

Effect of Surfactants on the Particle Sizes of Red #170 Polyurea Microcapsules

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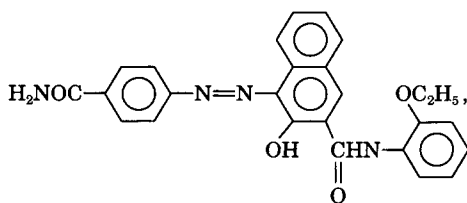
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SYNOPSIS

Red #170 (pigment) polyurea microcapsules have been successfully prepared at our laboratory. Both core and shell of these microcapsules are demonstrated to be red #170 pigment and polyurea, respectively, by infrared (IR) spectra. The number-average particle sizes of these microcapsules are seen to decrease with increasing concentration and the ethylene oxide chain length of nonylphenylpolyoxyethylene ether (NP_n; *n* = 6, 8, 10, 12, 16) as an emulsifier in the water phase used for making microcapsules. Experimental results indicate that the average particle sizes of red #170 polyurea microcapsules are smaller for the system with NP₁₆ than for the system with NP₄ (in the oil phase) and/or NP₁₆ (in the water phase) and that, in the presence of NP_n, these particle sizes are seen to be slightly smaller for use of methylcellulose than for use of sodium carboxymethylcellulose as a protective colloid. It is also interesting to note that the released amounts of red #170 pigment from polyurea microcapsules in di-*n*-butylphthalate solvent is lower for a system with NP₁₆ than for a system with methylcellulose, as a result of good emulsification leading to decrease the interaction between toluene diisocyanate and water molecules. This may further cause more crosslinkage to take place at the urea groups, resulting in a decrease in the porosity of the capsules. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Red #170 pigment,



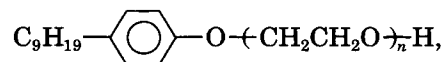
similar to surfactants having both hydrophobic and hydrophilic properties, is not soluble in aqueous solution. These dual properties enable red #170 at high concentration to form aggregates on the surface of leather in the process of coloring. However, these aggregates are likely to decrease the chroma and lightness of red #170 pigment on leather. To over-

come this problem, the use of red #170 microcapsule may be one of the best ways to color leather. Therefore, we attempt to investigate the preparation of red #170 polyurea microcapsules and the effect of surfactants¹ on the average particle sizes of these microcapsules by the interfacial polymerization²⁻⁵ technique.

EXPERIMENTAL

Material

Nonylphenylpolyoxyethylene ether (termed NP₆, NP₈, NP₁₀, NP₁₂, NP₁₆; the subscript represents the moles of ethylene oxide),



was received from Sino-Japan Chemical Co. Both methylcellulose (termed MC) and sodium carbox-

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ymethylcellulose (CMC) were obtained from Kan Chemical Co. and Wako Pure Chemical Co., respectively. Toluene diisocyanate (Called TDI), ethylene diamine, and dibutyltin dilaurate were supplied by Merck Co. Triethylamine and di-*n*-butylphthalate (DBP), reagent grade, were purchased from Merck Co. and Nihon Shiyaku Ind., Ltd., respectively. Red #170 pigment was obtained from Hoechst, Germany. All these chemicals were used without further purification.

Preparation

Nonylphenylpolyoxyethylene ether (0.5, 1.0, and 2.0 g) with different moles of ethylene oxide (EO) (i.e., NP₂ and NP₄) as an emulsifier was added, respectively, to a 250-mL beaker containing 0.2 g red #170 pigment suspended in 30 g DBP nonaqueous solution with 10 g TDI under agitation. The pH of this nonaqueous solution was adjusted to around 7 by NaOH solution. This neutralized nonaqueous solution was charged into a four-necked 1000-mL pyrex glass flask containing 4 g MC ($[\eta] = 6.0$ mL/g) or 4 g sodium CMC ($[\eta] = 27.6$ mL/g) as a protective colloid dissolved in 150 g H₂O in the presence and absence of NP with different EO chain lengths under agitation with a speed at around 900 rpm. Ethylene diamine (3.5 g) present in 10 g H₂O was then added to the above liquids to undergo interfacial polymerization reaction for 3 h at 70°C.

