

SYNTHESIS AND CHARACTERIZATION OF SINGLE HOLLOW OPAQUE  
POLYMER PIGMENTS

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POLYMER PIGMENTS**

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## ABSTRACT

### SYNTHESIS AND CHARACTERIZATION OF SINGLE HOLLOW OPAQUE POLYMER PIGMENTS

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In the present work opaque polymer pigments with single hollow structure were synthesized by osmotic swelling method. The hollow pigment is composed of an outer shell and an inner void space which can be filled with air or water. The osmotic swelling process involves synthesizing of a core polymer containing carboxylic acid group on the backbone, and encapsulating it with another polymer which functions as shell. The swelling of the polymer is provided by neutralization of the core with a base. Methyl methacrylate and methacrylic acid mixture is used as core monomer, and styrene is used as shell monomer. Sodium hydroxide is used for neutralization of polymer particles.

The optimal experimental conditions such as alkali treatment time and the pH were investigated. The results indicated that pH plays an important role in void generation. Hollow morphology appeared when pH was above 10 but no hollow morphology was observed when pH is below 10. Also, it was seen that extending alkali treatment time was beneficial to get the swelling equilibrium of the polymer particles.

The effect of the crosslinker content, acidity of the monomer, and the amount of surfactant on particle size and morphology of pigment were also investigated. When the carboxyl content of the core exceeded a certain value sedimentation of particles was observed. Furthermore, it was observed that low concentration of surfactant resulted in sedimentation of particles. The maximum pigment diameter was observed when crosslinker content was 2% w/w, methacrylic acid content 20% w/w, and the weight ratio of surfactant to water was 0.97.

The surface morphology of the pigments was characterized by scanning electron microscope and the inner hollow structure was confirmed by transmission electron microscope. The analysis indicated that single hollow opaque polymer pigments and colored single hollow polymer pigments were successfully synthesized.

The opacity, the L\*a\*b\* color, and the gloss properties of polymer pigments were examined by color spectrophotometer and glossmeter. Single hollow polymer pigments without any other additive provided up to 93.8% opacity with 50% v/v solid content.

**Keywords:** osmotic swelling, emulsion stability, single hollow polymer, opaque polymer pigment, colored hollow pigment

## ÖZ

### TEK BOŞLUKLU OPAK POLİMER PİGMENTLERİN ELDESİ VE ÖZELLİKLERİNİN BELİRLENMESİ

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Bu çalışmada, ozmotik şişirme yöntemiyle tek boşluklu yapıda opak polimer pigmentleri elde edilmiştir. Boşluklu pigment, içi su veya havayla dolu olan bir boşluk ve dış kabuktan oluşmaktadır. Ozmotik şişirme işlemi yapısında karboksilik asit grubu içeren bir çekirdek üretilmesi ve bu çekirdeğin kabuk olarak işlev gören başka bir polimerle kaplanmasını içermektedir. Çekirdeğin bir baz kullanarak nötrleştirilmesiyle polimerin şişmesi sağlanır. Çekirdek monomeri olarak metil metakrilat ve metakrilik asit, kabuk monomeri olarak stiren ve polimer parçacıklarının nötrleştirilmesi için sodyum hidroksit kullanılmıştır.

Alkaliyle işlem süresi ve pH gibi değişkenler için en uygun deney koşulları araştırılmıştır. Sonuçlar pH' nin boşluk üretiminde önemli bir rol oynadığını göstermiştir. pH' nin 10' dan yüksek olduğu durumlarda boşluklu yapı gözlemlenmiş fakat 10' dan düşük olduğu durumlarda boşluklu yapı gözlemlenmemiştir. Ayrıca, alkali işlem süresinin uzatılmasının polimer parçacıklarının şişme dengesine erişmesinde yararlı olduğu görülmüştür.

Çapraz bağlayıcı miktarının, monomerin asitliğinin ve yüzey aktif maddesinin miktarının pigment boyutuna ve yüzey özelliklerine etkisi de incelenmiştir. Çekirdeğin karboksil içeriği belli bir değerin üzerine çıktığında parçacıkların çöktüğü gözlemlenmiştir. Yüzey aktif maddesinin düşük derişimlerinde parçacıkların çöktüğü gözlemlenmiştir. En büyük pigment çapı çapraz bağlayıcı oranı kütlece %2, metakrilik asit miktarı kütlece % 20 ve yüzey aktif maddenin suya kütlece oranı 0.97 iken gözlemlenmiştir.

Pigmentlerin yüzey özellikleri taramalı elektron mikroskobu ile incelenmiş ve içlerindeki boşluk yapıları geçirimli elektron mikroskobu ile doğrulanmıştır. Analizler tek boşluklu opak polimer pigmentlerinin ve tek boşluklu renkli pigmentlerin başarıyla elde edildiğini göstermiştir.

Polimer pigmentlerinin opaklık,  $L^*a^*b^*$  renk ve parlaklık özellikleri renk spektrofotometresi ve parlaklık ölçer ile incelenmiştir. Tek boşluklu polimer pigmentleri hiçbir katkı maddesi içermeden % 93,8' e kadar (katı üzerinden hacimce % 50 oranında) opaklık sağlamışlardır.

**Anahtar sözcükler:** ozmotik şişme, emülsiyon kararlılığı, tek boşluklu polimer, opak polimer pigment, boşluklu renkli pigment

To my family  
&  
Can

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## LIST OF SYMBOLS AND ABBREVIATIONS

BaSO <sub>4</sub>	Barium sulfate
CaCO <sub>3</sub>	Calcite
CMC	Critical micelle concentration
C/M	Weight ratio of crosslinker to monomer
DLS	Dynamic light scattering
DLVO	Derjaguin-Landau-Verwey-Overbeek Theory
EGDMA	Ethylene glycol dimethacrylate
FTIR	Fourier transform infrared spectroscopy
MAA	Methacrylic acid
MEK	Methyl ethyl ketone
METU	Middle East Technical University
MMA	Methyl methacrylate
N <sub>p</sub>	Number of particles
R <sub>p</sub>	Rate of polymerization
rpm	Rotate per minute
PS	Polystyrene
PMMA	Polymethyl methacrylate
SEM	Scanning electron microscopy
SDBS	Sodium dodecyl benzene sulfonate
SPS	Sodium persulphate

S/M	Weight ratio of surfactant to monomer
S/W	Weight ratio of surfactant to water
TEM	Transmission electron microscopy
$T_g$	Glass transition temperature
TiO <sub>2</sub>	Titanium dioxide
W	Watt
w/w	Weight ratio
ZnO	Zinc oxide
ZnS	Zinc sulfide

## CHAPTER 1

### INTRODUCTION

Pigments are used for providing color, hiding the substrate and modifying the performance of coating. Titanium dioxide, calcite, zinc sulfide, and zinc oxide are the most used white opacifying pigments used in coating technology. These pigments are inorganic in nature, and cause paint defects such as agglomeration because of the high density difference between organic vehicle and inorganic pigment. Although organic pigments are used at very low percentages as 1-3% mostly for color delivery, inorganic pigments are used both for coloring and filling materials in coating industry.

Preparation of hollow particles as opaque polymer pigments has received great attention because of its properties such as low density and compatibility with polymeric binder in the paint. Opaque polymer is a great option to inorganic white pigment because of the intensive light scattering caused by the difference of refractive index between shells and air inside the voids [1-6]. The void scatters the light and provides opacity [7-12] or affects the mechanical properties of paint such as gloss [13-16]. Hollow opaque pigment is less expensive than titania ( $\text{TiO}_2$ ) and causes much less agglomeration, and also produces more scrub-resistant coating than  $\text{TiO}_2$  [17, 18].

Hollow particle with the surrounding polymeric shell is transparent to light, but, there is a large difference between the refractive indices of the polymeric shell and the void inside. A part of the incident light is scattered when it hits the surface and another part is refracted into the air void. It is refracted again in the polymeric shell as it leaves the void. These multiple scatterings increase the hiding power of the paint film.

The earliest opaque polymer pigments as developed by Kowalski and Vogel are mainly produced by osmotic swelling mechanism and commercialized as ROPAQUE opaque polymer by Rohm and Haas Company. Osmotic swelling mechanism involves synthesizing a carboxylated core and outer shell, followed by neutralization of the core with a base, which, results in the swelling of the polymer [19].

In this work also carboxylated polymer particles with different ingredients and different morphologies have been synthesized by osmotic swelling method. Additionally, hollow pigment was colored using organic pigment, which is incorporated by emulsion process.

The optimal experimental conditions such as the composition of monomer mixture, the crosslinker content, the pH, the acidity of monomer, and the amount of surfactant were investigated. The morphology and the size of the particles were examined using transmission electron microscopy, dynamic light scattering size measurement, and scanning electron microscopy. It is found that the hollow polymer particles were synthesized successfully. The opacity, the gloss, and the color properties of polymer pigments on styrene-acrylic water based clear resin were investigated.

## CHAPTER 2

### LITERATURE REVIEW

In this chapter, the properties and the methods of synthesis of hollow opaque polymer pigments were described, and the previous studies in the literature were surveyed. The scattering mechanism which creates opacity was explained in detail. Emulsion polymerization and osmotic swelling methods used to produce hollow opaque polymer particles were explained, and the stability of emulsions was discussed briefly.

#### 2.1 Hollow Polymer Pigments

Hollow polymer particles received much attention in many industrial fields such as in medical therapy, catalyst, white pigment, hiding and opacifying agent. In pigment industry the preparation of hollow particles has attracted increasing research interest due to the ability of hollow particles to scatter light caused by the difference of refractive index between the shell and air inside the void [1-6]. Hollow polymer particles which have void inside are very useful in surface coating as they can be used as opaque pigments. Hollow pigments provide white appearance due to scattering of light which contributes to the coating opacity [7-12], and contribute to the properties of the coating affecting performance variables such as gloss [13-16].

Titanium dioxide is the most important white pigment due to its very high refractive index compared to the coating binder polymers. It is also known to have the highest refractive index among all other pigments of industrial importance. Although it provides very high opacity it has poor stability and easily degrades. Other white pigments used in paint industry are zinc sulfide (ZnS), zinc oxide (ZnO), barium sulfate (BaSO<sub>4</sub>), and calcite (CaCO<sub>3</sub>) [17]. The properties of these pigments are given in Table 2.1.

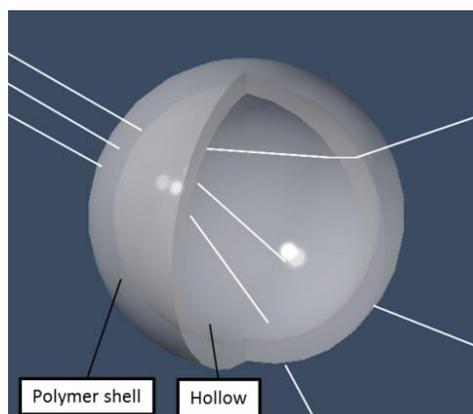
**Table 2.1** Refractive index and density of some white pigments.

<b>White Pigments</b>	<b>Density (g/cm<sup>3</sup>)</b>	<b>Refractive index</b>
Titanium dioxide (Rutil) (TiO <sub>2</sub> )	4.23	2.70
Zinc sulfide (ZnS)	4.09	2.40
Zinc oxide (ZnO)	5.60	2.00
Barium sulfate (BaSO <sub>4</sub> )	4.50	1.64
Calcite (CaCO <sub>3</sub> )	2.71	1.49-1.66

Inorganic pigments are usually incompatible with organic resins. This incompatibility causes agglomeration and reveals difficulty in the dispersion of pigments. In addition, the high densities of inorganic pigments result in settling under gravity.

Titania is quite expensive and costs to a third to half of the total material cost of latex paints. It is usually used in combination with extender pigments like calcite (CaCO<sub>3</sub>) or barite (BaSO<sub>4</sub>). One prominent alternative to partially substitute titania and improve compatibility in paint is to use hollow polymer pigment which is first developed in the early 1980s by Rohm and Haas. Hollow opaque pigment is less expensive than titania (TiO<sub>2</sub>) and causes much less agglomeration, and also produces more scrub-resistant coating than TiO<sub>2</sub> [18].

Hollow latex particles are first filled with water which evaporates later leaving air in the center of each particle [19]. Hollow particle shell film is transparent to light, but the difference in refractive index ( $\eta$ ) between the air void ( $\eta_{\text{air}}=1.0$ ) and the polymeric shell ( $\eta_{\text{resin}}=1.59$ ) results in the scattering of light [20, 21]. The light falling onto the spherical shell is partly scattered around and partly refracted. The light coming out of the hollow core is scattered a second time. In fact multiple scatterings take place inside and outside the hollow particles causing heavy interference which produces white color and hence opacity. Figure 2.1 shows a representative single hollow polymer pigment and the scattering of light.



**Figure 2.1** Single hollow opaque pigment [22].

There are some studies made to find out the optimum size of hollow pigments from light scattering theory [20, 21]. They calculated that the optimum diameter size of the hollow pigment must be 0.5–0.6  $\mu\text{m}$  and the void 0.25–0.3  $\mu\text{m}$ . The commercial pigments usually have an average particle size between 0.4–0.5  $\mu\text{m}$  and have a void volume fraction of 25–40%.

