Emulsion Polymers of Core-Shell Styrene-Butyl Acrylate: The Effect of Feeding and Aging Time on Particle Size Distribution

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Abstract: *Core-shell polymers in the particle size range 200–300 nm having a monodisperse distribution and opal color are prospective materials for coating applications. The emulsion polymerization of the core-shell was done using two monomers with significantly different refractive indices styrene for the hard monomers and butyl acrylate for the soft monomers. The feeding and aging time were varied, with particle size shown to increase with decreasing feeding time. Increasing the aging time increased conversion but had no effect to the particle size even after two hours producing particles in the 200–300 nm range. The obtained core-shell emulsion polymers were characterized by determining particle size and polymers morphology by TEM.*

1. INTRODUCTION

The ability to control particle properties like size and morphology has increased research interest in emulsion polymerization. The desired outcome depends on the physical properties of starting polymers, such as glass transition temperature and chemical properties, structure and monomer chain length.[1]

Polymers are used to effect color in coating application and monomer type and polymerization technique are important controlling parameters. There has been much research done in this area. One method to control color is by selective reflection, usually accomplished with chemical dyes containing chromophore groups. The color effect from polymers core-shells is caused by the (111) plane reflection of the face-centered cubic (fcc) lattice. Particle diameter must be 200 < D < 300 nm, so that the light will be reflected in the range of visible light. The latest research on core-shell emulsion polymers uses two co-existent polymers phases to select the color used in coating applications.[5,6,7]

A decade ago, research on the color effect of film crystals based on the theory of light reflection is originated from the work of Yablonovitch and John. Yablonovitch and John predicted that three dimensional crystals with lattice

spacing of the light wavelength scales and a strong periodic refractivity modulation exhibit photonic band gaps. Light within these gaps cannot propagate in these photonic crystals, so external light is reflected and the internal light emitted locally by flourescence at lattice defects. These properties make photonic crystals the optical equivalent of semiconductors. The optical properties depend on the difference in refractive index between the particle spheres within the matrixs.[3,4,5]

Much of the past work on the color effect of polymers reflecting light in the visible, region focuses on emulsion polymerization of styrene and methacrylate derivatives without a surfactant.[8,9,10] Recent research by that Ruhl et al.[6,7] showed that it is possible to obtain color effects using injection molding of plastic products.

Examination of the phenomena of the light reflection of colloid crystal films was made using latex emulsion particles, which have the potential for use in new materials for their effect on color. The color effect caused by monodisperse particle in the crystal lattice reflects visible light. These polymers are called colloid crystals or opal, taken from name of opal gems that are perhaps the best-known example of photonic band structures in nature. Latex emulsion particles can be fabricated that resemble the colloid crystals. To use emulsion particles that replicate the crystal colloid opal structure, the structure must consist of a hard core and a soft shell. Hard core forms the crystalline lattice while the soft shell forms a matrix around them. There is no free space between the spheres. The color effect is caused by plane reflection (111) of the fcc lattice. The colloid crystals material is analogous to the periodic structure of the simple salt NaCl crystal. The fcc is a simple example that reflects light and is shown in Figure 1.

Figure 1 shows that the fcc lattice is characterized by the next-neighbor distance d. The normal vector q111 of the (111) plane runs through one space diagonally. This (111) plane almost always extends parallel to the film surface in
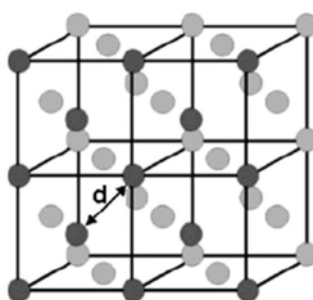

Figure 1: Fcc crystal structure.