Both the core and shell of red #170 polyurea microcapsules were analyzed by using Fourier transform/infrared (FT/IR) spectrometry (JASCO FT/IR 5300, Japan), an ultraviolet (UV) spectrophotometer (Shimadzu UV-240, Japan) and polarized microscope (Olympus Optical Co. Ltd., Japan). The number-average particle sizes of red #170 polyurea microcapsules were measured at $25 \pm 0.05^\circ\text{C}$ by a Coulter counter (Electronic Limited Multisizer, England) designed to analyze the particle size range from 3 to 200 μm . The experimental errors for the measurements of a much wider range of capsule sizes covered are estimated to be within ± 0.5 .

RESULTS AND DISCUSSIONS

The IR spectra for TDI and red #170 and red #170 polyurea microcapsules are shown in Figure 1–3, respectively. The TDI reacted with ethylene diamine to form the urea linkage and is illustrated by the formation of the absorbance peaks at around 3300 cm^{-1} (NH) and 1720 cm^{-1} (C=O) in Figure 3 and by the disappearance of the absorbance peak at around 2275 cm^{-1} (NCO) shown in Figure 3 in comparison to that of Figure 1. In addition, the absorbance peaks at 1670 cm^{-1} (C=O), 1140 cm^{-1} (Ar—OH), and 3400 cm^{-1} (N—H) for red #170 given in Figure 2 are almost the same as the corresponding peaks shown in Figure 3. These results may suggest

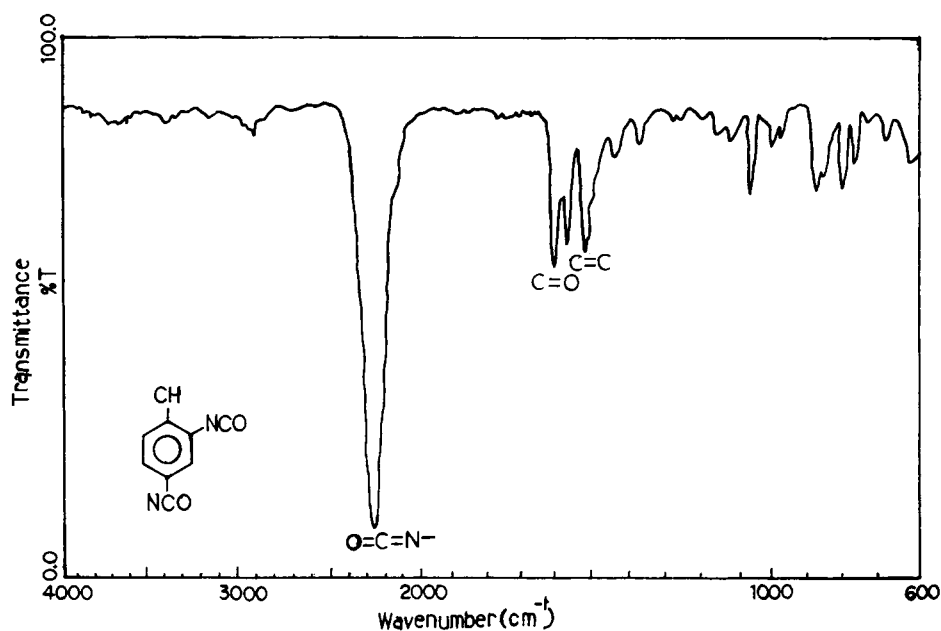


Figure 1 Spectra of toluene diisocyanate at $25 \pm 0.05^\circ\text{C}$.