Opaque polymers can replace  $\text{TiO}_2$  in pigment industry due to their properties like unique compatibility with organic resins and lower density. Refractive index difference in polymer–air interface is lower than  $\text{TiO}_2$ –polymer interface. Hence, scattering efficiencies of hollow polymer pigments were lower than  $\text{TiO}_2$ . So they can be best used to partially replace titania in paints.

## 2.2 Emulsion Polymerization

Emulsion polymerization, which is a heterogeneous polymerization process unlike bulk or solution polymerization, is a method widespread used in the industry. The hydrophobic monomer is dispersed in water by an emulsifier, and the polymerization is carried out using water soluble initiators such as sodium persulfate. In the emulsion polymerization; the monomers like styrene and methyl methacrylate are emulsified in water–surfactant solution. The reverse process in which the water soluble monomers are polymerized in organic solvents can also be used. But this process is not common as conventional emulsion polymerization [23, 24].

The bulk polymerization leads to cleaner polymers because there is no addition of foreign materials like surfactants or stabilizer. However, bulk polymerization process is very hard to control due to difficulty in the removal of polymerization heat especially for bulky volumes. On the other hand emulsion polymerization is very easy to control as heat generated in the tiny particle can be easily transferred to water used as dispersant phase. Owing to the better process control, the emulsion polymerization can lead to a variety of polymer morphologies, very high

weight polymer chains and polymer particle sizes [23, 24]. Primary characteristics of bulk polymerization and emulsion polymerization are given Table 2.2.

**Table 2.2** Primary characteristics of bulk polymerization and emulsion polymerization [23].

Parameter	Bulk polymerization	Emulsion polymerization
Reaction System	Homogeneous	Heterogeneous
$R_p/MW^*$	Slow/High or Fast/Low	Fast/High
Temperature control	Poor	Good
Viscosity of medium	High	Low

\* $R_p$  and MW are the rate of polymerization and molecular weight of polymer, respectively.

The reaction mixture becomes very viscous and very hard to stir at higher extent of bulk polymerization. Because of this situation, improper distribution of heat, autoacceleration and runaway reactions can be observed. On the other hand, emulsion polymerization does not suffer from these limitations of viscosity and heat control. One can easily stir the reaction mixture even at high monomer conversion at emulsion polymerization because the polymerization in water as a dispersion medium keeps the viscosity of the reaction medium low. In emulsion polymerization the polymerization heat generated can easily be transmitted or distributed uniformly all over the reaction vessel and the temperature can be easily controlled by cooling the jacket of the reaction vessel [24].

For high polymerization rates the large number of radicals must be increased but it results in the formation of low molecular weight polymers. So,  $R_p$  is inversely proportional to the molecular weight of polymer in bulk polymerization. However, the rate of polymerization ( $R_p$ ) and the molecular weight (MW) may be simultaneously high because of the segregation of radicals by compartmentalization within polymerizing particles in the emulsion polymerization. The molecular weight of polymer can be increased without slowing the polymerization rate in emulsion polymerization. The amount of surfactant in the emulsion is a key parameter for this situation because it leads to a different number of particles and, depending on the number of the particles, the polymerization rate is also affected [24, 25].

There are also some disadvantages of the use of emulsion polymerization. The polymer which is produced with emulsion polymerization, has large amount of surfactant on the surface, also the final mixture consists of a dissolved surfactant, dissolved initiator and unreacted monomer [24].

### (i) Surfactants

The surfactant, also referred to as emulsifier, soap or stabilizer, are amphiphilic molecules which comprise both hydrophilic and hydrophobic groups. The hydrophilic group can be nonionic or ionic and it specifies the type of surfactant [23-26]. Surfactants can be classified according to their hydrophilic part carried [23-26]:

- Anionic surfactants, where the hydrophilic part is anion (e.g., sodium dodecyl benzene sulfate, sodium benzene sulfate, sodium stearate)
- Cationic surfactants, where the hydrophilic part is cation (e.g., hexadecyltrimethylammonium bromide)
- Amphoteric surfactants, where the properties of hydrophilic part is dependent on the pH (e.g., sodium lauriminodipropionate, disodium lauramphodiacetate)
- Non-ionic surfactants, where the hydrophilic part is a non-ionic component (e.g., i-octophenol polyethoxylate)

Three major functions of surfactants are: (i) to stabilize the particle nuclei generated during early stage of emulsion polymerization, (ii) to generate micelles, (iii) to stabilize the growing polymer particles leading to a stable end product [23-26]. Surfactant can be dissolved in aqueous phase and adsorbed on the water-air interface at low concentrations. If the concentration of surfactant increased above the critical surfactant concentration, the excess surfactants begin to form molecular aggregates which are termed as micelles. This surfactant concentration is named as critical micelle concentration (CMC). The surface tension of solution decreases with the surfactant addition. Thus, the critical micelle concentration is determined from the sudden change of surface tension upon incremental addition of surfactant. Surfactants have different CMC values so one should be careful in the selection of surfactant type and the amount of surfactant for effective stabilization of various polymerization systems [23, 24].

The droplet size and emulsion stability are affected by surfactant type and the amount of surfactant. According to the past studies, decreasing the amount of surfactant increases the droplet size and reduces the emulsion stability [5, 6]. Yuan et al. investigated the effect of the amount of SDBS (sodium dodecyl benzene sulfate) used as surfactant on droplet size in osmotic swelling. In order to synthesize the core as large as possible the polymerization of metacrylic acid should not be restricted by excess amount of surfactant, therefore the amount of surfactant must be below the CMC. However in the preparation of shell the CMC must be acquired otherwise emulsion stability may not be achieved [29].

### (ii) Types of emulsion polymerization

There are three types of emulsion polymerization; conventional emulsion polymerization, miniemulsion polymerization, and microemulsion polymerization emulsion. There is also inverse emulsion which is a variation on these emulsion polymerizations. All types have

different particle nucleation, growth mechanism, and kinetics as a result of different initial conditions. The differences between these three methods are given in Table 2.3 [25].

**Table 2.3** Comparison of emulsion polymerization methods [25].

<b>Property</b>	<b>Conventional emulsion</b>	<b>Miniemulsion</b>	<b>Microemulsion</b>
Droplet size range	>1 $\mu$ m	50 to 500 nm	10 to 100 nm
Duration of stability	Seconds to hours	Hours to months	indefinitely
Diffusional Stabilization	Kinetic	Kinetic	Thermodynamic
Nucleation mechanism	Micellar, Homogeneous	Droplet	Droplet
Emulsifier concentration	Moderate	Moderate	High
Costabilizer type	None	Hexadecane, Cetyl Alcohol	Hexanol, Penthanol
Homogenization method	None	Mechanical or ultrasonic	None
Particle size range	50 to 500 nm	50 to 500 nm	10 to 100 nm
$N_p$ * range (per L $H_2O$ )	$10^{16}$ to $10^{19}$	$10^{16}$ to $10^{19}$	$10^{18}$ to $10^{21}$

\* $N_p$  is the number of particles.

Conventional emulsion polymerization is the most widely used technique for emulsion polymer synthesis. In this technique, water soluble monomer droplets, which allow the diffusion of monomer to the polymerization medium, are dispersed in a continuous aqueous phase. Monomer droplets are kept colloidal stable against coalescence through the use of a surfactant. Conventional emulsions are milky white emulsions. Micellar nucleation and homogenous nucleation mechanism prevail in conventional emulsion polymerization. Acrylics, methacrylics, styrene, and vinyl acetate, which have relatively low water solubility, have been polymerized by conventional emulsion polymerization and used in paints, textile binders etc. [23, 25].

Microemulsions are transparent or translucent reaction systems which are thermodynamically stable. The droplets of microemulsions are tiny and have a large oil-water interfacial area ( $\sim 10^5 \text{ m}^2\text{dm}^{-3}$ ). Microemulsions are synthesized from water and monomer and contain large amounts of surfactants. The combination of surfactants like alcohol and an anionic surfactant is the mostly used stabilization system. The most important disadvantage of microemulsion polymerization is the necessity for high concentration of surfactant for the preparation of microemulsion. The large amount of surfactant leads to the existence of unpolymerized monomer inside the micelles after the polymerization is over. The smallest particle size is obtained via microemulsion polymerization. Since the particle diameter of microemulsions are smaller than the wavelength of visible light, their appearance is usually transparent. The most important difference between microemulsion and conventional and miniemulsions is the resultant polymers' very high molecular weight. Microemulsions emulsion polymerization method is especially used for producing calibration standards and potential biomedical applications [23, 25].

Monomers are colloidal stabilized by a surfactant against coalescence to produce miniemulsions which are submicron dispersion of monomer. Costabilizers such as hexadecane which are a low-molecular weight hydrophobic species are used to impart the osmotic pressure effect on the emulsion system to delay the diffusion of monomer molecules from smaller droplets to larger ones (i.e., the degradation of monomer droplets or Ostwald ripening effect). Therefore kinetically stable miniemulsions, which are stable more than long enough for the polymerization performed, are produced. During the production of miniemulsions, larger droplets are broken down into smaller droplets by homogenization. Hence, more droplets are produced due to the intensive shear forces and energy. Miniemulsions which do not contain costabilizer but homogenized is called homogenized emulsions [23, 25].

Miniemulsion polymerization has two major advantages over conventional emulsion polymerization. The major potential advantage of miniemulsion polymerization is the nucleation mechanism. Conventional emulsion polymerization is carried out by micellar nucleation while miniemulsion is carried out by droplet nucleation. Micellar nucleation depends on lots of parameters such as amount of surfactant, amount of initiator, agitation speed, temperature of the polymerization reaction, mode of addition of the monomers, etc. The amount of surfactant and costabilizer along with shear affect the number of final particles in miniemulsions. The initiation system does not affect the number of final particles in miniemulsions. As a result of all these, it is easier to control miniemulsion than conventional emulsion polymerization. Another advantage of miniemulsion is the no need of monomer which can be highly water-insoluble and directly polymerized, and other reagents to be transported through the aqueous phase. Most used monomers for forming miniemulsions are hydrophobic monomers such as styrene, methyl methacrylate, and butyl acrylate. Miniemulsion polymerization is used to produce automotive coatings, binders for photocopier/laser printer toners, printer inks, etc. [24, 25]

Several methods which are based on miniemulsion polymerization method, are developed to produce hollow opaque pigment [30]. These methods involve osmotic swelling, solvent

swelling [31-34], incorporation of a blowing agent [35-42], water in oil in water emulsion methods [43, 44], encapsulation of a non-solvent hydrocarbon for the polymer being synthesized [25], and phase separation of the two polymers in a common solvent [46-48].

In this study hollow opaque pigments are synthesized by osmotic swelling method, so in this chapter it will be explained briefly.

### 2.2.1 Stability of emulsion polymerization

Stability can be described as the ability of colloidal system concerned to withstand some break down process, induced by the presence of forces acting externally on, or internally within the system. Gravity, centrifugal, electrostatic or magnetic fields are the examples of external forces [26, 31]. These forces and the types of breakdown processes are listed in Table 2.4.

**Table 2.4** Breakdown process in colloidal dispersion [49].

Type of force	Type of breakdown process
External forces (e.g. gravity, centrifugal, electrostatic, magnetic)	Particle migration (e.g., sedimentation or creaming), leading to a non-uniform concentration distribution
Interparticle (repulsive or attractive)	Aggregation
Interfacial tension (arising from the imbalance of intermolecular forces at an interface)	Coalescence or sintering; Ostwald ripening

Stability depends on some parameters, such as [50-53];

- Nature of surface active agents,
- Size and distribution of droplets,
- Viscosity of the dispersed phase,
- Viscosity of the continuous phase,
- Existence of a steric or an electric barrier,
- Dispersed phase volume fraction,
- Temperature,
- Density difference of two phases.

Five breakdown processes are described in literature: (i) Sedimentation or creaming, (ii) Ostwald ripening, (iii) Aggregation, (iv) Coalescence, (v) Phase inversion.

(i) Sedimentation (Creaming)

Sedimentation or creaming occurs when gravity centrifugal, electrostatic or magnetic force act on the droplets. Density difference of dispersed droplets and the continuous phase cause the sedimentation or creaming [26, 49].

If the density of the oil phase is higher than density of water, then sedimentation occurs and droplets settle down. On the other hand, if the density of the oil phase is smaller than density of the water, the creaming occurs and droplets move to the top of continuous phase [32, 36]. The Stokes equation is used for defining the rate of sedimentation or creaming:

$$v_s = \frac{2\pi\Delta\rho g a^2}{9\eta} \quad 2.1$$

where  $v_s$  is the steady-state velocity of droplet,  $\Delta\rho$  is the density difference between the dispersed and continuous phase (positive for sedimentation, negative for creaming),  $\eta$  is the viscosity of the continuous phase,  $g$  is the acceleration due to gravity and  $a$  is the droplet radius [49].

As seen on Stokes equation, droplet size has biggest effect but  $\eta$  is the only parameter which can be adjusted to reduce  $v_s$ . The rate of sedimentation or creaming can be reduced by increasing the continuous phase viscosity. This may be achieved by adding thickener to continuous phase.