opal films. Important planes, besides (111), are the (-111) family [-111, 1-11, 11-1], the (200) family [200, 020, 002] and the (220) family [220, 202, 022]. Each family consist of three planes 120^0 apart, with a spacing a_{hkl} and forms an angle φ_{hkl} with the film surface of four of these planes, as indicated in Figure 1 edge-on. The spacing a_{hkl} and angle φ_{hkl} are given by:

$$a_{hkl} = d\sqrt{\frac{2}{h^2 + k^2 + l^2}} \quad , \quad cos\varphi_{hkl} = \frac{h + k + l}{\sqrt{3(h^2 + k^2 + l^2)}} \quad (1)$$

Light entering an opal film surface at an angle θ is refracted according to Snells law and proceeds in the film at an angle δ:

$$n = \frac{cos\theta}{cos\delta} \quad (2)$$

where n is the average refractive index, which depends on wavelength (λ).

White light consists of wavelengths λ inside the window (400–700 nm). To place the interval $(\lambda_{min}, \lambda_{max})_{111}$ into this visible window, the diameter of the latex spheres is given by:

$$D = d\sqrt[3]{\frac{3\sqrt{2}}{\Pi}} \cong 1,1d \quad (3)$$

Diameter of the latex particle must be in the range $200 < D < 300$ nm. For $D \cong 180$ nm, only violet is observed at $\theta = 90^o$ and for $D \cong 400$ nm, only red at $\theta = 0^o$.[6,7]

This study on the emulsion polymerization core-shell is done in two steps for two monomers with different refractive indices for application in coatings. The hard monomer is styrene (Tg, 100°C), and the soft monomer is butyl acrylate (Tg,–54°C), with sodium lauryl sulfate (SLS) used as surfactant and ammonium persulfate (APS) as the initiator. In the experiment, both the feeding and aging time were varied. The feeding time was shown to effect particle size, which increased with decreasing feeding time obtained. The aging time is post polymerization, and it is estimated that at this step, propagation and termination are occurring and will be effected. Increasing the aging time lengthens the propagation step and slows down termination, the resulting polymer will have a higher solid content and the particle size will remains in the 200–300 nm range.

2.   EXPERIMENTAL

2.1   Materials

Styrene and butyl acrylate were used as monomers, sodium lauryl sulphonate as the surfactant, APS as the initiator and acrylic acid as the stabilizer. The cross-linking agent was made up of glycidyl methacrylate, potassium hydroxide (KOH) and deionized water.

2.2   Procedures

Process equipment used in the emulsion polymerization were a mini reactor equipped with a reflux condenser, agitator/stirrer, thermometer, dropping funnel (through which the monomer feed was added to the reaction mixture), analytical balance and glassware. Characterization was determined using an oven for the determination of solid content (SC), Malvern Zeta Nano Particle Analyzer Nano Series (Nano S) for measuring particle size and a Shimadzu Transmission Electron Microscopy (TEM) for polymers morphology.

2.3   Polymerization of Core-Shell Styrene-Butyl Acrylate

Emulsion polymerization of the core-shell structures was prepared using a two-steps polymerization process. The first step is the formation of a polymer core that is encapsulated with a cross-linking agent. In the second step, the butyl acrylate monomer is polymerized to styrene core to produce the final emulsion polymers core-shell. The process was done in a semi-continuous seeded reaction system. The reactor vessel was filled with a seeded mixture of water, surfactant and styrene monomer. The composition of styrene in the seed was less than in the overall mixture. The mixing speed was held constant at a rate of 200–300 rpm. The reaction temperature was set to 75°C, which is the decomposition temperature of the initiator APS to form free radical sulfate ions.

3.   RESULTS AND DISCUSSION

3.1   Emulsion Polymerization of Core-Shell Styrene-Butyl Acrylate with Varying of Feed Time

Synthesis of core-shell styrene-butyl acrylate emulsion polymers in this research was done using the seeding technique, where the reactor was filled with an initial charge or seed and heated until 75°C for one hour, and then the initiator was charged for 10 min. Pre-emulsion took place in the dropping funnel under continuous flow into the reactors at constant speed. The rate of pre-emulsion or

feeding was kept constant to maintain small droplets, and influenced the particle size of the emulsion polymers.