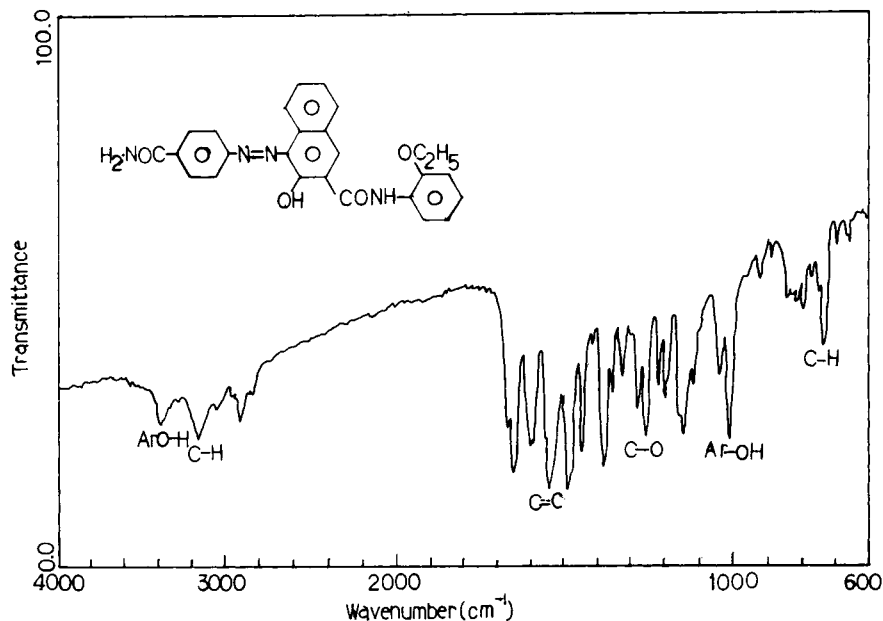


Figure 2 Spectra of red #170 at $25 \pm 0.05^\circ\text{C}$.

that both the core and shell of the microcapsule prepared at our laboratory are considered to be red #170 and polyurea, respectively.

The surface tension as a function of NP nonionic surfactants with different EO chain lengths present in water containing ethylene diamine is given in Figure 4. It clearly indicates that, for NP_n's aqueous

solutions, the surface tensions drastically decrease with increasing concentrations as a result of more hydrophobics of NP_n adsorbed at the air-water interface. Furthermore, the surface tension is seen to be higher for NP with longer EO chain length than for NP with shorter EO chain length. This is because more hydrogen bonding formed between the EO

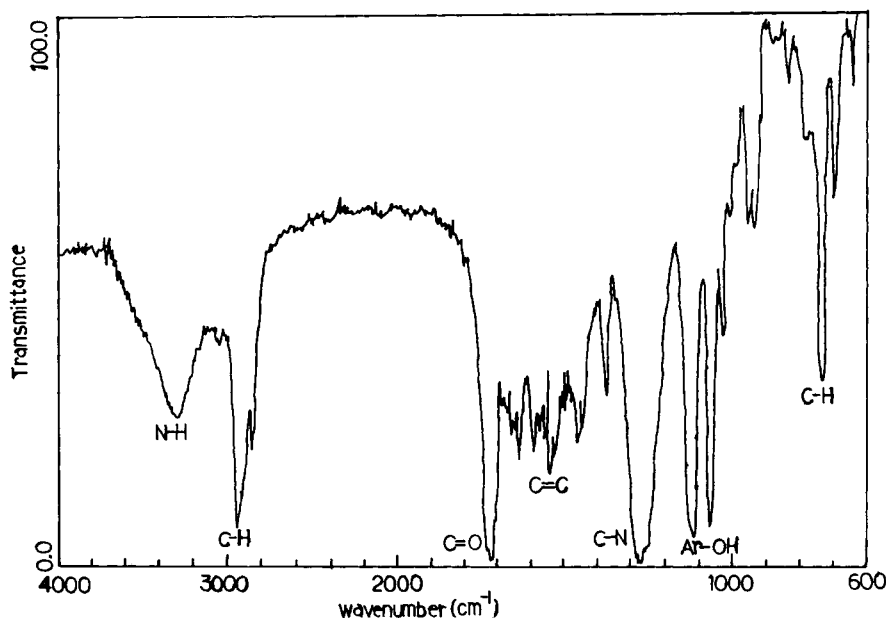


Figure 3 Spectra of red #170 polyurea microcapsule at $25 \pm 0.05^\circ\text{C}$.

