STUDIES ON SEEDED EMULSION POLYMERIZATION OF ACRYLATE MONOMERS USING PMMA LATEX PARTICLES

By

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CERTIFICATE

This is to certify that the thesis entitled **"Studies on Seeded Emulsion Polymerization of Acrylate Monomers using PMMA Latex Particles"** being submitted by **Ms. Sujata Mishra** to the Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by her. Ms. Sujata Mishra has worked under our supervision and has fulfilled the requirements for the submission of this thesis, which to our knowledge has reached the requisite standard.

The results contained in the thesis are original and have not been submitted in part or full, to any other University and Institute for the award of any degree or diploma.

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ABSTRACT

This thesis describes the synthesis and characterization of seeded emulsion polymerization of acrylate monomers using PMMA seed latex. Various copolymer emulsions were prepared by varying BA: MMA ratio ranging from 84:15 to 59:40 in the presence of acrylic acid/ methacrylic acid/ 2-hydroxyethyl acrylate/ or glycidyl methacrylate as functional monomers. Percentage of functional monomer was varied from 2-5% (w/w). Emulsions having methacrylic acid/ or glycidyl methacrylate as functional monomers have been investigated in details because of their excellent storage stability.

In the seeded emulsion polymerization, poly(methyl methacrylate) seed having particle size in the range of 55-60 nm was used for the preparation of copolymer emulsion using BA:MMA:MAA or GMA in varying ratio. Copolymers of BA: MMA: MAA were prepared using surfactants like sodium lauryl sulphate (SLS), alkyl diphenyl oxide disulphonate (Dowfax 2AI)/ and sodium salt of di-octyl sulphosuccinate (OT-50). None of these surfactants gave stable emulsions when used alone whereas it gave stable emulsion when mixture of Dowfax 2AI: OT-50 (in the ratio of 50:50, 40:60 and 60:40) was used as surfactant. Dowfax 2AI: OT-50 mixture [60:40] gave the best combination of properties and hence the effects of other reaction parameters were investigated using their mixture at a concentration of 2.1% (w/w). Similarly the effect of various type of thermal and redox initiators such as ammonium persulphate (APS), potassium persulphate (PPS), combination of tert-butyl hydroperoxide with sodium formaldehyde sulphoxylate (t-BHP/ SFS) or potassium persulphate and sodium metabisulphite (PPS/ SMBS) were also investigated in the

seeded emulsion polymerization of BA/ MMA/ MAA and APS was found to give better results at a concentration of 0.5% (w/w).

The emulsions were characterized for solid content, viscosity, pH, particle size, number of polymer particles, gel content, molecular weight, glass transition temperature and adhesive strength. Spectroscopic characterization was carried out using FTIR, ^{1}H- and ^{13}C-NMR. Morphological characterization of all the emulsions was done using scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The effect of surfactant type [SLS and mixture of (Dowfax 2AI / OT-50)], total surfactant concentration [1.5, 2.1 3.0% (w/w)], initiator concentration [0.21, 0.35, 0.5, 0.64 and 0.85% (w/w)], monomer feeding time[3 h, 4 h and 5 h], temperature [70 °C, 80 °C], chain transfer agent [1- dodecanethiol; 0, 0.1, 0.15, 0.2, 0.25, 0.3 and 0.35% (w/w)] and different ratio of BA: MMA [84:15, 79:20, 74:25, 69:30, 64:35 and 59: 40] on polymerization rate and different properties were investigated. Kinetics study of the polymerization showed that reaction rate increased with increase in initiator concentration and temperature whereas the rate decreased with increase in CTA concentration. Surfactant concentration and monomer feeding time was found to have negligible effect on polymerization rate. But the presence of surfactant in the seed enhances the rate of polymerization. The monomer feed composition had little effect on the polymerization rate. The average number of radicals per particle increased during the conversion which suggests, it follows Smith-Ewart case-III kinetics ($n >> 0.5$) for such emulsion polymerization.

The sol molecular weight (Mw) measured using Gel Permeation Chromatography decreased with increase in temperature and concentration of initiator and CTA. Gel content of the polymer reduced significantly in the presence of CTA. Particle size of

emulsion was measured using dynamic light scattering technique. Lowering in temperature enhances the formation of smaller particles whereas initiator concentration, CTA concentration, monomer composition of BA: MMA had no effect on the particle size of the emulsions.

In order to evaluate the effect of process variables i.e. initiator concentration, monomer concentration (solid content), surfactant concentration, reaction temperature, monomer feeding time and holding time on the emulsion polymerization of PMMA seed latex, experiments were conducted using fractional factorial design. Sixteen experiments were carried out using the low and high levels of each process variables to study the effect of these parameters. From this analysis, surfactant and 2-way interaction effect of initiator and monomer feed time was found to be the important parameters affecting all the properties of emulsions.

In the second-stage, nine stable seeds prepared using the fractional factorial method were used to prepare the copolymers [BA: MMA: MAA = 74: 24: 2]. Effect of seed properties on seeded emulsion polymerization of BA: MMA: MAA was investigated. It was found that surfactant-based seed affects the polymerization rate, particle size and molecular weight of the final latex in comparison to surfactant-free seed latex. Increase in polymerization rate was observed in the sample having a surfactant-based seed. A good agreement of both theoretical and experimental value of final particle size was observed in copolymers having small-size seeds. The glass transition temperature of all the samples was in the same range of –23°C to –27°C as all the reactions were carried to approximately 90 ±1% conversions.

The effect of seed concentration (prepared using surfactant), nature of seed [PMMA/PS/or mixture of PMMA and PS] on final properties of emulsion was also investigated. The polymerization rate, molecular weight increased with increase in

seed concentration. Number average molecular weight (Mn) of samples decreased with increase in seed concentration whereas weight average molecular weight (Mw) increased resulting in broad distribution. Morphological characterization of all emulsions using SEM and TEM showed perfect core-shell morphology.

Emulsions prepared using varying amount of MAA or GMA as functional monomer were evaluated as laminating adhesives. Corona treated PE (20 μm) and polyester (12 μm) were used as substrates and T-peel strength was measured using emulsions having varying amount of functional monomers. Peel strength increased with increasing concentration of chain transfer agent and was found to be dependent on the nature and concentration of functional monomer.

TABLE OF CONTENT