(ii) Ostwald ripening

Ostwald ripening, is the process where larger particles grow at the expense of smaller particles by molecular transfer through the dispersion medium. This is simply because of the fusion of smaller droplets into bigger ones due to Laplace pressure effect [28]. The solubility of monomer is defined by Kelvin [55] and the pressure difference is defined by Laplace:

$$C_{m,droplet} = C_{m,bulk} \exp\left[\frac{4\sigma V_m}{RTd_d}\right] \quad 2.2$$

where;  $C_{m,droplet}$  and  $C_{m,bulk}$  are the solubility of monomer in the aqueous phase with a droplet diameter of  $d_d$ , and the solubility of the bulk monomer in water, respectively.  $d_d$  is the average diameter of monomer droplets,  $\sigma$  is the monomer droplet-water interfacial tension,  $V_m$  is the molar volume of monomer,  $R$  is the gas constant, and  $T$  is the absolute temperature. According to the Kelvin equation; the solubility of monomer in continuous phase decreases with increasing diameter of monomer droplet.

The Laplace equation for spherical droplets is given by:

$$\Delta p = \frac{2\gamma}{r} \quad 2.3$$

where;  $\Delta p$  is pressure difference across a curved liquid/liquid interface,  $r$  is the radius of curvate and  $\gamma$  is interfacial tension. According to the Laplace equation  $\Delta p$  is smaller for larger droplets. Thus, smaller droplets diffusing in the aqueous phase fuse into larger droplets. This process reduces the total free energy of the system and it is called Ostwald ripening [49].

The Ostwald ripening effect can be reduced by the addition of a chemical component which is insoluble in the continuous phase into the droplet [49].

### (iii) Aggregation

Aggregation is a process in which particles come together in temporary or permanent contact. If the aggregation is irreversible (permanent contact) the process is called ‘coagulation’, and if the aggregation is reversible (temporary contact) the process is called ‘flocculation’ [26].

Aggregation can be described in terms of paired potential energy between particles which is the potential energy of any two mutually approaching particles as a function of their separation [26]:

$$F(h) = - \frac{dV(h)}{dh} \tag{2.4}$$

where,  $V(h)$  is the potential energy which is derived from the Van der Waals attraction between the particles, and  $F(h)$  is a function of distance. This is called Derjaguin-Landau-Verwey-Overbeek or DLVO theory. Colloidal stability is controlled by the more long-ranged interparticle with respect to DLVO theory. Irrespective of the chemical nature of the particles or the medium is operated by a long range van der Waals forces. If the particles are similar, this force is always attractive. So, most colloidal particles acquire a charge either from surface charge groups or by specific ion adsorption from the solution. For similar particles this charge leads to repulsive double- layer force. This theory has two basic principles [26]:

when;  $h > 0 \longrightarrow V$  at  $V_{max}$   
 $h = 0 \longrightarrow V$  at  $V_{min}$

For larger values of  $V_{max}$ , the dispersion will be kinetically stable for aggregation. If the  $V_{min}$  is small, then the dispersion will be thermodynamically stable. Thus, if  $V_{min}$  has large values, then aggregation will be irreversible and the process is called ‘coagulation’. On the other hand, if  $V_{min}$  has small values, then aggregation will be reversible and process is called ‘flocculation’ [26].

### (iv) Coalescence

Two droplets can fuse each other and give a bigger droplet when the solution is turbulently mixed. The high inertial energy can overcome the electrostatic repulsion between the particles

and cause coalescence [49]. The rate of coalescence in emulsion is given by Davies and Rideal [56] as flows:

$$\frac{d\bar{V}}{dt} = \frac{4}{3} \frac{V k T}{\eta} e^{-E/kT} \quad 2.5$$

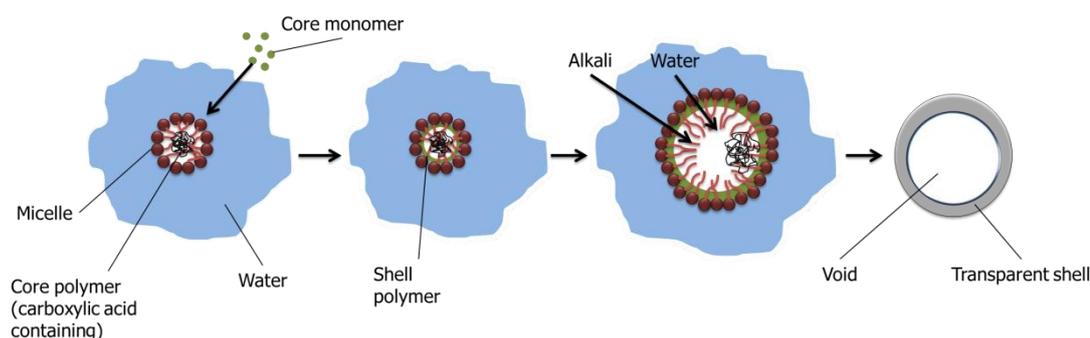
where;  $\bar{V}$  is the mean volume of droplet,  $k$  is the Boltzman constant,  $\eta$  is viscosity,  $V$  is the volume fraction of dispersed phase and the  $E$  is the energy term. They derived this equation using Smoluchowski theory [52]. According to this equation coalescence stability is highly dependent on the temperature, viscosity and volume fraction of dispersed phase.

(v) Phase inversion

Phase inversion is the process signifying water-in-oil emulsion to oil-in-water emulsion, or vice versa. There are two primary mechanisms for phase inversion. First one is transitional phase inversion which is observed by the change in the conditions. For example, change in temperature, salt concentration, or a change in surfactant composition can cause phase inversion. The second inversion is catastrophic phase inversion which results in by a large change in the relative volume fraction of the two components [49].

### 2.3 Osmotic Swelling Method

Osmotic swelling is one of the most known methods to produce hollow pigment. The hollow pigment is composed of an outer shell and an inner void space which can be filled with air or with a liquid phase such as water [30, 57]. The process involves (i) a core polymer which is synthesized inside micelles containing carboxylic acid containing group on the backbone, and (ii) capsulating it with another polymer which functions as shell. The core usually contains 10-30% ionizable compound which is later neutralized with an alkali and converted into a polyelectrolyte [30, 58]. The polymeric salt thus obtained delivers much higher osmotic pressure than the unneutralized polymer. The osmotic pressure expands the core, and upon removal of water void is created inside the shell. The hard shell must be thermally stable and be permeable to water. Thermoplastics such as styrene or styrene and methyl methacrylate copolymer is usually used in the preparation of shell [30, 59]. A schematic illustration of osmotic swelling is shown in Figure 2.2.



**Figure 2.2** Steps of osmotic swelling method [22].

The composition of core and shell and core/shell ratio must be well established in order to produce stable hollow polymer particle. The morphology can be further stabilized using cross-linking monomers that minimize the interdiffusion of polymer chains. Another critical parameter is the temperature of the medium in which swelling is carried out. Emulsion must be heated above the softening point (i.e.  $T_g$ ) of the shell while swelling is carried out for diffusion of base into core. When temperature is decreased back to the ambient temperature, the shell, which has significant cohesion and thermoplastic flow properties, avoids the collapse of polymers [30, 59].

Some basic requirements must be met to produce hollow latex by osmotic swelling [30, 60]:

- The volume of the carboxylated core of the particle should be sufficient to form a micro void inside the particle to scatter the light. The diameter of the void relative to the wavelength of visible light and thickness of the shell are the parameters that affect the efficiency of light scattering. Volume fractions of expansion which are obtained by the osmotic swelling method are in the range of 30-50%.
- The shell should allow the transport of water and base into the interior of the particle.

### 2.3.1 Patents and literature review

The earliest process for making hollow particles by osmotic swelling mechanism were developed by Kowalski and Vogel and then commercialized as ROPAQUE™ in Rohm & Haas Company [61, 62]. As described in their patents, they synthesized a structured particle with a carboxylated polymer core and one or more outer shells. The core polymer is then neutralized with a base to form an organic salt which resulted in the expansion of the particle upon attracting water.

Vanderhoff et al. prepared hollow particles by heterocoagulation process for the particle growth mechanism. They produced hydrophilic/hydrophobic core/shell particles with soft alkali swelling core and hard crosslinked shell [63].

Okubo et al. developed an alternative method to produce hollow [65] and multihollow [66-71] polymer particles. They named this method as stepwise alkali/acid method. The main difference of this method is the swelling mechanism of polymer. Hollows are generated in a single reaction, directly from uniform carboxylated polymer particles by addition of base and an acid respectively. The particles swell with the addition of a base to the system and ionic polymers move toward the outside of the particle due to its hydrophilic character. When acid is added to the system, particles begin to shrink to give hollow particles of smaller size than the original beads. While single hollow particles can be produced by osmotic swelling, multihollow particles can be produced by alkali/acid swelling methods. Okubo et al. used reverse alkali/acid method in which the particles are treated first by an acid and then by a base. They used this method to produce multihollow particles [71].

Okubo et al. produced hollow particles with emulsion copolymerization. They used styrene and methacrylic acid as a monomer. In alkali treatment step, they increased the pH of the latex with the addition of aqueous potassium hydroxide and heated for various hours at different temperatures. Then, the latex was cooled down to ambient temperature. They investigated the effect of methacrylic acid content, pH, time and temperature in the alkali treatment on the formation of multihollow particles. They named this method as an alkali/cooling method. The expansion becomes significant above 10% (mole basis) methacrylic acid, and increases linearly with its amount. The total hollow volume increased with an increase in the treatment time, and there was almost no expansion at pH values below 10.5. The maximum expansion was observed at a pH value of 11.5 [70].

Kong et al. prepared hollow particles by a similar method to alkali/acid treatment. They synthesized core and shell particles with or without acrylic acid by emulsion polymerization. After alkali treatment, particles without acid in the core and particles with acid in the core increased by volume 42% and 23%, respectively, with acid containing shell. They claimed that the presence of carboxylic acid in the shell make the swelling process possible. [72].

Khan et al. synthesized single hollow polymer particles by using osmotic swelling method. They used butyl acrylate–methacrylic acid as core monomers and styrene-acrylonitrile as shell monomers; and neutralized polymer particles with ammonia. They were able to decrease TiO<sub>2</sub> content by 15% without lowering opacity by introducing hollow polymer pigment [73].

## **2.4 Pigment Opacity**

Opacity is the desirable property of a coating that results from light being scattered at an interface between substances of different refractive index (e.g. the interface between air and polymer). Hollow pigments provide opacity by the similar mechanism as the light is bended and scattered at interfaces. Although colored pigments achieve opacity by absorbing visible light, hollow pigments provide opacity by scattering the light. If a polymer contains large number of voids, it appears to be opaque. The degree of opacity is dependent on microvoid concentration, microvoid size and distribution, and refraction index difference between air and polymer [74].

Electric and magnetic moment induced in a particle by the fields of the incident electromagnetic wave. Light scattering originates from this process [75]. Light scattering is performed by refraction and diffraction of light while it passes through or near the hollow pigments.

Light travels more slowly through the high refractive index pigment than the low refractive index polymer in which the pigment is dispersed. So, the light bends as it hits the polymer particle. Refraction is generated from an apparent bending of light. Equation 2.6 shows the refraction of light [75, 76]. For the light passing through different media that have refractive indexes of  $n_1$  and  $n_2$ , Snell expressed the law of refraction as:

$$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_2}{n_1} \quad 2.6$$

where;  $\theta_1$  is the angle of incidence and  $\theta_2$  is the angle of refraction. According to this equation, when the difference between the refractive index of the pigment and the polymer matrix in which it is dispersed is increased, light scattering efficiency will be increased [76].

Diffraction is another factor that affects the scattering of light from pigment. Diffraction occurs when the light falls onto the pigment that has a similar size with the wavelength of light [76]. As a light beam hits a pigment particle, it bends because of the pigment's ability to scatter light in an adjacent area several times larger than the cross sectional area of the pigment. So, particle size of the pigment is very important parameter for light scattering phenomenon because of the diffraction of light. If the particle is too large or too closely spaced, diffraction occurs at a lower extent. If the particle is too small, the light will pass from near the particle because light will not see the pigment.

As a result, shape and size of the particle, refractive index differences between medium and particle, wavelength of the light, and the number of particles which acts as scattering centers are the parameters that all affect the scattering efficiency [77, 78].

There are many studies about the preparation of coatings that include opaque hollow pigment. Seiner et al. [79] optimized the microvoid size using a model system developed by El-Aasser et al. [80]. Durbin et al. produced latex paint which can be replaced 50%  $\text{TiO}_2$  to yield hiding power [81].

## 2.5 Encapsulation of Opaque Polymer Pigments

Organic pigments such as carbon black phthalocyanines or azo-based dyes have numerous applications in coatings, optics, and catalysis due to their photosensitivity and color strength [82-84]. Colored organic pigments can be encapsulated and then used in polymeric materials to immobilize them in the polymeric materials or in surface coating. There are many techniques for encapsulating method such as conventional emulsion, dispersion and

miniemulsion polymerization [83, 84]. While dispersing the water-insoluble pigments in the aqueous phase, they often tend to agglomerate due to their high surface area [82, 83].

Miniemulsion polymerization has more advantages than both conventional emulsion polymerization and dispersion polymerization. Miniemulsions usually have diameters in the range of approximately 50–500 nm. Direct miniemulsions can be synthesized by shearing the system in the presence of a surfactant, oil, water and a hydrophobe like hexadecane whose role is to stabilize the emulsion against the diffusion degradation, the so-called Ostwald ripening [85]. The size of monomer droplets are too small in miniemulsions than the size of monomer droplets of revealed in conventional emulsion polymerization. Polymerization occurs by radical entry into the preexisting miniemulsion droplets without the formation of new particles. The size of the droplets can be controlled in miniemulsion technique in a much better way than in conventional emulsion technique. Therefore, miniemulsion polymerization is a successful application for the encapsulation reaction of any compound which can be suspended into the monomer phase [86].

