of the distribution was within the range of 2.7 to 4.1 μm with 95% confidence limits. The standard deviation of the mean of the distribution was 3.4 μm.

Figure 4 shows the surface topography of the microcapsules, mapped by atomic force microscope. The scanned area was 1 μm^2. According to this figure, the maximum surface roughness was around 50 nm. Also, as the surface area was scanned, no pores were observed on the surface. Therefore, it appears that the microsphere wall structure is not porous.

Thermal stability of the microcapsules was investigated with TGA/MS as a function of temperature, at a heating rate of 10 °C/min. Figures 5 and 6 show the molecular ion current for molecular fragments 271, 269, 238, and 175 daltons as a function of temperature for unencapsulated and microencapsulated alachlor, respectively. The molecular ion current is directly proportional to the amount by weight of each molecular fragment given off as the sample was heated. Since the molecular weight of alachlor is 270 daltons, the molecular fragments with mass numbers 271 and 269 correspond to the entire alachlor molecule before fragmentation or degradation in which the molecule is ionized by abstracting or loosing hydrogen. The molecule fragment with mass number 238 is due to

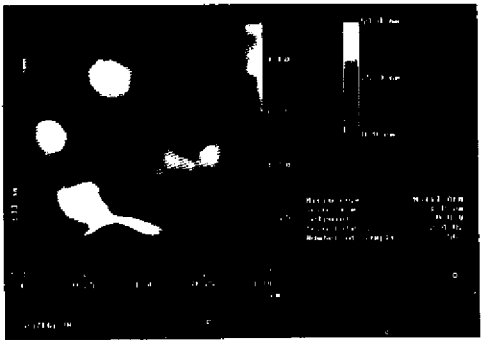

Figure 4. AFM micrograph of the surface topography of the synthesized polyurea microcapsules. The scanned area was 1 μm^2. Maximum surface roughness was around 50 nm.

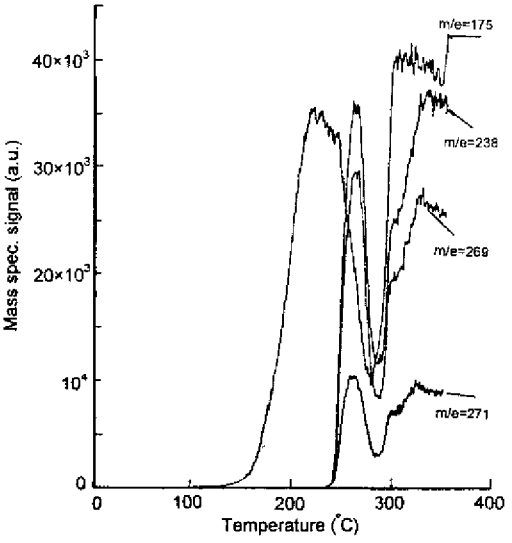

Figure 5. Molecular ion current as a function of temperature for unencapsulated alachlor as an active agent for molecular fragments of 271, 269, 238, and 175 daltons.

fragmentation and loss of carbon dioxide from alachlor, as the temperature is raised above 200 °C.

The molecule fragment with mass number 175 is due to fragmentation and oxidative degradation of alachlor in the presence of oxygen in the gas mixture.

According to Figure 5, oxidative degradation of unencapsulated alachlor, displayed by the ion current of the molecular fragment with mass number 175, commences at 160 °C and it peaks at temperatures between 210-220 °C. According to the same figure, fragmentation of the alachlor, displayed by the ion current of the molecular fragment with mass number 238, and vaporization, displayed by the ion current of the molecular fragments with mass numbers 271 and 269, commences concurrently at 240 °C and they peak at 260 °C.