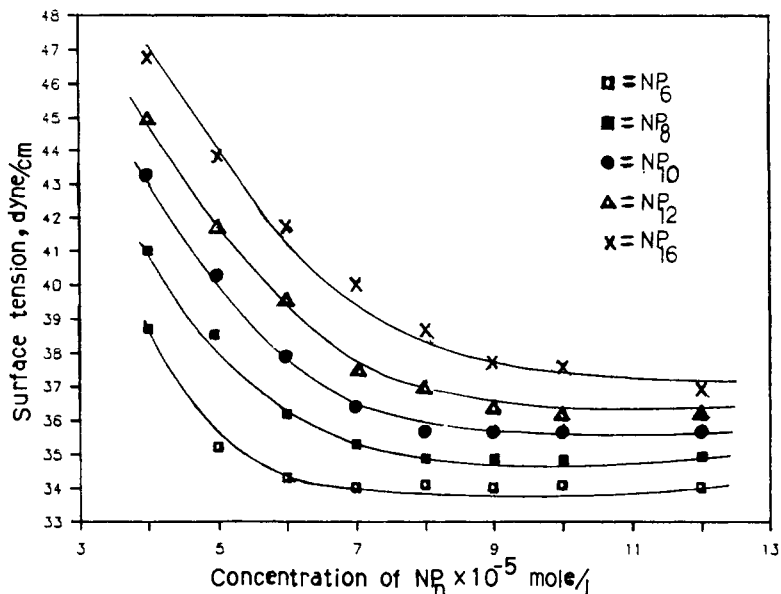


Figure 4 Plot of the surface tension versus the concentration of NP with different EO chain lengths present in water containing ethylene diamine at room temperature.

chain and the water molecules makes micelles with minimum surfaces to be formed at the higher concentrations. This is why the surface tension for NP nonionic surfactant with longer EO chain length is higher.

The number-average diameter of red #170 polyurea microcapsule, prepared by polymerization of TDI with ethylene diamine in the presence of a fixed

amount of MC (4.0 g) as a function of NP₆, NP₈, NP₁₀, NP₁₂, and NP₁₆, respectively, at the oil-water interface, is given in Figure 5. It indicates that the average particle size of red #170 polyurea microcapsule is seen to decrease with increasing concentrations of NP_n's nonionic surfactants and EO chain length as well. However, at the same concentration of NP_n's nonionic surfactants present in the water

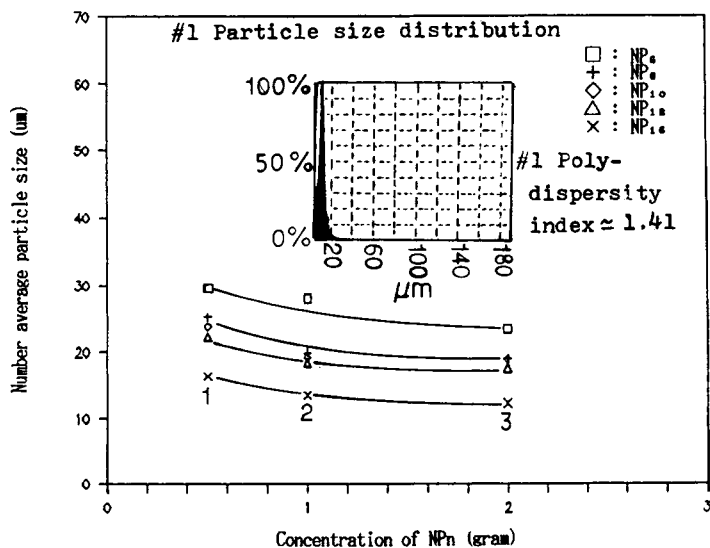


Figure 5 Plot of the number-average particle size vs. the respective concentration of NP₆, NP₈, NP₁₀, NP₁₂, and NP₁₆ present in a fixed amount of MC (4.0 g) used for preparing red #170 polyurea microcapsule at room temperature.

phase the particle size of red #170 polyurea microcapsule prepared appears to be smaller for NP with longer EO chain length (i.e., NP₁₆). This is because NPs with longer EO chain lengths will generate better emulsification at the oil-water interface. This good emulsification resulting in greatly reducing the interaction between unbound water and TDI may enhance the interfacial polymerization to complete fast. Therefore, the number-average particle size of red #170 polyurea microcapsule becomes smaller. Based on the number-average particle size distribution of red #170 polyurea microcapsule (sample 1) given in Figure 5, the polydispersity, calculated to be approximately 1.41, is considered within the reasonable range.

