# Chitosan Encapsulation of Poly(*n*-butyl acrylate-*co*-methyl methacrylate) Particles

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**Summary:** Poly(*n*-butyl acrylate-*co*-methyl methacrylate) particles encapsulated with chitosan were synthesized at 1:1 monomer ratio using potassium persulfate as an initiator. Effect of concentration and molecular weight of chitosan on particle encapsulation process was investigated. Chitosan concentration was varied from 0.5%, 1%, and 1.5% w/v, while molecular weights were 120, 370, and 850 kDa, respectively. The results showed that the particle diameter of the copolymer particles with chitosan encapsulation was increased when the concentration and molecular weight of chitosan were increased. The average particle size and zeta potential were obtained in a range of 144–625 nm and +27 – +47 mV, respectively. TEM micrographs suggested a presence of the chitosan encapsulation layer on the particles.

**Keywords:** chitosan; copolymerization; encapsulation; methyl methacrylate; *n*-butyl acrylate

## Introduction

Chitosan, a β-(1,4)-2-amino-2-deoxy-D-glucopyranose, is a deacetylated form of chitin which can be obtained from the shells of crabs, shrimps and other crustaceans. Chitosan is a cationic biopolymer that has many potential applications in food, medical, and pharmaceutical industries because of its polycationic nature. It possesses antibacterial property against various bacteria through ionic interaction. Moreover, it can adsorb on surface of lipid droplets, functioning as a surfactant.[1] The amount of chitosan adsorption control emulsion stability through electrosteric repulsion between the droplets. It has been reported that core-shell type polymer particles that are composed of poly(butyl acrylate) core and poly(methyl methacrylate) shell are found to be very effective for an improvement of impact strength for thermoplastic resins.[2] A block copolymer of primary alkyl acrylate and methyl methacrylate is considered as a good candidate of thermoplastic elastomers with resistance to UV irradiation and thermal degradation.[3] Lately, core-shell particles with poly(*n*-butyl acrylate) cores and chitosan shells have been prepared as a new antibacterial coating for textiles.[4] The cotton treated with such particles demonstrates an excellent antibacterial activity with bacterial reduction more than 99%. Therefore, the current research interests in preparation of poly(*n*-butyl acrylate-*co*-methyl methacrylate) particles encapsulated with chitosan via emulsion polymerization using potassium persulfate as an initiator. Influences of concentration and molecular weight of chitosan on particle encapsulation process are studied. Chitosan concentration is varied from 0.5%, 1%, and 1.5% w/v, while molecular weights were 120, 370, and 850 kDa, respectively. Colloidal and film formation properties of the resultant particles are characterized. Thus, such copolymer particles with chitosan encapsulation can be served as a new alternative for antibacterial coating.

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## Materials

Methyl methacrylate (MMA) and *n*-butyl acrylate (*n*-BA) were purchased from Fluka, Germany. Inhibitors in the monomers were removed prior to the polymerization. Chitosan (MW 120, 370, and 850 kDa, 87–88% deacetylation) were obtained from Koyo Chemical, Japan, and potassium persulfate (KPS) (Ajax Finechem, Australia) was used as received as an initiator.

## Experimental Part

Poly(*n*-butyl acrylate-*co*-methyl methacrylate) or P(BA-*co*-MMA) encapsulated with chitosan was synthesized via emulsion polymerization. A 250 mL round-bottomed, four-necked flask equipped with a condenser, a teflon stirrer, and nitrogen inlet was immersed in a water bath with a control temperature at 80°C. Chitosan solutions were prepared at 0.5%, 1%, and 1.5%w/v by dissolving the chitosan in 1%v/v acetic solution. The chitosan solution was first added into the flask and the monomers (at ratio 1:1 of BA:MMA) were added afterward. The resultant mixture was purged with nitrogen. Next, a solution of potassium persulfate at 0.1 wt% was added, and the mixture was heated at 80°C for 2 hours under nitrogen. Particle size and zeta-potential of the particles were characterized by Malvern Instrument, Zetasizer Nano Series, Germany. TEM photograph was performed by using JEOL, JEM-2100, Japan. The sample was stained with a small drop of 2% phosphotungstic acid (PTA) before analysis. For proton NMR characterization, the chitosan encapsulated copolymer and the copolymer were first extracted with 1%v/v acetic solution for 16 hours to remove the adsorbed chitosan on the particles, and further extracted with chloroform for 16 hours to remove any homopolymers. After extraction, the obtained copolymer and chitosan grafted copolymer were separately dissolved in $CDCl_3$ and $CDCl_3$/acetic acid-$d_4$, respectively, and subsequently characterized by nuclear magnetic resonance technique (INOVA, U.S.A). Surface roughness of the films prepared from the encapsulated copolymer particles was studied using a scanning probe microscope (Nanoscope IV, Germany). The film was allowed to air-dry at ambient temperature for 7 days prior to the measurement.