On the other hand, according to Figure 6, oxidative degradation, fragmentation and vaporization of the encapsulated alachlor commences concurrently at 260 °C, which is 20 °C higher, and they peak at 290 °C, which is being 30 °C higher than the unencapsulated alachlor. For encapsulated alachlor, no peak was

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observed at temperatures below 220 °C due to oxidative degradation, and only a shoulder was observed at temperatures ranging from 180 °C to 220 °C due to 3–5% unencapsulated alachlor in the encapsulated sample. Since the peaks for the encapsulated alachlor are relatively sharp, it indicates that the active agent is released from the microcapsules by the rupture of the capsule wall or the capsule structure and molecular diffusion plays a minor role as the release mechanism. Comparison of Figures 5 and 6, clearly indicates that encapsulation substantially reduces volatility and oxidative degradation of the active agent and increases its thermal stability.

The release behaviour of the microcapsules were studied in deionized water and 9.5% w/w calcium chloride aqueous solution at 25 °C. Approximately 1 g of the spray-dried microcapsules were dissolved in 200 mL of deionized water or calcium chloride aqueous solution, extracted for 30 min, filtered through a Whatmen No.4 filter paper, and allowed to dry under ambient conditions. Figures 7 and 8 show the SEM micrograph of the microcapsules extracted with deionized water and calcium chloride aqueous solution, respectively, after 24 h of drying under ambient conditions at 2000 magnification.

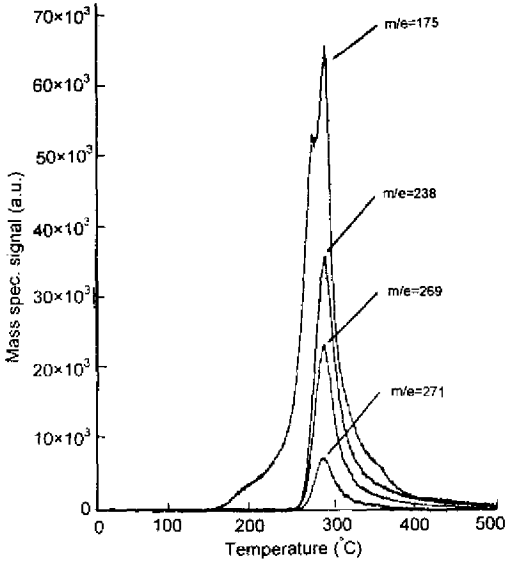

Figure 6. Molecular ion current as a function of temperature for the synthesized polyurea microcapsules with alachlor as an active agent for molecular fragments of 271, 269, 238, and 175 daltons.

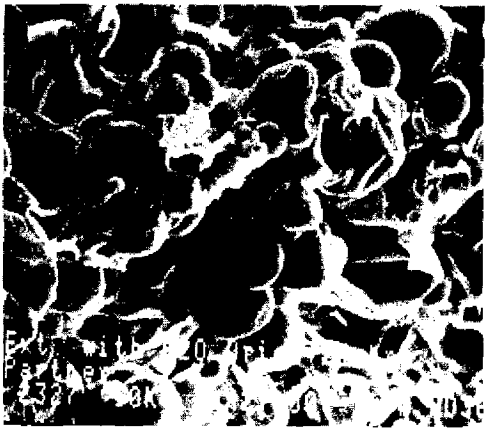

Figure 7. SEM micrograph of the synthesized polyurea microcapsules after extraction with deionized water and drying for 24 h under ambient conditions at 2000 magnification.

Comparison of these figures indicated that

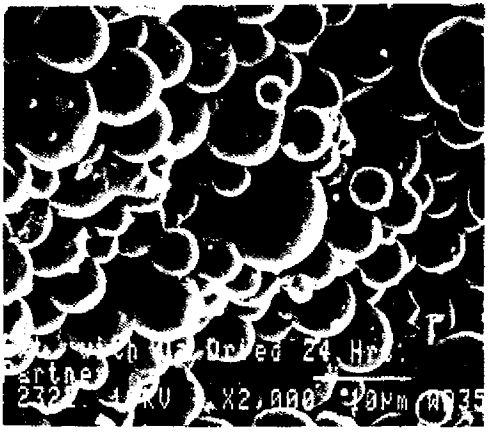

Figure 8. SEM micrograph of the synthesized polyurea microcapsules after extraction with 9.5% calcium chloride aqueous solution and drying for 24 h under ambient conditions at 2000 magnification.

