

Nanoparticles Formation of Poly (Styrene Acrylate) Emulsion by Two-Stage Polymerization Process

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Abstract. Nowadays, phenol containing poly (styrene acrylate) is getting less preferably due to unpopular effects to the environment issues despite the materials still have wide applications and readily available products. In order to account for the less desirable impact to the materials, phenol free poly (styrene acrylate) is becoming one of the subject of current research interest. In this paper, we report some results of synthesized phenol free poly (styrene acrylate) materials with the main focus of research is to duplicate some physical properties of phenol containing with that of phenol-free containing poly(styrene acrylate). These are including particle formation with ultra fine mean size and characterization of poly (styrene acrylate) emulsion after replacement of non-ionic surfactant nonylphenol emulsifier with polyethylene glycol ether based emulsifier. It was found that nanoparticles formation took place when the anionic and non ionic emulsifier was introduced during initiation reaction of feeding process for monomer and polymer formation stages. The feeding process and feeding time of monomer during initiation reaction influenced the mean particle size of polymer. The presence of the combined emulsifier caused the mean particle size of polymer decreased to much smaller value than that of original. However, a significant change in mean particle size was only obtained after the second stage ceased and the extension of feeding time. The mean particle size of formed polymer was reduced progressively towards the desired size. It is shown that when combined surfactant between anionic and non-ionic has the concentration ratio 3:1. The polymer particles were formed which followed by a significant mean size reduction from as large as 594 nm to as low as 57 nm. Variation in concentration ratio 3:1 during the feeding process caused the formation of polymer progressed in a much slower rate. The latter is believed to be the reason of ultra fine particle size formation in phenol free material under synthesis.

Keywords: copolymer styrene acrylate; polymer emulsion; non-ionic emulsifier; anionic emulsifier; particle size

Introduction

Poly (styrene acrylate) emulsion is commonly used in paper, textile, metal primers, adhesives, paints, magnetic tape industries. Generally, the poly (styrene acrylate) emulsion has found at wider applications [1]. A coating industry is one of the major user of poly

(styrene acrylate). Basically, this application requires a polymer with small particle sizes since interfacial properties of materials are important in the coating process. The coating materials thus must have a large interfacial area which can be obtained from materials with nanoparticles.

Modification of polymerisation process of polystyrene is depend on the application area, particle size value, etc. Polymer nanoparticles could be prepared through preparation techniques and size-control parameters [2]. Polymer nanoparticles has been a subject interest of some researchers to get new properties of polystyrene. Leena S, et.al [3] introduced polystyrene based through cross-linked reaction between polystyrene and ethylene glycol acrylate resin. This new copolymer has function at Polypeptide Syntheses. Various techniques have been introduced to produce nanoparticle polymer [4,5,6]. Solans et al [4] reported on results of an nano emulsion formation by a phase inversion temperature (PIT) method. It was shown that minimum droplet size and complete solubilization of the oil in a micro emulsion bicontinuous phase has resulted ultra fine particles with size in the range 20–200 nm. Much finer particle size ~ 10 nm of polymer was obtained by Horgan following synthesized polystyrene nanoparticles through graft copolymers technique between poly (butyl methacrylate-g-methoxypoly (ethylene glycol)) and poly (methyl methacrylate-g-methoxypoly (ethylene glycol)). Control of the monomer concentration and polymerization temperature during polymerizations reaction was the key to obtain spherical nanosize latex particles with similar size to those of the micelle precursors [5]. In emulsion polymerisation process, all the components of the system have an influence on the nucleation mechanisms and colloidal stability, and therefore on the final particle size distribution (PSD). In this report, we discussed a new synthesis method of Poly (Styrene Acrylate) Emulsion with ultra fine particles and with phenol free [6]. Nanoparticles polymer also was reported by M. Hazarika et al who studied a nanoparticles formation of a new blend system consisting of an amorphous polymer poly benzimidazole (PBI) and an ionomer sodium salt of sulfonated polystyrene (SPS-Na). According to this polymer blending technique is obtained the particle size of polymer ~ 70 nm [7].

Experimental

Emulsion polymer of poly (styrene acrylate) was prepared through emulsion polymerization technique using a two stage process. This process involved 25.00% of

styrene and 20.00% of ethyl acrylate as monomer, 0.20% of ammonium persulphate as catalyst, combination of two type surfactant by composition are 2.25% of sodium lauryl sulphate as anionic surfactant and 0.75% of nonyl phenol with 30 mole ethylene oxide as non-ionic surfactant and 52.05% of distillate water. In the first stage, the emulsion polymerization was conducted through a batch process. The initiation reaction was occurred in which only 10 % of respectively the total number of catalyst and 40% of each monomer used in the whole process involved in this stage. In addition, a half of total surfactant was also added during initiation reaction. In the second stage, the propagation reaction was occurred through a continuous process in which the remain ingredients are 90% of rest catalyst and 60% of rest each monomer then continuously feed to the batch for 5 hours at temperatures 72-75°C. Extra time reaction was given to let reaction between remaining monomer and catalyst ceased. The additional terminating agent was then added to stop the propagation chain. This was conducted by a quenching to stop the reaction completely. The temperature process during the whole reaction was kept at 72-75°C. Agitator speed was kept constant at 30 rpm to avoid foaming. To compare effect of non-ionic surfactant by doing the same process with same composition but nonyl phenol with 30 mole ethylene oxide as non-ionic surfactant is replaced by alkyl polyethylene glycol ether with 28 mole ethylene oxide.