Different feeding times were used over the course of this work; it was observed that short feeding times yield bigger particle sizes with higher solid content. This was in agreement with work by Bao et al.[11] who found that short feeding times result in larger particle size. A two steps feeding process was used where the first is for the formation of the core styrene and the second is for grafting butyl acrylate to the styrene core to complete the shell (ratio of core-shell to feeding time). The results of the conversion and particle size to the ratio of the feeding time are given in Table 1.

Table 1 shows that as the feeding time of the core and shell increases, so does conversion and the results are presented in Figure 2. For the feeding time ratio 2:2, the conversion is low, and increasing the ratio to 2:3 increases the conversion, however further increases in the feeding time ratio do not significantly affect conversion. The feeding time optimum was obtained with the ratio 2:3, which is a feeding time of 2 h for the core styrene and 3 h for the shell butyl acrylate. Figure 2 also shows the influence of feeding time ratio on particle size.

Table 1: The conversion and particle size for different ratios of feeding time.

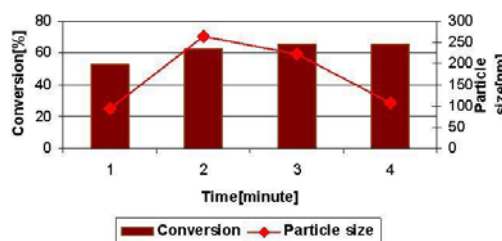| Ratio of feeding time (Core:Shell)	Feeding time of core styrene (h)	Feeding time of shell butyl acrylate (h)	Conversion (%)	Particle size (nm)
2:2	2	2	50.5	94.1/798.6
2:3	2	3	62.4	264.7
3:4	3	4	65.5	222.5
3:5	3	5	65.5	108.2

Figure 2: Conversion and particle size of feeding time.

The particle size distributions for the different feeding times are presented in Figure 3. For ratio of feeding time 2:2, the particle size distribution is polydisperse or polymodal, with peaks at 94.1 nm and 798.6 nm [Fig. 3(a)]. This is because the feeding time of 2 h is too short to complete the grafting of butyl acrylate to the styrene core, which is only partially completed; a secondary core is formed by the homogeneous nucleation from droplets of monomer or oligomer with the termination of the external of micelle.

Figure 3(b) shows the particle size distribution for the feeding time ratio 2:3, with a peak of 264.7 nm. This is a relatively big particle size, the feeding time for formation of core styrene 2 h and 3 h for the grafting of butyl acrylate is optimum for the formation of the polymer core-shell. Figure 3(c) shows the particle size distribution for the ratio 3:4, and gives a particle size 222.2 nm. This particle size is still within the desired range, meaning that the feeding time ratio is still suitable for the formation of polymer core-shells. For Figure 3(d), the particle size decreases to 108. 2 nm, indicating that the increase of feeding time for butyl acrylate to 4 h results in particle sizes of the polymers core-shell that are too small.

3.2 Emulsion Polymerization of Core-Shell Styrene-Butyl Acrylate with Various Aging Time

The conversion results of core-shell polymers at various feeding times are low, so the aging time was increased in an attempt to improve this. Aging time is the time at which the feeding has finished (post polymerization step). Aging is strongly influential in the process for the final polymerization result. In
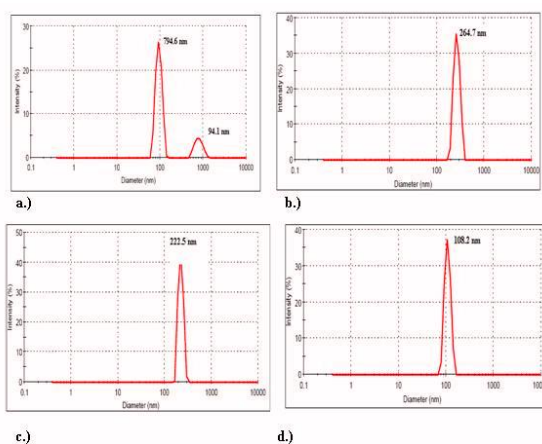