## Results and Discussion

### Particle Size and Zeta Potential

Monomer conversion and total solids content were determined by gravimetric analysis method.[4] The total solids content and monomer conversion of the P(BA-*co*-MMA) encapsulated with chitosan were found to be in a range of 12–13% and 87–91%, respectively. As the chitosan concentration is increased, the larger sizes of particles are attained (Figure 1). A pronounced effect is observed with the medium and the highest molecular weights. These may be attributed to the low viscosity of the aqueous solution using low molecular weight of chitosan, which can diffuse in the aqueous medium more easily and deposit onto the surfaces of formed copolymer particles, resulting in a smaller size of the encapsulated particle.[5] From the surface charge measurement, it suggests that the positive charge is present on the surface of copolymer particle due to the amino groups ($NH_2$) in the chitosan molecule which is protonated forming $NH_3^+$ in the acidic solution. Furthermore, the amount of positive charge is enhanced corresponding to the chitosan concentration more than the molecular weight (Figure 2). The reason could be that chitosan with higher molecular weight has more acetyl groups on molecular chain, which simultaneously lead to a significant decrease in charge density.[6]

### TEM Micrographs of the Particles

TEM micrographs of P(BA-*co*-MMA) particles encapsulated with chitosan show that the particles obtained are spherical as seen in Figure 3. Since the particles are

 

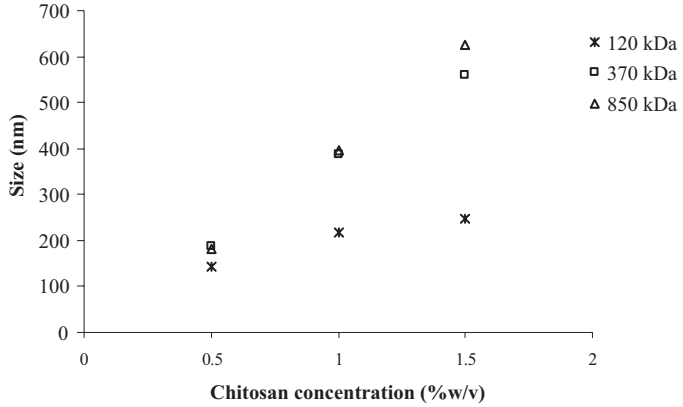


***Figure 1.***
Particle sizes of P(BA-*co*-MMA) at 1:1 monomer ratio encapsulated with different concentrations and molecular weights of chitosan.

stained with 2% phosphotungstic acid, the encapsulation layer of chitosan becomes obvious, suggesting a presence of chitosan encapsulation layer on the particle surface.[4] It is also observed that having the chitosan layer on the particle surfaces results in a particle size increment. The particles encapsulated with the highest molecular weight of chitosan gain the largest layer thickness in which the largest size is obtained with the highest concentration (1.5%) and molecular weight (850 kDa).

**NMR Spectrum of the Particles**

It is previously reported that, in the case of poly(*n*-butyl acrylate), the $-OCH_2$ proton appears around δ 4.0 ppm, and α-CH, β-$CH_2$, and $^4CH_3$- protons appear at δ 2.2–2.4 ppm, δ 1.8–2.0 ppm, and δ 0.91–0.96 ppm, respectively. In case of poly(methyl methacrylate), an $-OCH_3$ resonance signal appears around δ 3.5 ppm, β-$CH_2$- protons around δ 2.0 ppm, and α-$CH_3$ protons between δ 1.5 and δ 1.0 ppm.[7] In the case of the copolymer, the peak between δ 3.89 and δ 3.97 ppm is due to

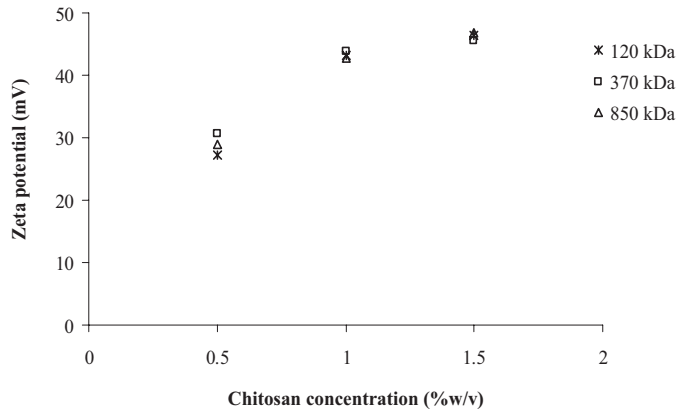


***Figure 2.***
Zeta potential of P(BA-*co*-MMA) at 1:1 monomer ratio encapsulated with different concentrations and molecular weights of chitosan.