Encapsulation of organic pigments in the monomer such as styrene is possible when the pigment content is about 10% w/w in the monomer phase. Otherwise the increase of viscosity makes dispersion rather difficult. Therefore when pigment content is less than 10% w/w, it can be dispersed in styrene [82, 84, 85]. Miniemulsion can be successfully achieved by using casonification [87]. Contrary to dispersing pigment directly in the monomer, it is dispersed in water using surfactant [83]. Then, this dispersion is mixed with stabilized monomer miniemulsion. Encapsulation of organic pigment in the monomer droplets is processed by a fusion/fission process which is initiated by ultrasonication [87].

In this research work miniemulsion technique was used to encapsulate the copper phtalocyanine pigment in the shell of hollow pigment produced.



## CHAPTER 3

### EXPERIMENTAL

In this chapter, the materials used in the study were described. Also given are detailed information on the steps of the procedure for synthesis of opaque polymer pigment. Furthermore, the characterization methods used were presented.

#### 3.1 Materials

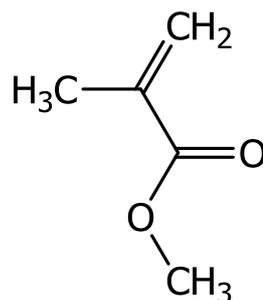
- Methyl methacrylate (MMA)
- Methacrylic acid (MAA)
- Ethylene glycol dimethacrylate (EGDM)
- Styrene
- Sodium dodecylbenzenesulfonate (SDBS)
- Sodium persulphate (SPS)
- Methyl ethyl ketone (MEK)
- Copper phthalocyanine

##### 3.1.1 Monomers

Methyl methacrylate (Sigma Aldrich) and methacrylic acid (Sigma Aldrich) mixture was used for the production of core polymer, and styrene is used for the production of shell polymer. Poly(methyl methacrylate) (PMMA) is widely used in coatings due to its excellent optical properties such as high light deterioration resistance, high light transmittance, high Abbe number (lower wavelength dependence of refractive index) [88, 89]. High chemical resistance and weathering corrosion resistance are other important properties of PMMA [90, 91]. The properties of MMA and its structure are given in Table 3.1, and in Figure 3.1, respectively.

**Table 3.1** Properties of MMA.

<b>Chemical formula</b>	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$
<b>Molecular weight (g/mole)</b>	100.12
<b>Density (g/cm<sup>3</sup>) (25 °C)</b>	0.94
<b>Refractive index</b>	1.4118
<b>Viscosity (20 °C)</b>	0.6 mPa.s

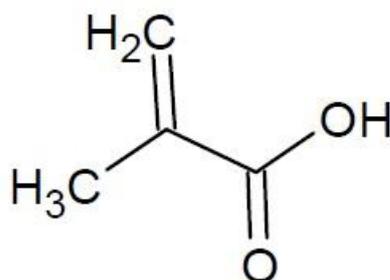


**Figure 3.1** Structural formula of MMA.

MAA is used to make acidic polymer which can swell the core. The properties of MAA and its structural formula are given in Table 3.2, and in Figure 3.2, respectively.

**Table 3.2** Properties of MAA.

<b>Chemical formula</b>	CH <sub>2</sub> =C(CH <sub>3</sub> )COOH
<b>Molecular weight (g/mole)</b>	86.09
<b>Density (g/cm<sup>3</sup>) (20 °C)</b>	1.014
<b>Refractive index</b>	1.4288
<b>Viscosity (20 °C)</b>	0.54 mPa.s

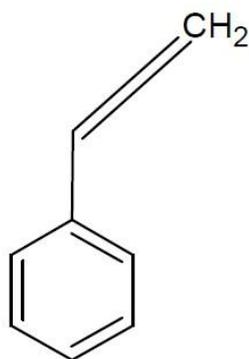


**Figure 3.2** Structural formula of MAA.

Polystyrene (PS) (Sigma Aldrich) is thermally stable and permeable to water, increases the toughness and impact strength of the polymer. Therefore, it is a suitable polymer to be used as the shell material. The properties and structural formula of styrene are given in Table 3.3, and in Figure 3.3, respectively.

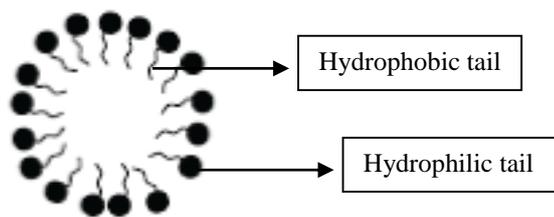
**Table 3.3** Properties of styrene.

<b>Chemical formula</b>	C <sub>8</sub> H <sub>8</sub>
<b>Molecular weight (g/mole)</b>	104.15
<b>Density (g/cm<sup>3</sup>) (20 °C)</b>	0.906
<b>Refractive index</b>	1.546
<b>Viscosity (20 °C)</b>	0.8 mPa.s



**Figure 3.3** Structural formula of styrene.

The inside of the micelle consists of hydrophobic tails of surfactant, therefore the interface of the micelle's inner part is more hydrophobic than the outer of the micelle. PS is more hydrophobic than PMMA. So, PMMA is located in the core part and PS is located in the shell part.



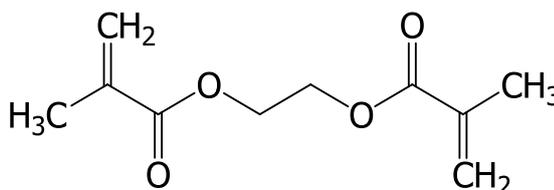
**Figure 3.4** Scheme of micelle.

### 3.1.2 Crosslinker

Ethylene glycol dimethacrylate (Merck) is used as crosslinker. EGDM yields gel at relatively low concentration. The properties and structural formula of EGDM are given in Table 3.4, and in Figure 3.5, respectively.

**Table 3.4** Properties of EGDM.

<b>Chemical formula</b>	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)=\text{CH}_2$
<b>Molecular weight (g/mole)</b>	198.22
<b>Density (g/cm<sup>3</sup>) (25 °C)</b>	1.051
<b>Refractive index</b>	1.454
<b>Viscosity (25 °C)</b>	3.45



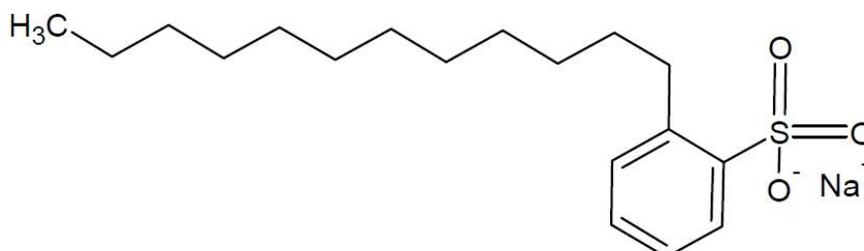
**Figure 3.5** Structural formula of EGDM.

### 3.1.3 Surfactant

Sodium dodecyl benzene sulfonate (Sigma Aldrich) is used as surfactant to form micelles. Sodium dodecyl benzene sulfonate is soluble in water so the aqueous solution of surfactant was used in this work. The properties and structural formula of SDBS are given in Table 3.5, and in Figure 3.6, respectively.

**Table 3.5** Properties of SDBS.

<b>Chemical formula</b>	$C_{18}H_{29}NaO_3S$
<b>Molecular weight (g/mole)</b>	348.48
<b>Density (g/cm<sup>3</sup>) (20 °C)</b>	1.00
<b>Refractive index</b>	1.5256



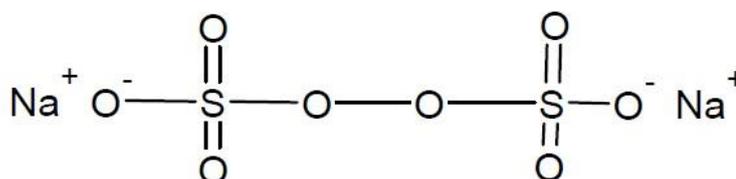
**Figure 3.6** Structural formula of SDBS.

### 3.1.4 Initiator

Sodium persulphate (Merck) is used as water soluble initiator in this study. The properties and structural formula of SPS are given in Table 3.6 and in Figure 3.7, respectively.

**Table 3.6** Properties of SPS.

<b>Chemical formula</b>	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>
<b>Molecular weight (g/mole)</b>	238.10
<b>Density (g/cm<sup>3</sup>) (20 °C)</b>	2.4



**Figure 3.7** Structural formula of SPS.

### 3.1.5 Swelling agent

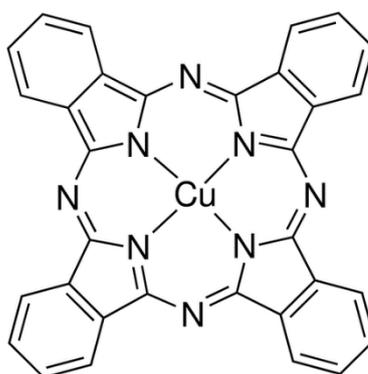
Methyl ethyl ketone (MEK) is used as swelling agent to increase the size of hollow pigment. Chemical formula of MEK (Sigma Aldrich) is C<sub>4</sub>H<sub>8</sub>O.

### 3.1.6 Organic pigment

The copper phthalocyanine blue pigment (Sigma Aldrich) is used for coloring the opaque hollow pigment. The encapsulation of copper phthalocyanine with MMA is unfeasible but it can be introduced to styrene successfully due to  $\pi$ - $\pi$  interactions. So, coloring of hollow pigment with copper phthalocyanine can be carried out by incorporating it into shell. The properties and structural formula of copper phthalocyanine are given in Table 3.7 and in Figure 3.8, respectively.

**Table 3.7** Properties of copper phtalocyanine blue pigment.

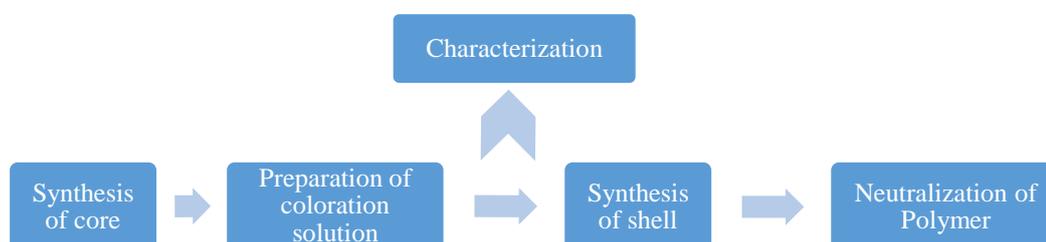
<b>Chemical formula</b>	$C_{32}H_{16}CuN_8$
<b>Molecular weight (g/mole)</b>	576.07



**Figure 3.8** Structural formula of copper phtalocyanine blue pigment.

### 3.2 Procedure

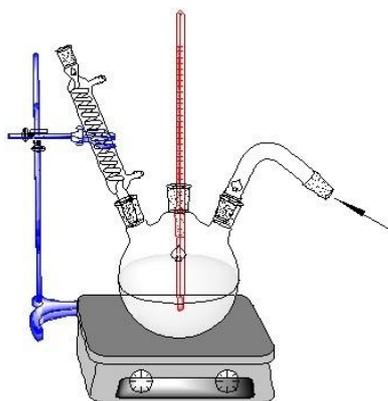
In this study; the preparation of opaque polymer was carried out in four main steps; these are (i) synthesis of core part, (ii) preparation of coloration solution, (iii) synthesis of shell part, (iv) neutralization of core polymer. Step (ii) was not performed during the synthesis of white opaque pigment. The general flow diagram is shown in Figure 3.9:



**Figure 3.9** General flow diagram.

### 3.2.1 Synthesis of core part

Methyl methacrylate and methacrylic acid is used as core monomers. Poly (methyl methacrylate-co-methacrylic acid) were prepared by emulsion polymerization at 80°C for 24 h in a four-necked 250 ml round-bottom flask equipped with an inlet of nitrogen gas and a condenser. The experimental setup is given in Figure 3.10.



**Figure 3.10** Experimental setup.

In the very first step water and SDBS solution was added to the reactor, then the solution was stirred at 250 rpm under a nitrogen atmosphere for 30 minute at 80°C. MMA and MAA are poured into this solution, and the reaction was continued for 30 minutes at 80°C. Then SPS (0.5 w/w ratio to monomer) is added to the reactor to start polymerization. Four hours later water and SDBS solution was added again to the reactor. After 30 min MMA, MAA and crosslinker were added to the system and the solution was stirred at 250 rpm at 80°C for half an hour, and then SPS was added into the reactor. Complete polymerization takes place in 16 hours. Both the compositions of core used in this study and the name of the experiments were given in Table 3.8.