The concentration of NP₄ (0.5 g = 8.42×10^{-3} mol/L) as an emulsifier and of MC (4.0 g) as a protective colloid were fixed in the oil and water phases, respectively. The number-average particle size of red #170 polyurea microcapsule prepared at 70°C as a function of NP with different EO chain lengths present in the water phase is given in Figure 6. The results shown in Figure 6 illustrate that the number-average particle sizes of microcapsules decrease with the increase of concentration and EO chain length of NP present in water phase. The reason the particle size decreases is the same as described in Figure 5. However, the use of a fixed amount of NP₄ as an emulsifier in the oil phase is seen not to significantly affect the particle size of

red #170 polyurea microcapsule. On the other hand, the concentrations of NP_{*n*} (*n* = 6, 10, 16) and MC in the water phase are fixed, while the concentration of NP₄ in the oil phase is changed. Under this experimental condition, the particle sizes of microcapsules are also found to decrease with increasing concentration of NP₄ and are seen to be smaller for NP₄ with 0.5 g ($=3.99 \times 10^{-3}$ mol/L) NP₁₆ than for NP₄ with 0.5 g ($=6.89 \times 10^{-3}$ mol/L) NP₆ or 0.5 g ($=5.05 \times 10^{-3}$ mol/L) NP₁₀ shown in Figure 7. This is because NP₁₆ may provide better emulsification at the oil-water interface than NP₆ or NP₁₀, leading the polymerization reaction to be completed sooner.

To further investigate the effect of the protective colloids on the particle size of red #170 polyurea microcapsule, we replaced 4 g MC by 4 g CMC and changed the concentration of NP with different EO chain lengths in the water phase for preparing red #170 polyurea microcapsules only. Except for the substitution of MC by CMC, experimental conditions are the same as described in Figure 5. The experimental results given in Figure 8 indicate that the number-average particle size of red #170 polyurea microcapsule is seen to decrease with increasing concentration and EO chain length of NP_{*n*}'s but to slightly increase as the concentration of NP_{*n*}'s further increases.

At low concentrations of NP_{*n*} with different EO chain lengths, the adsorbance of charged CMC mol-

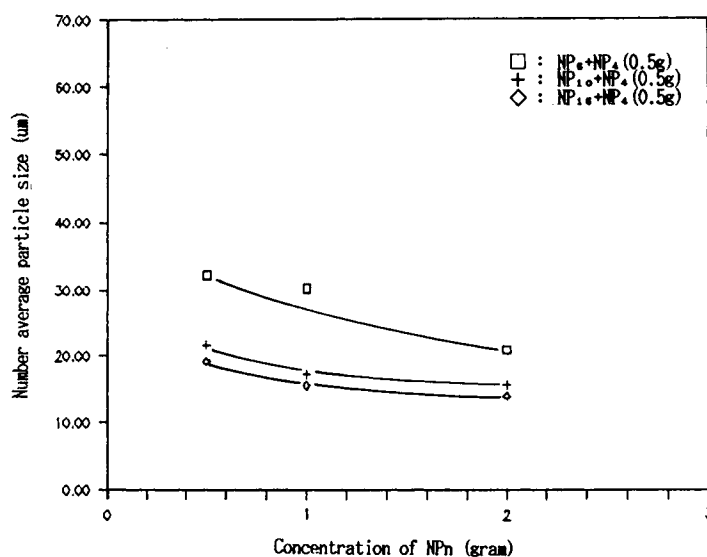


Figure 6 Plot of the number-average particle size vs. the respective concentrations of NP₆, NP₁₀, and NP₁₆ present in DBP containing red #170 and TDI reacted with aqueous solution in the presence of fixed amounts of MC (4.0 g) and NP₄ (0.5 g) to form polyurea microcapsule at room temperature.

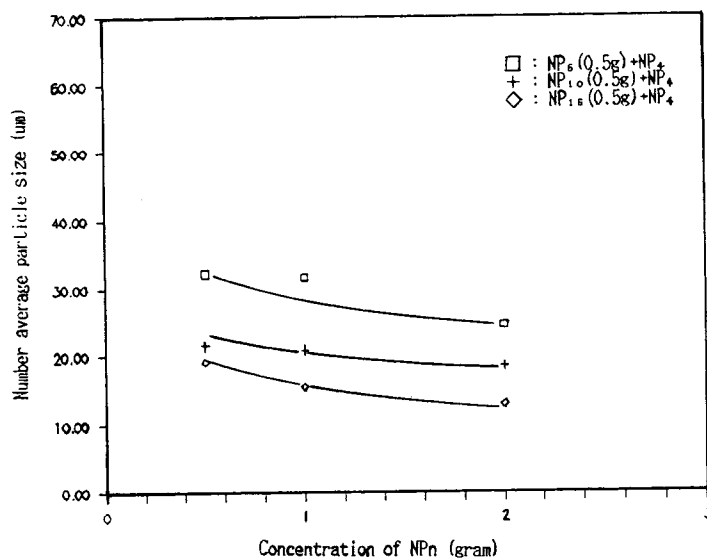


Figure 7 Plot of the number-average particle size vs. the concentration of NP₄ present in DBP containing red #170 and TDI reacted with 4.0 g MC aqueous solution in the presence of a fixed amount of NP₆, NP₁₀, and NP₁₆, respectively, to form polyurea microcapsule at room temperature.