 

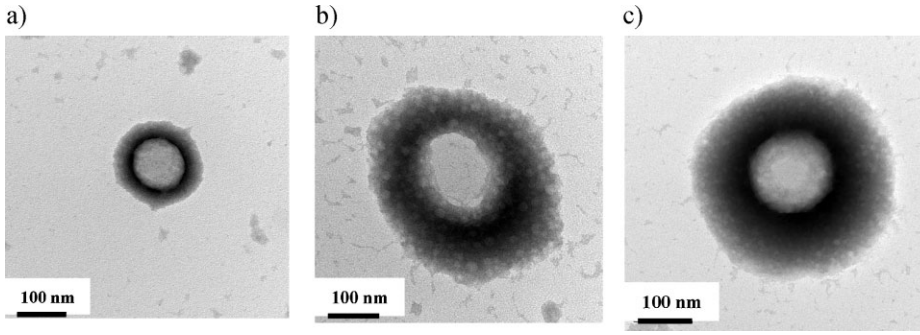


***Figure 3.***
TEM micrographs of P(*n*-BA-*co*-MMA) at 1:1 monomer ratio with different molecular weights of chitosan stained with 2%PTA: (a) 1.5% (120 kDa), (b) 1.5% (370 kDa), (c) 1.5% (850 kDa).

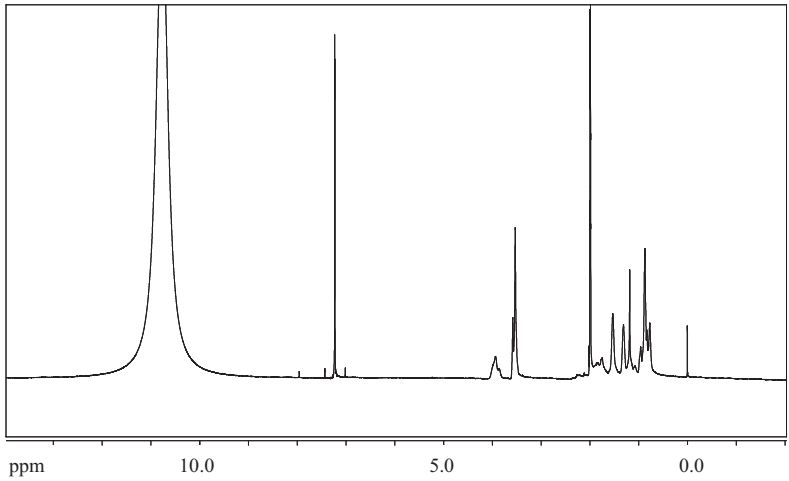


***Figure 4.***
$^{1}$H-NMR spectra of P(*n*-BA-*co*-MMA) at 1:1 monomer ratio encapsulated with chitosan (0.5% w/v, MW 370 kDa).

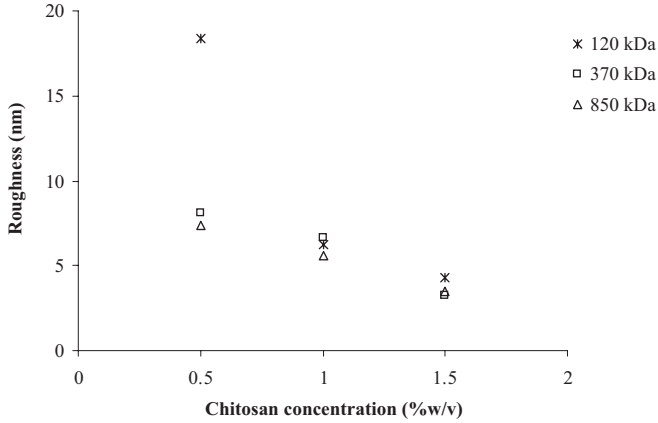


***Figure 5.***
Surface roughness of the films prepared from P(*n*-BA-*co*-MMA) at 1:1 monomer ratio encapsulated with different chitosan concentrations and molecular weights.