Result and Discussion

Figure 1 is series of particle size distribution of synthesized poly (styrene acrylate) which shows a successive decrease in mean particle size. It was obtained after series of treatment introduced during the polymerization process. When nonyl phenol emulsifier was replaced by alkyl polyethylene glycol ether with 28 mole ethylene oxide, the particles were formed with the mean size value 594 nm. This happened due to alkyl polyethylene glycol ether based has longer molecule chains and larger molecule structure than nonyl phenol based emulsifier. Consequently, the micelle size as home base of polymer explained the particle sizes of final polymer. When the modification process further progressed the particle size of polymer decreased and the final particle size was 57 nm. It was obtained due to the propagation of polymer chains which progressed through two stages. The first step was an initiation reaction contained a few amount of emulsifier but insufficient to form stable micelles. The second stage determined the size of micelles. Because it was conducted through a continuous process in which the propagation of polymer chain and polymer size

formation was occurred step by step with a slower rate. In addition to this, smaller particle size of final polymer also affected by the presence of anionic surfactant.

The batch and the continuous process of the polymerization caused the diffusion of monomers from the emulsified monomer droplets, through the aqueous medium, into the polymer particles for the ensuing polymerization. Adequate solubility of the monomers is therefore essential for the diffusion process to proceed effectively. Consequently, very hydrophobic monomers with extremely low water solubility cannot be readily incorporated by emulsion polymerization. Effective primary anionic emulsifiers for emulsion polymerization must be used in salt form such as ammonium, sodium, amine salt, etc. They have properties as classical particle size control

Alkyl polyethylene glycol ether with 28 mole ethylene oxide as non ionic surfactant was conducted by two stage of polymerization process can influence the viscosity value of emulsion, it was found that higher particle sizes of emulsion has higher viscosity value (7800 mPa.s) compared with that of small particle size (800 mPa.s). It indicates that the particle sizes of emulsion determined ability of fluid to the friction. Indirectly, particle sizes of Poly (styrene acrylate) also determined the rheology properties of emulsion.

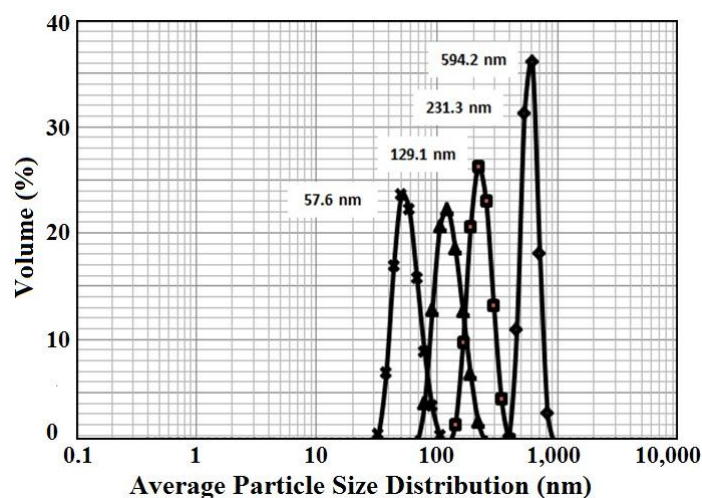


Figure 1. Decreasing Particle Size of Poly (Styrene Acrylate).

According to chemical function groups of polymer which is shown in FTIR spectrum, it was confirmed that the polymer emulsion contains nonyl phenol emulsifier which appear at the wavelengths respectively 1510 cm^{-1} and 1174 cm^{-1} . The polymer emulsion without containing any nonyl phenol based have no such peaks as indicated in figures 2 and 3.