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more than 50% of the microcapsules extracted with deionized water collapsed after 24 h of drying but relatively all of the microcapsules extracted with calcium chloride aqueous solution remained stable.

Figures 9 and 10 show the SEM micrograph of the same microcapsules after 14 days of drying under ambient conditions at magnification of 1000 and 2000, respectively. According to these figures, after 14 days of drying, almost all of the microcapsules extracted with deionized water collapsed but the majority of the microcapsules (more than 95%) extracted with calcium chloride aqueous solution remained stable.

When the same experiments were performed with sodium chloride aqueous solution with the same molarity as the calcium chloride solution, results similar to the extraction with deionized water were obtained. According to these results, the multivalent salt calcium chloride plays a major role in stabilizing the microcapsule structure, most likely by interacting with the anionic surfactant sodium lignin sulphonate.

To further investigate this interaction, viscosity of SLS aqueous solutions was measured as calcium chloride was added to the solution. Figure 11 shows the viscosity of a 40% w/w SLS aqueous solution as calcium chloride was added to the solution at 25 °C.

The abscissa in Figure 11 is the molar ratio of calcium to carboxylic and phenolic groups of the SLS. It is believed that the interaction between calcium chloride and SLS is mainly by electrostatic interactions between the positive calcium ions and the

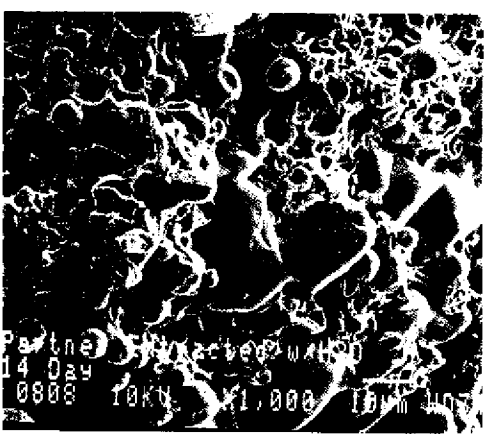

Figure 9. SEM micrograph of the synthesized polyurea microcapsules after extraction with deionized water and drying for 14 days under ambient conditions at 1000 magnification.

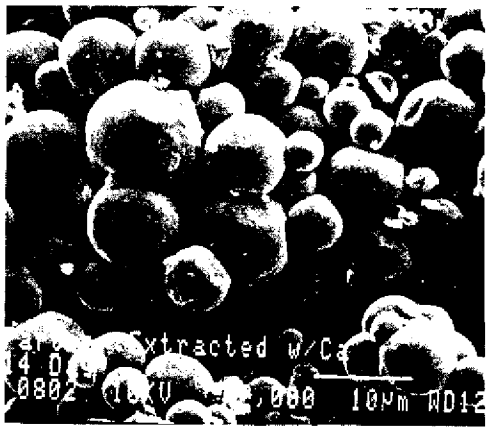

Figure 10. SEM micrograph of the synthesized polyurea microcapsules after extraction with 9.5% calcium chloride aqueous solution and drying for 14 days under ambient conditions at 2000 magnification.

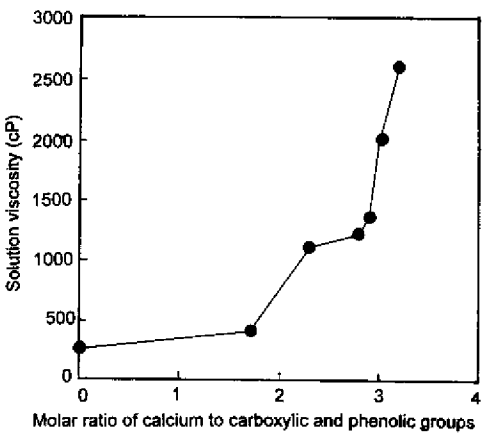

Figure 11. Viscosity of a 40 w/w (%) sodium lignin sulphonate aqueous solution as a function of calcium chloride concentration at 25 °C. The abscissa is the molar ratio of calcium to carboxylic and phenolic groups of the sodium lignin sulphonate.