 

$-OCH_2$ protons, and at δ 2.09 ppm due to α-CH, at δ 1.34 ppm due to $-^2CH_2-$, at δ 1.56 ppm due to $-^3CH_2$, and at δ 0.91 ppm due to $-^4CH_3$ of *n*-butyl acrylate. The peak obtained at δ 3.56 ppm corresponds to $-OCH_3$ and at δ 1.11 ppm and δ 1.23 ppm to α-$CH_3$ of methyl methacrylate. The β-$CH_2$ signal appears at δ 2.03 and δ 1.79 ppm. Similar signals are observed with $^1$H-NMR spectrum of the copolymer encapsulated with chitosan (MW 370 kDa), except a peak at 1.9 ppm, suggesting a presence of chitin acetyl proton in chitin (Figure 4). This result implies that a grafting reaction occurs between the chitosan molecule and the copolymer. Hence, the grafting percentage of chitosan on copolymer main chain is calculated using equation (1). The result shows that at 0.5% wt of chitosan concentration (MW 370 kDa), the grafting of chitosan is founded at approximately 52%. Typically, the use of chitosan, a cationic polysaccharide derived from chitin, results in a certain grafting percentage (approximately 45-56%).[8] This is attributed to that the amino group of chitosan is chemically bonded to the polymers.[9]

$$Grafting\ percentage = \frac{W_g}{W_t} \times 100 \qquad (1)$$

where; $W_g$ = Weight of the grafted chitosan copolymer
$W_t$ = Weight of the soluble polymer

### AFM Micrographs of the Particles

Surface roughness of the films of copolymer at 1:1 monomer ratio encapsulated with different chitosan concentrations and molecular weights are characterized and illustrated in Figures 5 and 6. The results indicate that the chitosan encapsulation has an impact on film formation of the P(*n*-BA-*co*-MMA) particles. Increasing in the concentration of chitosan leads to a reduction in the surface roughness of the films. It can be implied that the chitosan encapsulation helps promoting a smooth film formation. Moreover, the molecular weight of chitosan also has an effect on film formation in which higher molecular weight yields a smoother film. This is probably due to a rather thick

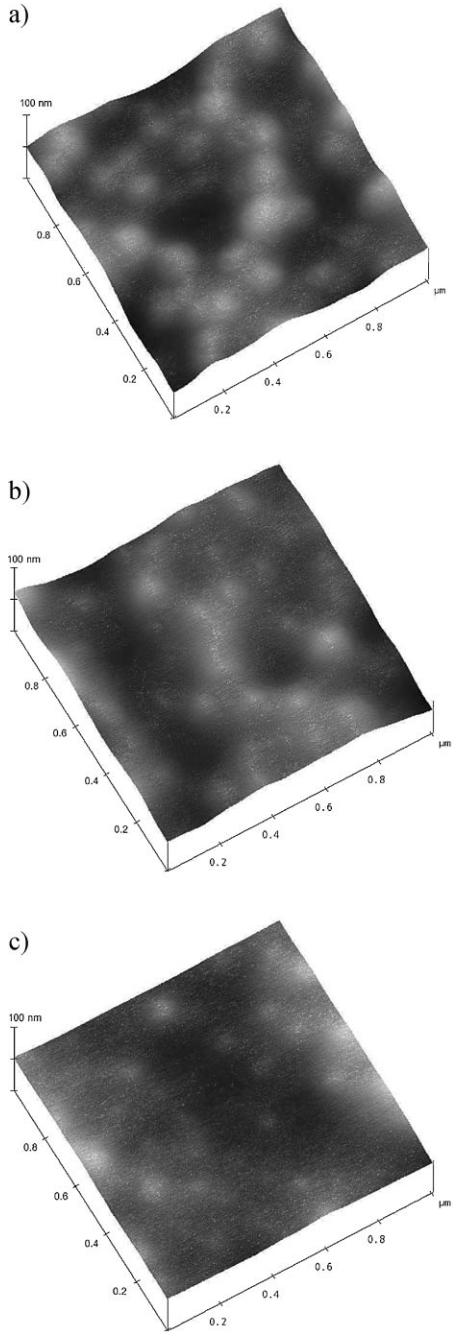


***Figure 6.***
AFM images of P(*n*-BA-*co*-MMA) at 1:1 monomer ratio encapsulated with different chitosan concentrations (370 kDa) (a) 0.5%w/v, (b) 1%w/v, (c) 1.5%w/v.

 

chitosan layer surrounding the copolymer particle, which might have sufficiently gathered on the top of film surface, influencing on film smoothness during film formation.

## Conclusion

The poly(*n*-butyl acrylate-*co*-methyl methacrylate) particles encapsulated with different chitosan concentrations and molecular weights are successfully prepared at high conversion and the colloidal properties of such copolymers are characterized. The average particle size of copolymers is increased when the chitosan contents and molecular weights are increased, while the positive charge is observed on the surface of the encapsulated particles. TEM micrographs exhibit the chitosan encapsulation layer of the particles. The layer gains more thickness according to the molecular weight of chitosan. Increasing in the concentration and molecular weight of chitosan leads to a reduction in surface roughness of the films.

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