**Table 3.8** Composition of core emulsion.

Name of experiment	Monomer percent by weight		C/M* %	(% w/w)	
	MMA	MAA	EGDM	S/W**	S/M***
S1A1C1	90	10	2	1.46	11.56
S2A1C1	90	10	2	1.35	10.71
S3A1C1	90	10	2	0.97	7.71
S4A1C1	90	10	2	0.65	5.14
S5A1C1	90	10	2	0.54	4.28
S1A2C1	85	15	2	1.46	10.94
S1A3C1	80	20	2	1.46	10.25
S1A4C1	75	25	2	1.46	9.62
S3A2C1	85	15	2	0.97	7.29
S3A3C1	80	20	2	0.97	6.83
S3A4C1	75	25	2	0.97	6.41
S4A2C1	85	15	2	0.65	4.86
S4A3C1	80	20	2	0.65	4.55
S3A1C2	90	10	3	0.97	7.71
S3A1C3	90	10	4.5	0.97	7.71
S3A1C4	90	10	9	0.97	7.71
S3A2C2	85	15	3	0.97	7.29
S3A2C3	85	15	4.5	0.97	7.29
S3A2C4	85	15	9	0.97	7.29

\*C/M: weight ratio of crosslinker to total monomer

\*\*S/W: weight ratio of surfactant to water

\*\*\*S/M: weight ratio of surfactant to total monomer

### 3.2.2 Preparation of coloration solution

Organic copper phthalocyanine blue pigment (2-3% w/w ratio to monomer) was dispersed in styrene and stirred by magnetic stirrer at 400 rpm for half an hour. The dispersion was added to the aqueous solution (S/W= 0.45 and S/M= 5) which is composed of surfactant and swelling agent (10% w/w ratio to monomer). The final mixture was stirred for 1 hour under the same conditions. Then, the mixture was ultrasonically homogenized for 4 min at 90% output power, to overcome the agglomeration (Bandalin Sonopuls HD2200, with maximum power of 200W).

### 3.2.3 Synthesis of shell

The amount of styrene used in the production of shell is taken to be about one third of the monomer used in the production of core, by weight. Water, SDBS (S/W= 3.33 and S/M= 33), styrene, and initiator (0.5% weight ratio to monomer) solution are charged by 5 equal portions. The first portion of water and SDBS solution was added at the very beginning of the synthesis of shell, and the temperature was increased to 90 °C. The reactor was agitated at 350 rpm. After half an hour the first portion of styrene is added into the reactor. First portion of SPS solution is added to the reactor half an hour after the addition of styrene. All steps were repeated 5 times by 1 hour intervals. Polymerization of shell was stopped and the reactor was cooled down to the ambient temperature after 16 hours passed from the completion of all stages. The product thus obtained is white opaque pigment.

For the preparation of colored hollow pigments; the solution containing coloring agent which is prepared as in step 3.2.2 is divided into 5 portions. The first portion of solution is added into the reactor for the synthesis of shell and the temperature of the reactor was increased to 90°C. The second portion is added one hour later after the first portion. This procedure was repeated five times. The polymerization was stopped 16 hours after the start, and the reactor was cooled down to the ambient temperature.

### 3.2.4 Neutralization of polymer

After the production of core-shell polymer water was added, and the mixture was stirred at 350 rpm under nitrogen atmosphere at 90°C. The pH of solution was adjusted to 10 using NaOH solution (pH=13). After addition of NaOH (pH=13) into the reactor, water is added to system for each hour. A sample is taken from the reactor before the addition of water to the system. . These samples are used for particle size analysis. When the particle size reached a constant value neutralization was ended.

### 3.2.5 Film application

Polymer pigment was mixed water based styrene acrylic resin (Betapol SA-5017B) hydroxyethyl cellulose was used as thickener which is provided from Betek Paint and Chemical Inc. The resin has 50% w/w solid content. The films were applied by using an

applicator at a wet thickness of 150  $\mu\text{m}$ . The optical properties of paint, namely opacity and gloss were determined 24 hours after drying the film at ambient temperature. The formulation given in Table 3.9 was used in coating.

**Table 3.9** Receipt of film.

Component	(% w/w)
Opaque Polymer Pigment	7
Water	70.5
Styrene-Acrylic Resin (50 %w/w)	15.5
Hydroxyethyl cellulose (2%)	7

### 3.3 Characterization Methods

Dynamic light scattering size measurement (DLS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), opacity, gloss and color measurements were the characterizations methods used in this study. These methods were briefly described below.

#### 3.3.1 Dynamic light scattering size measurement (DLS)

The size of core and core-shell emulsion particles, and hollow pigment were measured by using Malvern Zetasizer Nano ZS (Model No: ZEN3500,  $\lambda=633$  nm laser). The measurements were made in Nuclear Application Laboratory in Chemical Engineering Department of Middle East Technical University. The average particle size is the key parameter for the efficiency of light scattering.

The samples were washed with water (1:1 by weight) and quartz cells were used as sample holder.

DLS measures the size of particles based on their velocities as the large particles have slower motion than smaller particles. In fact, it measures the velocities of particles in Brownian motion.

#### 3.3.2 Scanning electron microscopy (SEM)

SEM is the technique which is used in the general characterization of pigments for their size and morphology. SEM (Model: FEI Quanta 200 FEG) is located in National Nanotechnology Research Laboratory in Bilkent University.

Pigments can be used directly for SEM sample after washing with water (1:1 by weight). SEM samples were coated with gold/palladium before analysis.

### 3.3.3 Transmission electron microscopy (TEM)

SEM and TEM are very similar to each other, but TEM gives information about the internal structure of specimen. So, hollow structure of opaque pigment was investigated by using TEM (Model: FEI Tecnai G2 F30). TEM is located in National Nanotechnology Research Laboratory in Bilkent University.

Pigments can be used directly for TEM specimen after washing with water (1:1 by weight). TEM samples were also coated with gold/palladium before analysis.

### 3.3.4 Fourier transform infrared spectroscopy (FTIR)

FTIR (Model No: Shimadzu IR Prestig-21) spectroscopy is used for determining the molecular structure of pigment.

### 3.3.5 Opacity and color measurement

Color spectrophotometer (Model no: X-rite Color I5) is used for opacity and color measurements of coating films. Spectrophotometer is located in Nuclear Application Laboratory in Chemical Engineering Department of Middle East Technical University. It has 360-750 nm spectral range, and its light source is CEI standard illuminant D65. The spectrophotometer measures opacity of film with respect to contrast ratio value. Contrast ratio is the ratio of lightness against black and white background, respectively.

### 3.3.6 Gloss measurement

Glossmeter (Model: Rhopoint, Novo-Gloss) is used to determine gloss value. Gloss values are measured at 20°, 60° and 85° angles of incident light to find out high, medium, and matt gloss respectively. If the gloss value of film is lower than 10, it is said to be matt whereas a gloss value higher than 70 indicates high gloss.



## CHAPTER 4

### RESULTS AND DISCUSSION

#### 4.1 Preliminary Studies on Emulsion Stability

The droplet size and emulsion stability are affected by the type and the amount of surfactant used. It is essential to select an appropriate surfactant type and its concentration in order to prepare a stable emulsion. Rapid coagulation of the particles is observed in the experiment S5A1C1 (S/W=0.54 and S/M=4.28, see Table 3.8) which is prepared using SDBS. The amount of surfactant used for synthesizing the core is increased to achieve emulsion stability. Preliminary experiments showed that the amount of surfactant is one of the main factors to have stable emulsion as low concentration of SDBS leads to the sedimentation of particles. The surfactant to monomer, surfactant to water weight ratios and the observed emulsion stability properties are given in Table 4.1.

**Table 4.1** Preliminary experiments for determining the amount of surfactant.

(% w/w)		Stability observation
S/W	S/M	
0.43	3.42	Sedimentation
0.54	4.28	Sedimentation
0.65	5.14	Stable
0.97	7.71	Stable

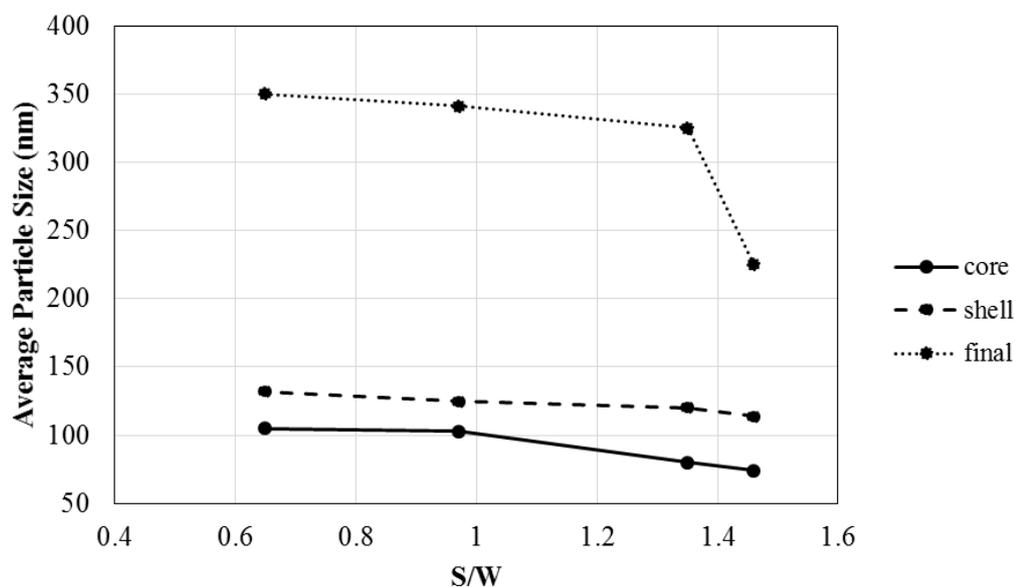
#### 4.2 Effect of S/W Ratio on Particle Size of Pigment and Emulsion Stability

A set of experiments were performed at different S/W and S/M ratios in order to understand the effect of the amount of surfactant on emulsion stability, particle size, and particle morphology. These ratios were arranged in such a way that the amount of monomer and water were kept constant, and the amount of surfactant was varied.

The size of polymer droplets was measured by DLS technique in core stage, shell stage and by one hour intervals in the swelling part. The size measurement results of core, shell, and pigment were given Table 4.2 and in Figure 4.1.

**Table 4.2** Influence of surfactant amount on particle size.

Name of experiment	Monomer percent by weight		C/M %	(% w/w)		Average particle size by volume (nm)		
	MMA	MAA		EGDM	S/W	S/M	Core	Shell
S1A1C1	90	10	2	1.46	11.56	74	114	225
S2A1C1	90	10	2	1.35	10.71	80	120	325
S3A1C1	90	10	2	0.97	7.71	103	125	341
S4A1C1	90	10	2	0.65	5.14	105	132	350
S5A1C1	90	10	2	0.54	4.28	Sedimentation	-	-



**Figure 4.1** The effect of surfactant concentration on particle size.

Particle size may be controlled by the amount and type of surfactant. The biggest particle size was observed at S/W ratio at 0.65, and the smallest particle size was observed at S/W ratio at 1.46.

SDBS plays a key role for hollow particle production. Greater amounts of surfactant offers better stabilization and produce smaller particle size. As the latex particles grow in both core and shell stage, more surfactant is needed to stabilize the emulsion. So, SDBS should be supplied gradually and slowly. The increase of the amount of surfactant affects both the structure and monodispersity of latex. When it was too low (S/W=0.54), sedimentation of the particles was observed.

Two droplet growth mechanisms influence the polydispersity of particles and emulsion stability; these are (i) Ostwald ripening, and (ii) coalescence. As the S/M ratio increases, surfactant can reduce monomer diffusion from one droplet to the other droplet. Therefore, S/M ratio affects both emulsion stability and particle size, and smaller particles can be produced at higher S/W weight ratio.

The effect of S/W ratio on particle size and particle morphology of pigment will be discussed again in concern to TEM images of pigment.

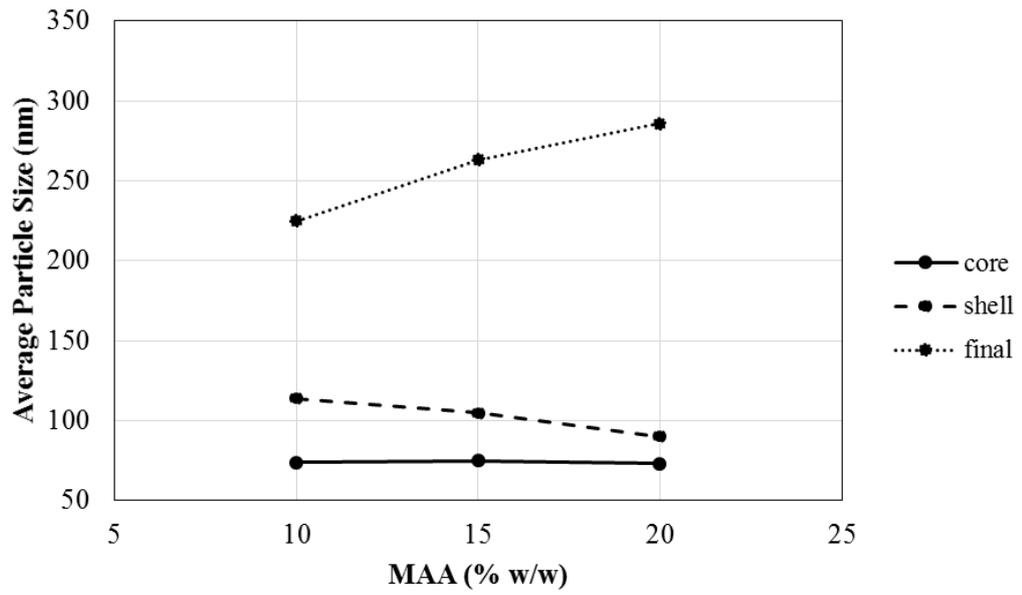
### **4.3 Effect of Acid Content on Particle Size of Pigment and Emulsion Stability**

Three set of experiments were designed to investigate the effect of the acid content. S/W was fixed at 1.46, 0.97 and 0.65 respectively, and the monomer concentration changed by increasing the acid content. In Table 4.3, the effect of acid (MAA) content on the particle size of latex is given.