Figure 3: Distribution of particle size for different experimental feeding time ratios. (a) 2:2; (b) 2:3; (c) 3:4; and (d) 3:5.

the aging step, propagation and termination occur, and if not completed, a low conversion is obtained. This research has shown that aging time significantly affects the polymerization result.

Figure 4 and Table 2 show the effect of aging time on the conversion of core-shell emulsion polymers. The results indicate that the conversion increases with aging time. An aging time of 30 min yielded low, leaving unreacted monomers in the propagation step. At an aging time of 120 min, the optimum conversion is observed and then no further increases are seen with increases in aging time.

In Figure 4, it is seen that an increase of aging time to 2 h significantly raises the conversion. This lengthened aging time gives more opportunity for the oligomer radicals to react during propagation. In addition to the effect of conversion, the impact on particle size is important. Results of core-shell polymers with aging times of 30 min and 2 h gave a particle size of 257.4 nm and 264.7 nm, respectively. It means that aging times up to 2 h do not affect the particle size. This is illustrated in Figure 4, as all particles fall within the 200–300 nm range.
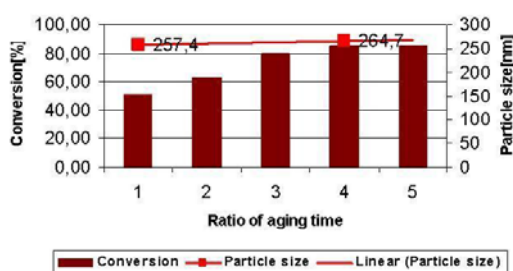

Figure 4: Plot of conversion and particle size as a function of aging time.

Table 2: Effect of aging time on the conversion of core-shell styrene-butyl acrylate polymers.

Ratio of Aging time (Core: Shell)	Aging time of core styrene (min)	Aging time of shell butyl acrilate (min)	Conversion (%)
1 [1:1]	30	30	50.5
2 [1:1]	60	60	62.4
3 [1:1]	90	90	80.0
4 [1:1]	120	120	85.0
5 [1:1]	180	180	85.0

3.3 Morphology of Core-Shell Styrene-Butyl Acrylate Polymers by TEM

Figure 5 shows the TEM of the core-shell polymer particles. The image shows that polymers consist of spherical structures, with the particle size distribution of 200–300 nm and is monodisperse.

4. CONCLUSION

The latest research on core-shell emulsion polymers is of interest because the properties of two co-existent polymers phases will be reflected in the color if used for coating application. In this work, the emulsion polymers that having a core-shell structure of styrene-butyl acrylate with monodisperse particle sizes from 200–300 nm have been explored.

The feeding time was shown to be an important parameter on particle size, which increased with decreasing feeding time. The study showed that, during the synthesis, using a feeding time for the formation of the styrene core of 2 h, and 3 h for the shell yielded polymer particles size of 264.7 nm.

Increasing the aging time was shown to increase conversion which was shown to be optimal at 2 h. Aging time was not shown to influence particle size, and times up to 2 h, all obtained particles were within the 200–300 nm range.
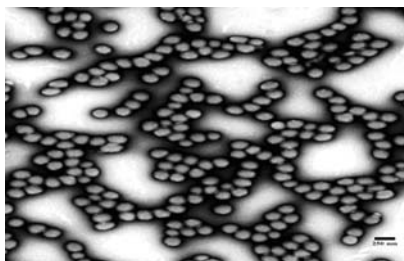

Figure 5: Morphology of core-shell polymer particles (5 000x).

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