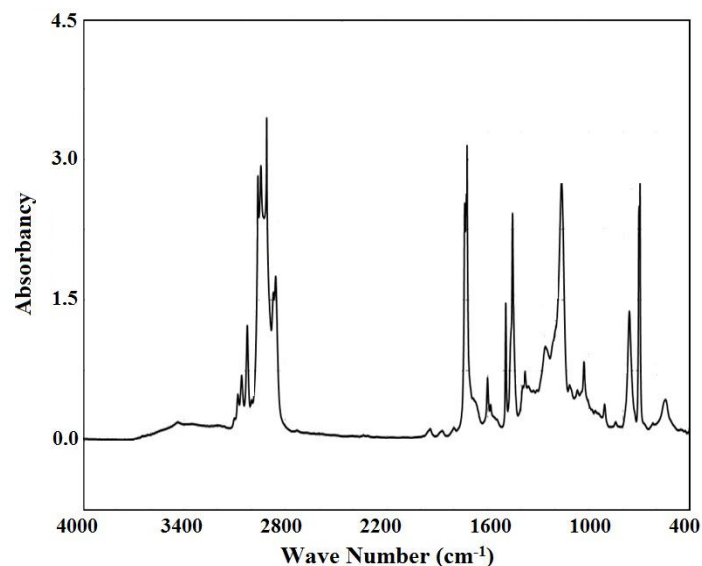


Figure 2. Spectrum FTIR of Poly (Styrene Acrylate) Nonyl Phenol Free.

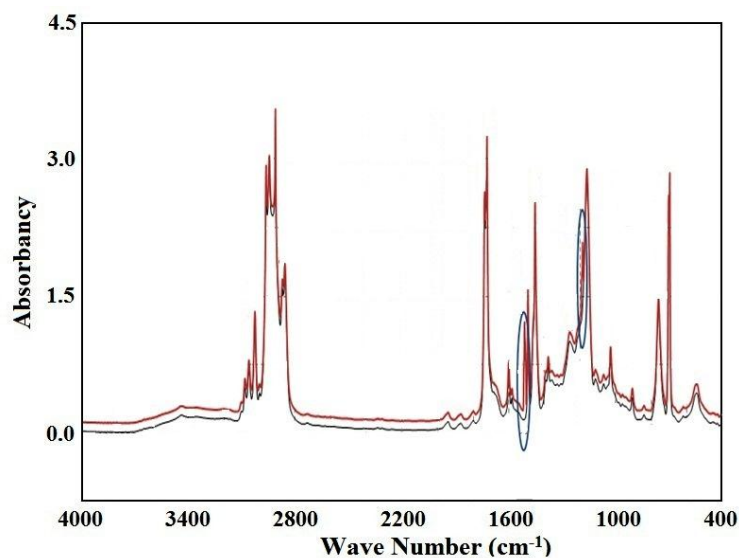


Figure 3. Spectrum FTIR of Poly (styrene acrylate)
■ Nonyl Phenol ■ Nonyl Phenol Free.

Figure 4 is a DSC spectrum which describes temperature properties of polymer obtained through the process. The glass transition, T_g of polymer which is shown in Figure 4 obtained from different polymerization technique and employing different emulsifier types derived the same T_g value. Based on this result it indicated that T_g value for polymer determined by T_g value of each monomer. T_g value theoretical of that polymer was approximately 23°C which was calculated based on T_g value of Styrene monomer and butyl acrylate. Thus, the present of Poly styrene acrylate is confirmed.

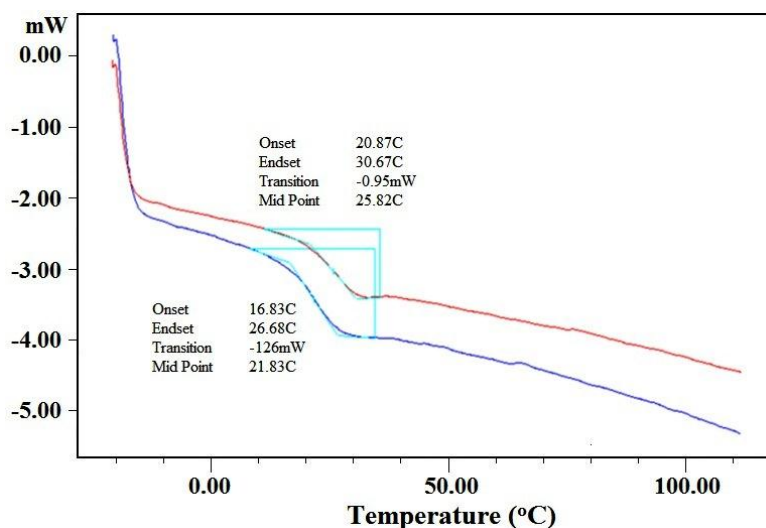


Figure 4. Tg Value of Poly (styrene acrylate)
■ Nonyl Phenol ■ Nonyl Phenol Free.

Conclusion

In order to get environmentally products, nonyl phenol emulsifier can be replaced by Alkyl polyethylene glycol ether based with 28 mole ethylene oxide. Small particle size could be obtained using alkyl polyethylene glycol ether based combined with anionic emulsifier. Nanoparticles of poly styrene acrylate emulsion can be synthesized through two-stage polymerization process.

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