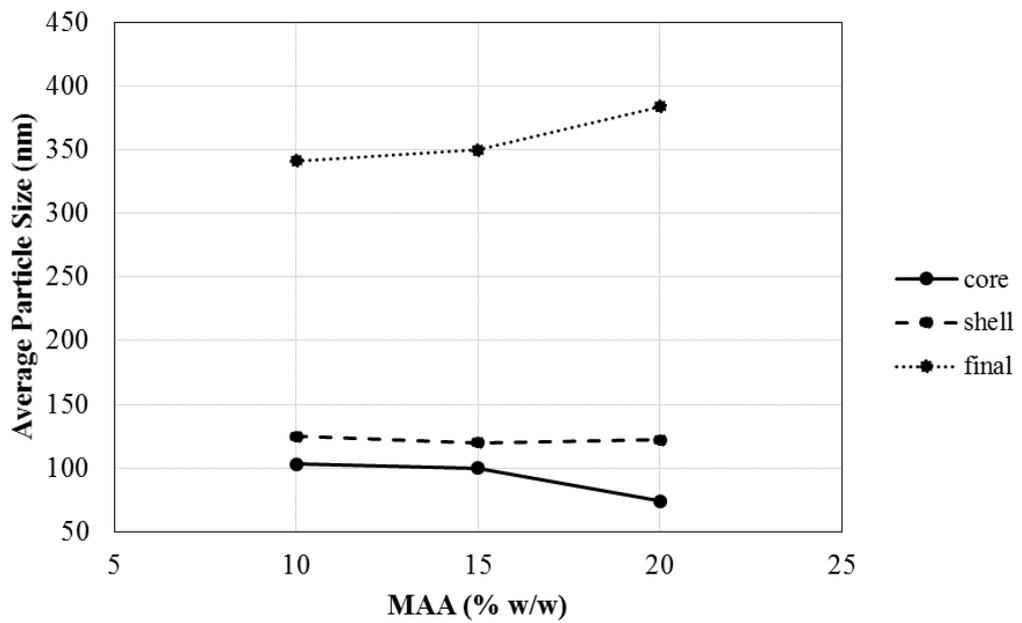
**Table 4.3** Influence of the amount of acid (MAA) on particle size.

Name of experiment	Monomer percent by weight		C/M %	(% w/w)		Average particle size by volume (nm)		
	MMA	MAA		EGDM	S/W	S/M	Core	Shell
S1A1C1	90	10	2	1.46	11.56	74	114	225
S1A2C1	85	15	2	1.46	10.94	75	105	263
S1A3C1	80	20	2	1.46	10.25	73	90	286
S1A4C1	75	25	2	1.46	9.62	72	Sedimentation	-
S3A1C1	90	10	2	0.97	7.71	103	125	341
S3A2C1	85	15	2	0.97	7.29	100	120	350
S3A3C1	80	20	2	0.97	6.83	74	122	384
S3A4C1	75	25	2	0.97	6.41	73	Sedimentation	-
S4A1C1	90	10	2	0.65	5.14	105	132	350
S4A2C1	85	15	2	0.65	4.86	83	129	371
S4A3C1	80	20	2	0.65	4.55	76	Sedimentation	-

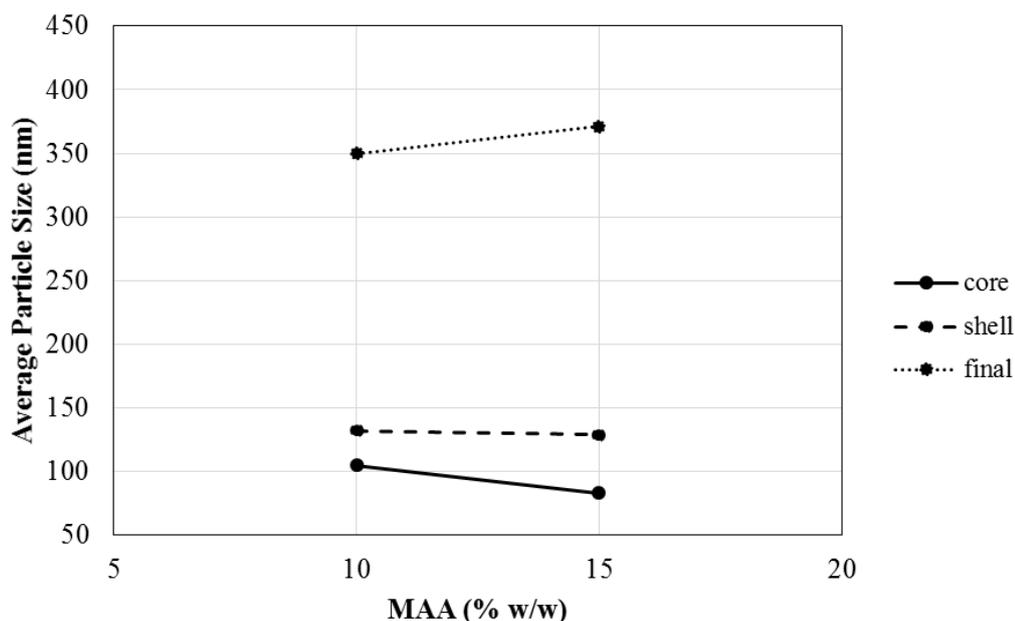
The results of size measurements of core, shell, and pigment were given in Figure 4.2, Figure 4.3, and Figure 4.4, respectively.



**Figure 4.2** The effect of acid content on particle size for S/W=1.46.



**Figure 4.3** The effect of acid content on particle size for S/W=0.97.



**Figure 4.4** The effect of acid content on particle size for S/W=0.65.

The increase of acidic monomer in the composition decreases the core size as seen from Figure 4.2, Figure 4.3 and Figure 4.4. The increased hydrogen bonding between the carboxylic groups may cause the decrease in particle size.

The incorporation of high levels of carboxylic acid into emulsion copolymer leads also to instability and coagulation as the surfactant may not be well adsorbed. Carboxylic acids formed oligomers may act as a dispersant or flocculants and they caused emulsion instability. However particle size analysis based on dynamic light scattering (DLS) technique does not give very dependable conclusions, because, the agglomerated particles are counted as a unique particle. The results given in these figures may denote the size of agglomerated clusters.

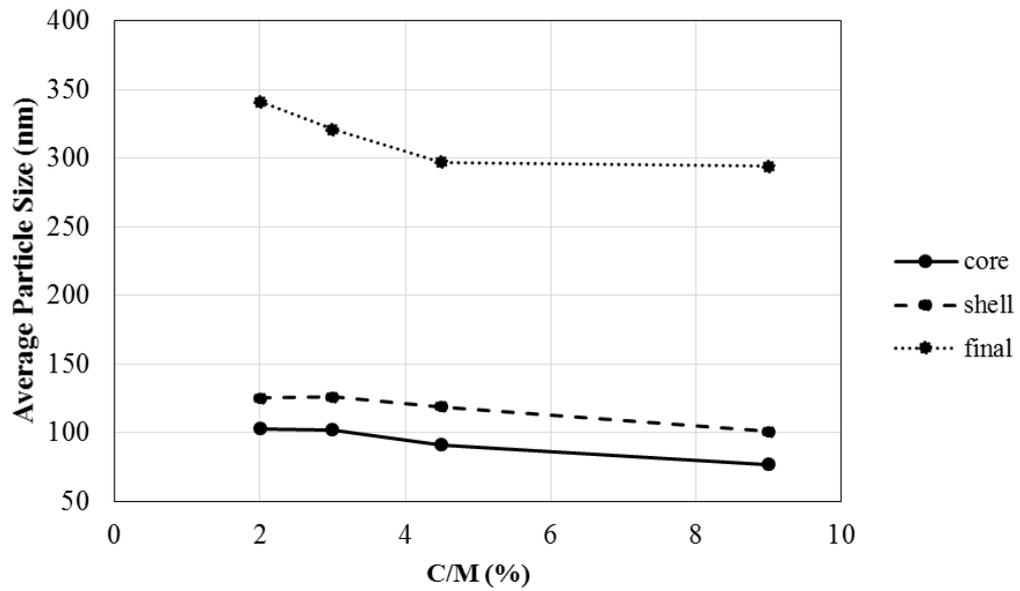
Encapsulation of core which is made of MMA and MAA copolymer with shell can be problematic due to instability of emulsion. The emulsion instability were observed in experiments (S1A4C1, S3A4C1, and S4A3C1) while generating shell.

#### 4.4 Effect of Crosslinker Content on Particle Size of Pigment

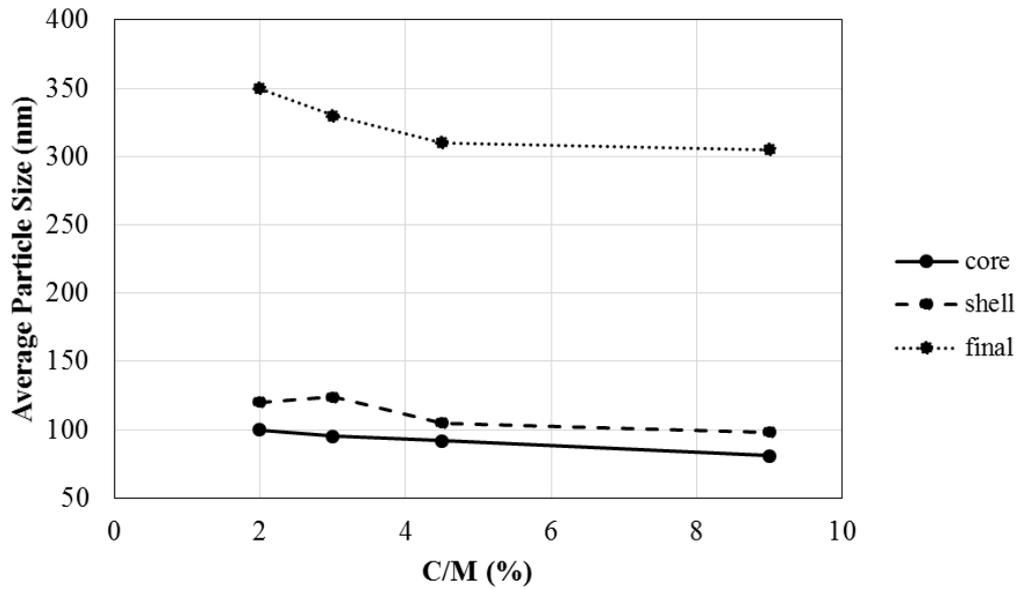
Two sets of experiments were performed for investigating the effect of crosslinker on size and morphology of particle. The size measurement results of core, shell, and pigment were given in Table 4.4, and Figure 4.5, and Figure 4.6, respectively.

**Table 4.4** Influence of crosslinker content on particle size.

Name of experiment	Monomer percent by weight		C/M %	(% w/w)		Average particle size by volume (nm)		
	MMA	MAA		EGDM	S/W	S/M	Core	Shell
S3A1C1	90	10	2	0.97	7.71	103	125	341
S3A1C2	90	10	3	0.97	7.71	102	126	321
S3A1C3	90	10	4.5	0.97	7.71	91	119	297
S3A1C4	90	10	9	0.97	7.71	77	101	294
S3A2C1	85	15	2	0.97	7.29	100	120	350
S3A2C2	85	15	3	0.97	7.29	95	124	330
S3A2C3	85	15	4.5	0.97	7.29	92	105	310
S3A2C4	85	15	9	0.97	7.29	81	98	305



**Figure 4.5** The effect of crosslinker content on particle size (10% w/w MAA).



**Figure 4.6** The effect of crosslinker content on particle size (15% w/w MAA).

S/W ratio is constant for both experiments but in the second set of experiments carboxylic acid content increases as seen from Table 4.4.

Sufficient amount of crosslinker will improve the heat resistance, solvent resistance, and the anti-blocking property of the coatings. As seen from Figure 4.6, when the amount of crosslinker is increased, the size of particles decreased as detected by DLS. The mobility of the carboxyl acid containing polymer chains, which move toward the outside of the latex particles while the alkaline solution penetrates inwards to the particles, will be limited if the particles were cross-linked.

#### 4.5 Effect of pH on Particle Size of Pigment

The effect of pH on particle size and morphology was done using S3A1C1 composition. The pH is adjusted by dropwise addition of NaOH. The size measurement results of core, shell, and pigment were given in Table 4.5.