ecules on NP_n molecules will make NP_n molecules become charged NP_n surfactant molecules. These charged NP_n molecules may push more ethylene diamine to the interface to react with TDI rapidly. Therefore, the average particle size of red #170 polyurea microcapsules becomes smaller. At high concentration of NP_n ($2 \text{ g} = 2.75 \times 10^{-2} \text{ mol/L}$ to $1.59 \times 10^{-2} \text{ mol/L}$), on the other hand, the charged

NP_n molecules, generating strong micelle-micelle interactions coupled with more hydrogen-bonding formation, may prevent some ethylene diamine molecules diffusing into the interface to react with TDI. Since the polymerization of TDI with ethylene diamine needs longer time to complete, therefore, the average particle size of red #170 polyurea microcapsules may increase slightly.

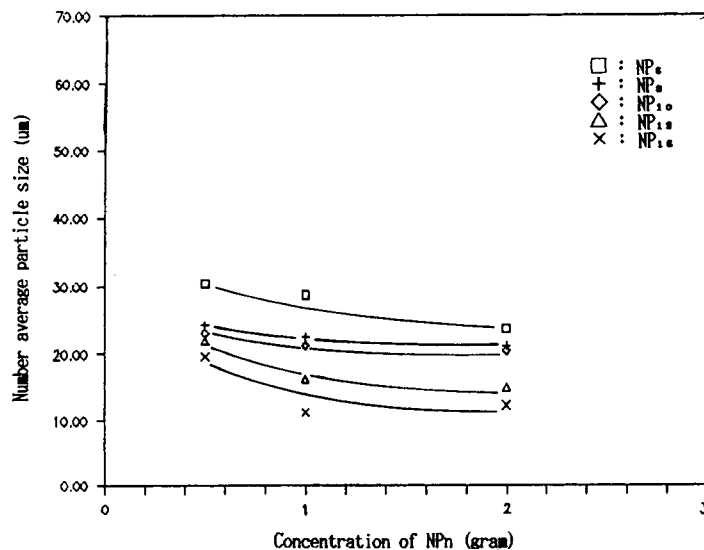


Figure 8 Plot of the number-average particle size versus the respective concentration of NP₆, NP₈, NP₁₀, and NP₁₆ present in a fixed amount of CMC (4.0 g) used for preparing red #170 polyurea microcapsule at room temperature.

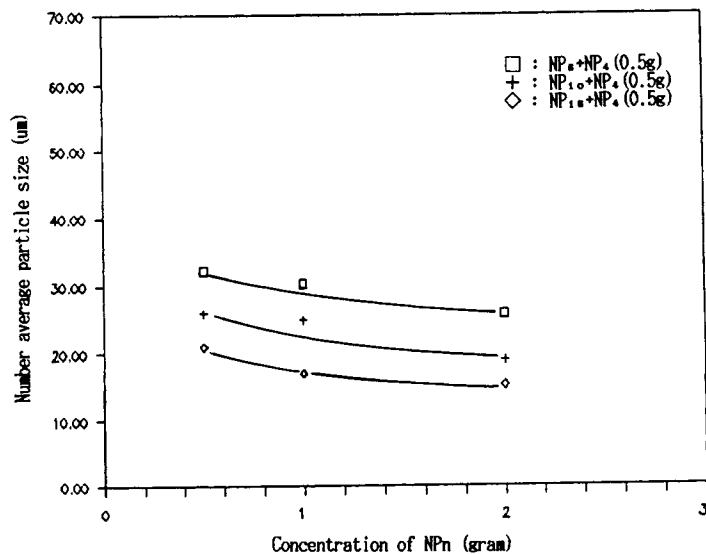


Figure 9 Plot of the number-average particle size vs. the respective concentration of NP₆, NP₁₀, and NP₁₆ present in DBP containing red #170 and TDI reacted with aqueous solution in the presence of fixed amounts of MC (4.0 g) and NP₄ (0.5 g) to form polyurea microcapsule at room temperature.