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negatively charged carboxylic and phenolic groups. According to this figure, the viscosity of SLS solution increased from 250 cP to 2700 cP as the molar ratio of calcium chloride to carboxylic acid and phenolic groups of SLS increased from zero to 3.2. This indicated that a physical gel was formed, as calcium chloride was added to the SLS solution. In fact, upon the addition of calcium chloride to SLS aqueous solution, two phases were formed in which one phase was concentrated and the other was dilute with respect to SLS.

Figure 12 shows the volume ratio of the gel phase to the dilute phase as calcium chloride was added to the solution. According to this figure, as the molar ratio of calcium to carboxylic acid and phenolic groups of the SLS increased from zero to 1.0, the volume percent of the gel to the dilute phase increased from zero to nearly 60%. This clearly indicates that the multivalent positive calcium ion physically cross-links the SLS chains by interacting with the negatively charged carboxylic and phenolic groups with subsequent phase separation of the physically cross-linked chains to form a concentrated gel phase.

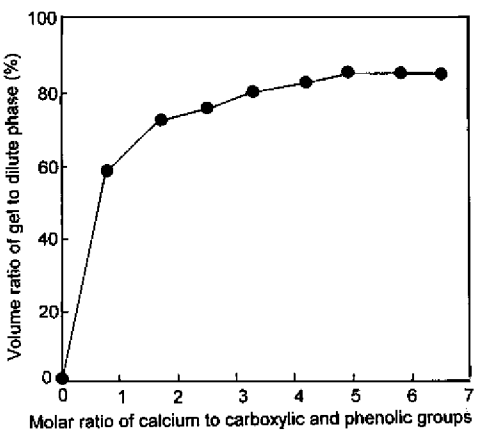

Figure 12. Volume ratio of the gel phase to the dilute phase as a function of calcium chloride concentration for a 40 w/w (%) sodium lignin sulphonate aqueous solution at 25 °C. The abscissa is the molar ratio of calcium to carboxylic and phenolic groups of the sodium lignin sulphonate.

According to the same figure, as the molar ratio of calcium to carboxylic and phenolic groups increased from 1.0 to 6.8, the volume percent of the gel phase to the dilute phase increased from 60% to 82%.

When similar experiments were performed with sodium chloride instead of calcium chloride, phase separation did not take place. These results indicate that as calcium chloride is added to the aqueous suspension of microcapsules containing SLS as the surfactant, a gel phase is formed. This gel phase encompasses the microcapsules and increases the stability and modifies the release behaviour of the microcapsules. When the microcapsule suspension is washed with calcium chloride aqueous solution and allowed to dry, the gel layer encompassing the microcapsules does not dissolve and therefore the microcapsules remain stable after drying. On the other hand, when the microcapsule suspension is washed with deionized water and allowed to dry, the calcium ions in the gel layer diffuse to the aqueous phase by the action of osmotic force, the gel layer dissolves, and the microcapsules rupture after drying.

The results of this research indicates that the ionic surfactants and their interaction with multivalent salts can play a significant role in stabilization and release behaviour of microcapsules prepared by the method of interfacial polycondensation.

CONCLUSION

Polyurea microcapsules containing 2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide as the active agent were prepared by the method of interfacial polycondensation with methylene bis(phenyl isocyanate) as the multifunctional isocyanate, hexamethylene diamine as a diamine, and anionic sodium lignin sulphonate as an emulsifying agent.

Results indicate that the interaction between ionic surfactants and multivalent salts can play an important role in stabilization and release behaviour of microcapsules prepared by the method of interfacial polycondensation.

As calcium chloride was added to the aqueous suspension of the synthesized polyurea microcapsules

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containing SLS as the surfactant, a gel phase was formed. This gel phase encompasses the microcapsules and increases the stability and modifies the release behaviour of the microcapsules.

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