**Table 4.5** Influence of pH on particle size.

Name of experiment	Monomer percent by weight		C/M %	(% w/w)		Average particle size by volume (nm)		
	MMA	MAA		EGDM	S/W	S/M	Core	Shell
pH=8	90	10	2	0.97	7.71	122	144	190
pH=9	90	10	2	0.97	7.71	122	144	201
pH=10	90	10	2	0.97	7.71	122	144	321
pH=11	90	10	2	0.97	7.71	122	144	324

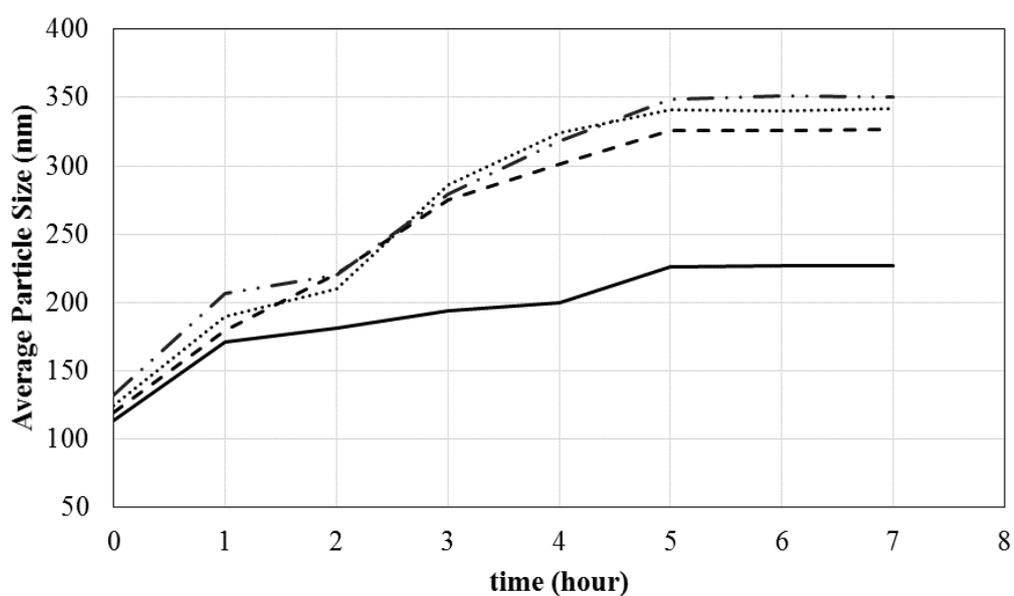
The pH change did not result in any significant difference on particle size but its influence on particle morphology will be discussed later using the TEM images.

#### 4.6 Effect of Alkali Treatment Time on Particle Size of Pigment

The size of polymer droplets of experiments S1A1C1, S2A1C1, S3A1C1 and S4A1C1 were measured in both core and shell stage by one hour intervals while swelling the pigment through alkali treatment. The results were given in Table 4.6, and Figure 4.7.

**Table 4.6** Influence of alkali treatment time on particle size.

Name of experiment	Average particle size by volume (nm)									
	Core	Shell	t= 1h	t= 2h	t= 3h	t= 4h	t= 5h	t= 6h	t= 7h	Final
S1A1C1	74	114	171	181	194	200	226	227	227	225
S2A1C1	80	120	180	221	275	301	326	326	327	325
S3A1C1	103	125	190	210	286	324	341	340	342	341
S4A1C1	105	132	207	220	279	318	349	351	350	350



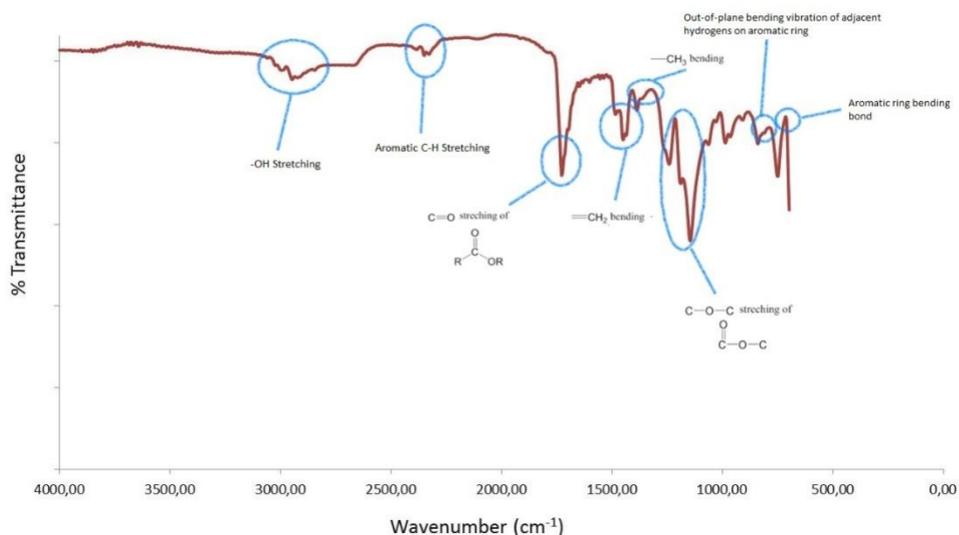
**Figure 4.7** The effect of alkali treatment time on particle size.

It was seen from Figure 4.7 that extending alkali treatment time was beneficial to get the swelling equilibrium of the polymer particles. It was seen that the particle size of the polymers increase till a certain time and then remain same. The experiments were not carried beyond this point. Polymers have different permeability at different temperature. Furthermore, in order to reach osmotic equilibrium at a given temperature a certain time is necessary. The time for

the movement of polymer chain segments can be shortened by increasing temperature of the system. So, neutralization time and temperature both affect the particle size.

#### 4.7 FTIR Spectrum of Polymer Pigment

The Fourier Transform Infrared (FTIR) spectrum of polymer produced is given in Figure 4.8.

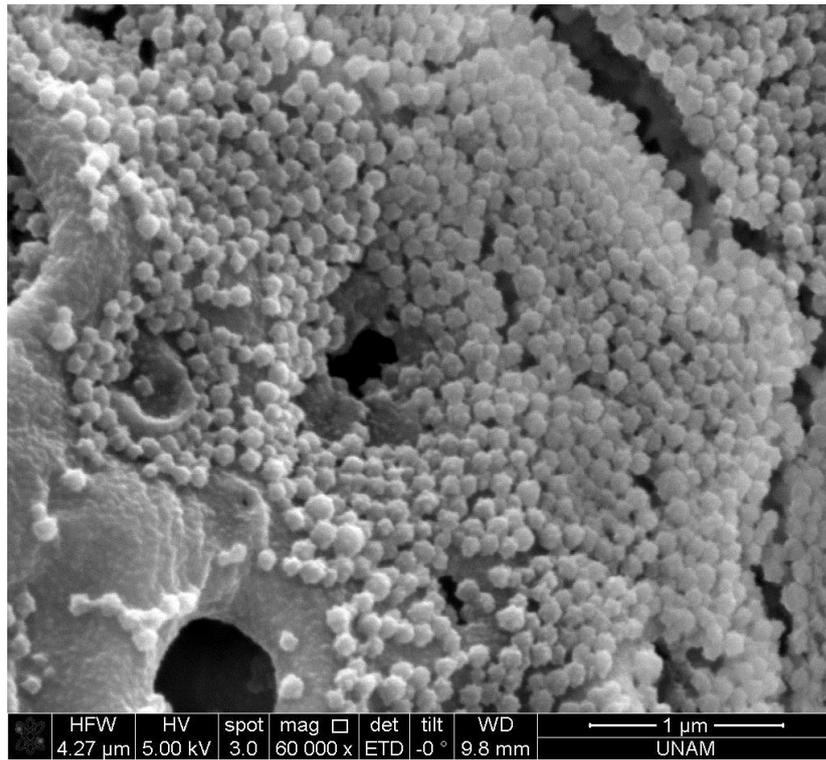


**Figure 4.8** FTIR spectrum of the synthesized polymer pigment.

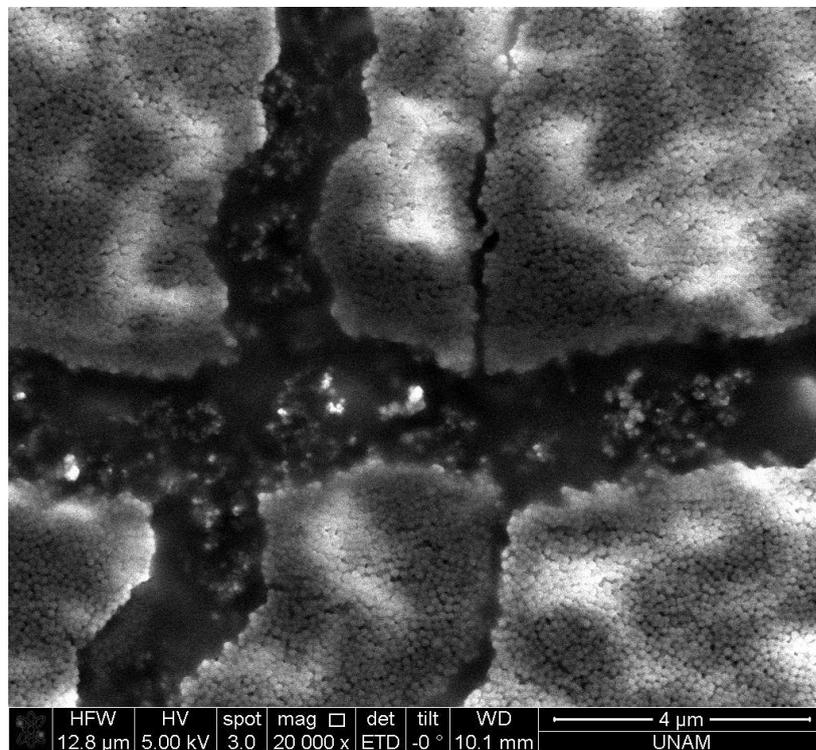
The (C-O) stretching peaks of PMMA appeared at 1276, 1185, and 1140  $\text{cm}^{-1}$ . In addition, the sharp intense peak at 1728  $\text{cm}^{-1}$  is due to stretching of carbonyl group (C=O) of ester. A peak at 698  $\text{cm}^{-1}$  (the benzene ring out-of-plane bending peak) appeared clearly. The peaks ranging from 975 to 700  $\text{cm}^{-1}$  are caused by the bending of C-H. This means that PMMA and PS were effectively synthesized while preparing the pigment.

#### 4.8 Particle Morphology

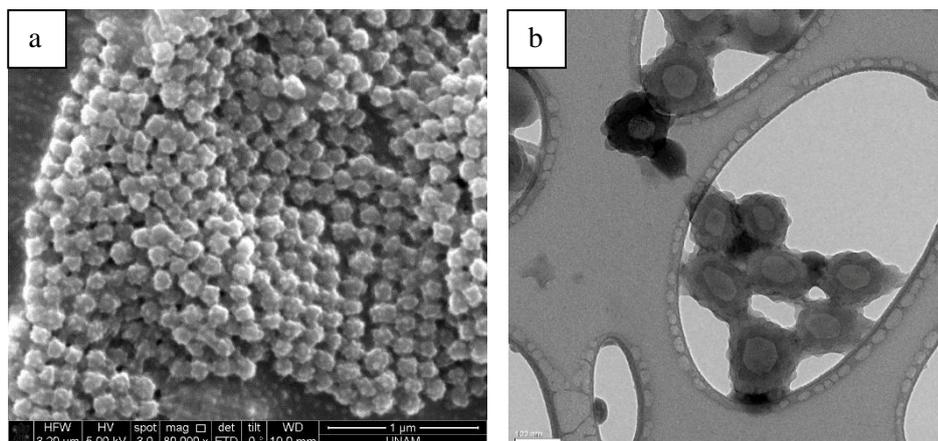
The surface morphology of particles was investigated by SEM and TEM analysis. The micrographs are given in Figures 4.9-11.



**Figure 4.9** SEM micrographs of the experiment S1A1C1.



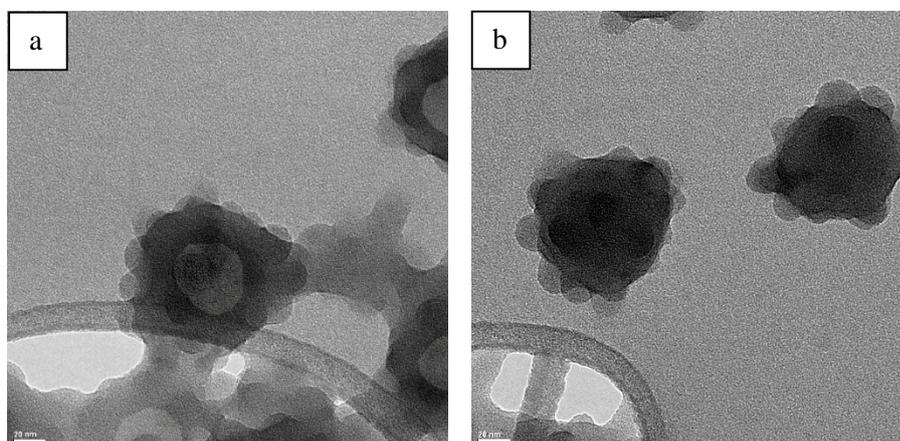
**Figure 4.10** SEM micrographs of the S1A3C1.



**Figure 4.11** (a) SEM micrographs of the colored pigment, (b) TEM micrographs of the colored pigment

All pigments have spherical structures as observed from the micrographs. Colored pigment is synthesized efficiently as seen in Figure 4.11.