With the exception of the substitution of MC by CMC as a protective colloid, the experimental conditions are the same as described in Figures 6 and 7. Experimental results given in Figures 9 and 10, very similar to that of Figure 8, show that the addition of a fixed amount of NP₄ as an emulsifier present in the oil phase or NP_n (i.e., $n = 6, 10, 16$)

present in the water phase does not significantly affect the average particle size of red #170 polyurea microcapsules. The explanation for these results is more or less the same as described in Figure 8. In comparison with Figures 6, 7, 9, and 10, although the curves are very similar, results of the particle sizes are slightly larger for the system with CMC

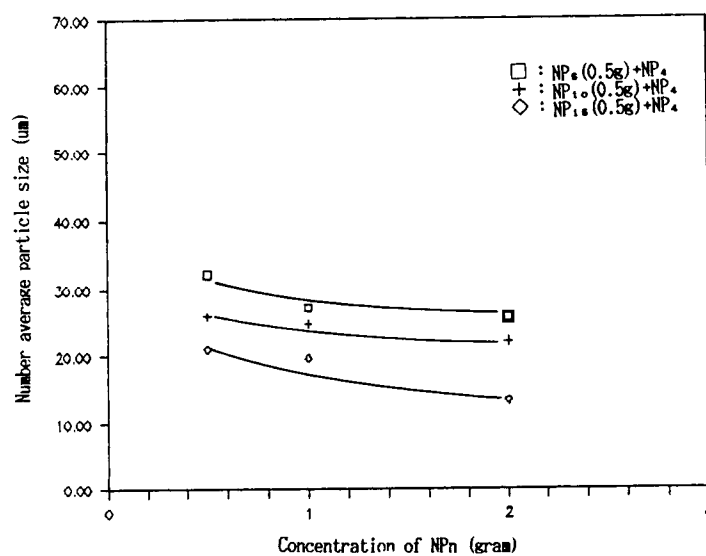


Figure 10 Plot of the number-average particle size vs. the concentration of NP₄ present in DBP containing red #170 and TDI reacted with 4.0 g CMC aqueous solution in the presence of a fixed amount of NP₆, NP₁₀, and NP₁₆, to form polyurea microcapsule at room temperature.

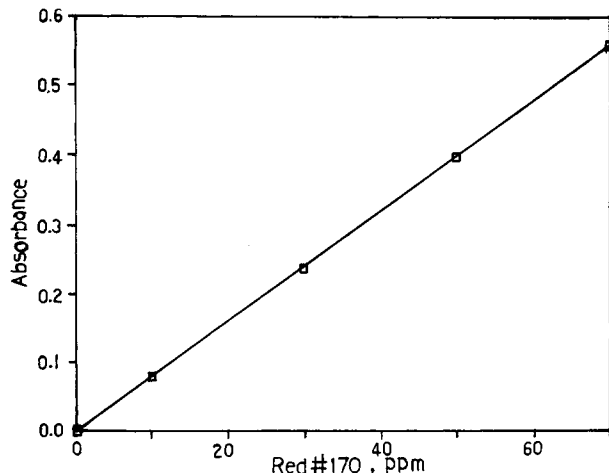


Figure 11 Plot of UV absorbance vs. the concentration of red #170 as a standard calibration curve at room temperature.

than for the system with MC. This may be attributed to the adsorbance of charged CMC molecules on NP_n micelles generating strong electrostatic repulsion among them. This strong repulsion, which may prevent some of ethylene diamine to react with TDI at the interface, enables the polymerization reaction to complete slowly. Therefore, the average particle size of red #170 polyurea microcapsules appears to increase slightly.