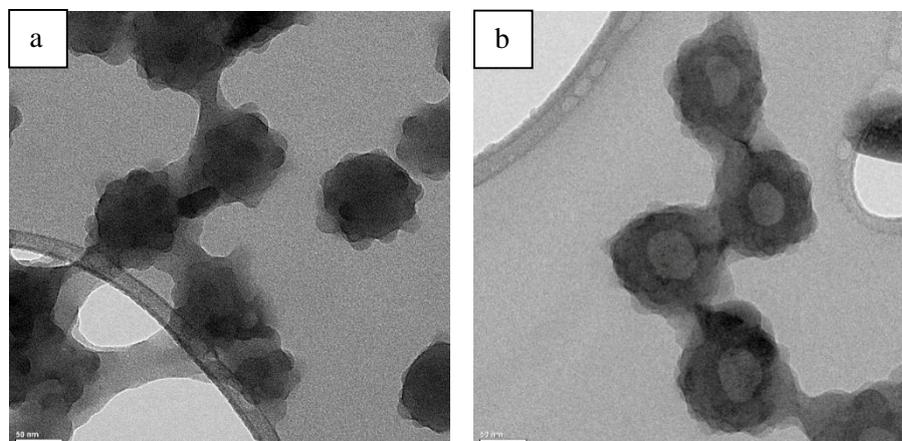
The TEM analysis of pigments was performed to investigate the existence of voids for sure, and the particle morphology of pigments. The TEM micrographs of hollow pigments are given in Figures 4.12-14.



**Figure 4.12** TEM micrographs of (a) S1A3C1 (20% w/w MAA and S/W=1.46), (b) S1A1C1 (10% w/w MAA and S/W=1.46).

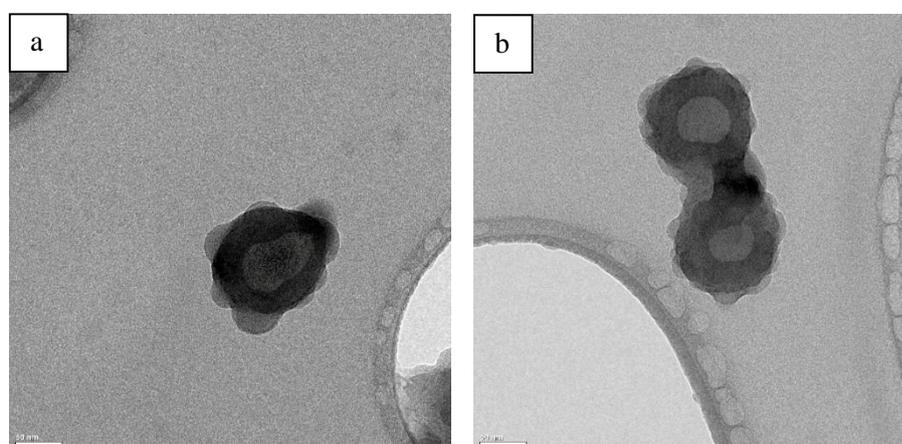
As observed from the TEM micrographs the hollow structured particles were obtained when MAA content was 20% w/w. The lower amounts of acid adversely affected the morphology

as seen from Figure 4.12b. No hollow morphology was observed when acid content was below 10% w/w.



**Figure 4.13** TEM micrographs of the pigment (a) pH=9, (b) pH=10

It can be seen from TEM images and DLS measurements, that no hollow particles were observed when pH is 9. The average particle size by volume was almost unchanged during neutralization of polymer at pH 8 and 9 as seen in Table 4.5. However, when the pH was increased to 10, the pores were generated and the average size of pigment by volume increased slightly during neutralization of polymer according to DLS measurements.



**Figure 4.14** TEM micrographs of (a) S3A1C4 (10% w/w MAA, S/W=0.97, C/M=9) (b) S3A1C1 (10% w/w MAA, S/W=0.97, C/M=2)

High degree of crosslinking of polymer particles resulted in smaller polymer particles as measured by DLS. According to the DLS results, the particle size of pigment decreased when

crosslinker content is decreased. However, the TEM micrographs show that the size of each bead was the same (Figure 4.14 a and b).

Particle size values revealed by TEM and DLS measurements are different. The reason for the higher DLS results was the bead positioning next to each other (Figure 4.14b). DLS measures the aggregated particles as a single particle.

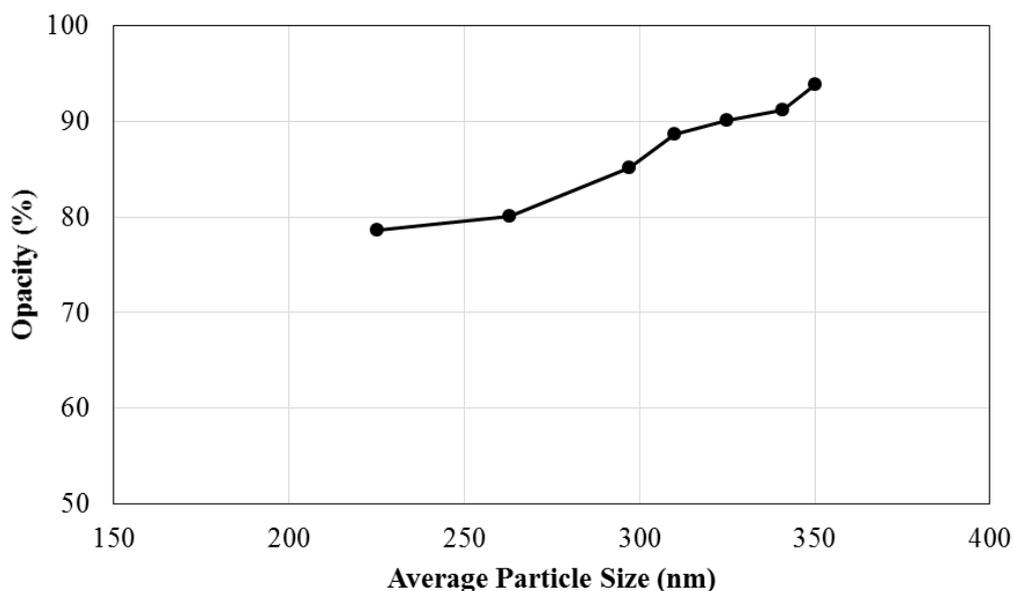
#### 4.9 Opacity Measurements

Opacity is the desirable property of coating that results from light being scattered at an interface between substances of different refractive index (e.g. the interface between air and a polymer). Hollow pigments contain voids which act as scattering centers and deliver opacity.

A film with titania was prepared with the same volume of polymer pigment for comparing the opacity properties. The opacity measurement results of synthesized hollow pigments and titania are given in Table 4.7.

**Table 4.7** Opacity measurement results of polymer pigments.

Name of experiment	Opacity	Average particle size by volume (nm)
TiO <sub>2</sub>	100	
S3A2C1	93.8	350
S3A1C1	91.2	341
S2A1C1	90.1	325
S3A2C3	88.7	310
S3A1C3	85.2	297
S1A2C1	80.1	263
S1A1C1	78.6	225



**Figure 4.15** Opacity measurements with respect to average particle size of polymer pigment.

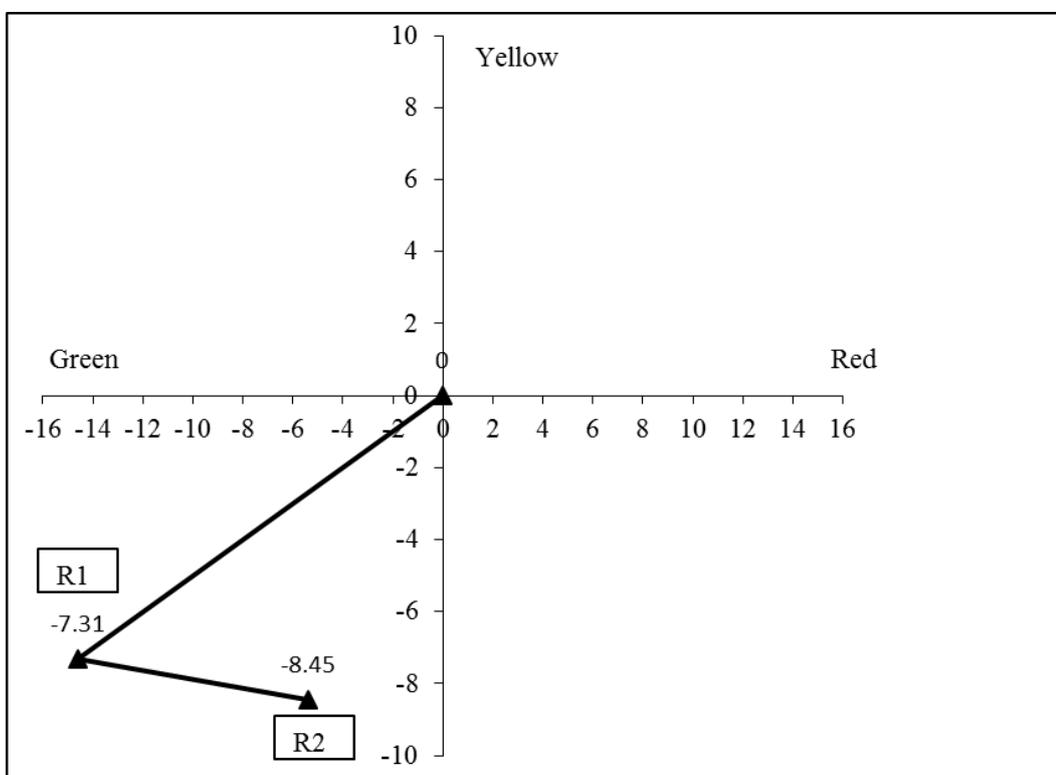
As seen from Figure 4.15, opacity performance of the polymer pigment was dependent on the size of polymer pigment. The results showed that, S3A2C1 and S3A1C1 delivered highest opacity values.

#### 4.10 Color Measurements

$L^*a^*b$  values of the samples were measured for characterization of color properties of paints. Lightness of the paint is shown by the  $L$  parameter.  $a^*$  is used to designate redness and  $b^*$  for the yellowness. Positive values of 'b' mean that paint is yellower than the sample; negative values are indications of the bluish samples. Similarly, positive values of 'a' mean that paint is redder than the sample; negative values are indications of the greenish samples.  $dL^*$ ,  $da^*$  and  $db^*$  indicate color difference between the sample and the standard. Two experiments (R1 and R2) are performed for characterization of color properties of paints. The amount of copper phthalocyanine blue pigment in R1 was 2% w/w in the monomer while it was 3% w/w in R2. Table 4.8 lists the values for each colored pigment. The comparative color properties of pigments based on different copper phthalocyanine content are shown in Figure 4.16.

**Table 4.8** The L\*a\*b values of paint.

Name of sample	dL*	da*	db*
Single hollow white pigment (standard)	0	0	0
R1	-10.74	-14.61	-7.31
R2	-31.49	-5.39	-8.45



**Figure 4.16** The comparative color properties of pigments based on different copper phthalocyanine content.

Single hollow white opaque pigment based paint is taken as the standard and it is shown at the origin. Green and blue shift is observed with the increase of the amount of copper phtalocyanine.

#### 4.11 Gloss Measurements

In Table 4.9, the gloss measurement at angles of 20°, 60°, and 85° are given. The porous structure of polymer pigments which lead to very high diffuse reflection caused very low gloss values.

**Table 4.9** Gloss values of opaque polymer pigments.

	20°	60°	85°
<b>S1A1C1</b>	1.8	2.9	2.3
<b>S1A2C1</b>	1.9	3.0	1.5
<b>S3A1C3</b>	1.8	2.7	1.8
<b>S3A2C3</b>	1.9	2.9	1.7
<b>S2A1C1</b>	1.8	2.6	1.5
<b>S3A1C1</b>	1.9	2.8	1.6
<b>S3A2C1</b>	1.9	2.7	2.4

## CHAPTER 5

### CONCLUSIONS

Hollow polymer pigment with carboxylated core (MMA-MAA) and outer shell (styrene) was prepared and the following conclusions can be drawn from the experiments done:

1. The particle size of pigment can be controlled by changing the amount of surfactant. The biggest size of particle was observed at S/W ratio of 0.65, and the smallest one was observed at S/W ratio of 1.46.
2. Surfactant to water (S/W) weight ratio had significant effect on emulsion stability. Low concentration of SDBS (below S/W=0.54) lead to sedimentation of particles.
3. The carboxyl group in the core helped water transport through the shell and swelling of the core during neutralization of pigment. The maximum particle size of pigment was observed when acid content was 20% w/w and S/W was 0.97. However, excess carboxylic acid content led to sedimentation in the shell forming stage.
4. No hollow morphology was observed when acid content was below 10% w/w.
5. High degree of crosslinking of polymer particles resulted in smaller polymer particles.
6. Hollow morphology was revealed when the pH is above 9.
7. The particle size of polymer pigment increased in the course of alkali treatment progressed but it stayed constant after a while.
8. Single hollow polymer pigment provided up to 93.8% opacity without any other additive at 50% v/v.
9. Colored pigment was synthesized efficiently.



## **CHAPTER 6**

### **RECOMMENDATIONS**

1. Methacrylic acid can be used while generating shell to acquire bigger particle size pigments.
2. Swelling agent such as methyl ethyl ketone (MEK) can be used to increase the size of void inside the pigment.



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