The plot of the absorbance versus the concentration of red #170 measured by UV spectra (at 341 nm) at $25 \pm 0.05^\circ\text{C}$ as a standard calibration curve is given in Figure 11. Released amounts of red #170

from polyurea microcapsules measured by UV can be obtained from the standard calibration curve. To test the effect of NP_n and MC on the release of red #170 from polyurea microcapsules in the presence of DBP solvent in order to determine the solidification of crosslinkage of red #170 polyurea microcapsule, we therefore made four samples with 4.0 g MC (in the water phase), 0.5 g ($=8.42 \times 10^{-3}$ mol/L) NP_4 (in the oil phase), 0.5 g ($=3.99 \times 10^{-3}$ mol/L) NP_{16} (in the water phase), and 0.5 g ($=8.42 \times 10^{-3}$ mol/L) NP_4 (in the oil phase) with 0.5 g ($=3.99 \times 10^{-3}$ mol/L) NP_{16} (in the water phase), respectively. The released amount of red #170 from these samples in DBP solvent at $25 \pm 0.05^\circ\text{C}$ as a function of time is shown in Figure 12. It appears that the released amount of red #170 from polyurea microcapsules in DBP solvent is in the order as follows: microcapsule prepared in the presence of 4.0 g MC $>$ 0.5 g ($=8.42 \times 10^{-3}$ mol/L) NP_4 $>$ 0.5 g ($=3.99 \times 10^{-3}$ mol/L) NP_{16} $>$ 0.5 g ($=8.42 \times 10^{-3}$ mol/L) NP_4 , and/or 0.5 g ($=3.99 \times 10^{-3}$ mol/L) NP_{16} .

This is because NP with long EO chain lengths will provide good emulsification at the interface, leading to small particle sizes of red #170 polyurea microcapsules. Furthermore, this good emulsification (i.e., good dispersion), which can prevent some of unbound water to react with TDI to form CO_2

and Nc1ccccc1, on the other hand, may indirectly help more crosslinkage to take place at the urea groups. This crosslinkage may result in de-

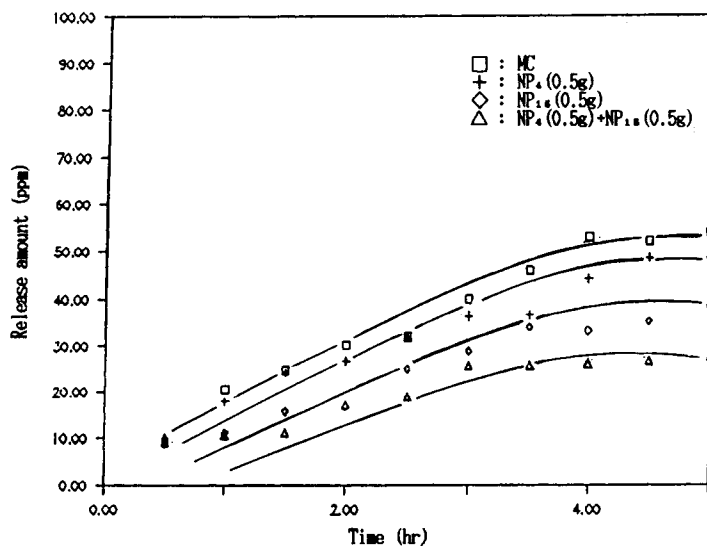


Figure 12 Plot of released amounts of red #170 from polyurea microcapsules present in DBP vs. time at $25 \pm 0.05^\circ\text{C}$.

creasing the porosity of red #170 polyurea microcapsules. Therefore, the released amount of red #170 from polyurea microcapsules in DBP solvent becomes lower for a sample with NP₁₆ than for a sample with NP₄. However, for a system with MC alone, it has relatively large particle sizes of microcapsules and has less crosslinkage to occur at the urea groups, as a result of poor emulsification occurring at the interface. Thus, the released amount of red #170 from polyurea microcapsules becomes higher.

CONCLUSION

We have successfully prepared microcapsules at our laboratory, and their core and shell are demonstrated to be red #170 pigment and polyurea, respectively, by IR spectra.

The number-average particle size of red #170 polyurea microcapsules prepared in the presence of a fixed amount of MC or CMC is seen to decrease with increasing concentration and EO chain length of NP_n. Use of NP₄ and/or NP₁₆ as an emulsifier in the oil and water phases, respectively, is not superior in making small particle sizes of microcap-

sules to NP₁₆ used in the water phase alone. In addition, our experimental results indicate that, for preparing red #170 polyurea microcapsules, replacing CMC with MC as a protective colloid in the presence of NP_n will not significantly decrease the particle size of red #170 polyurea microcapsules. However, interfacial polymerization is considered to be a good technique for preparing red #170 polyurea microcapsules.

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