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Statistical design strategies to optimize properties in miniemulsion polymerization of methyl methacrylate

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ABSTRACT

PMMA particles were synthesized by a miniemulsion polymerization method using hexadecane as costabilizer and sodium dodecyl sulfate as surfactant. Full factorial experimental design incorporating the linear regression analysis of the experimental values was used to illustrate the usefulness of this technique in miniemulsion polymerization studies. The effect of initiator concentration, costabilizer concentration, surfactant concentration, sonication time and amplitude, and their interactions on the particle size were identified. Costabilizer and surfactant concentrations influence both particle size individually whereas initiator concentration influences particle size via its interactions with the costabilizer and the surfactant. Sonication parameters influence also greatly the particle size. Two mathematical models were established, and have demonstrated the capability of predicting particle diameter from the synthesis conditions with a precision of 1–2 nm over a range from 75 to 180 nm.

1. Introduction

In recent years an increasing interest is observed in the development of environment-friendly paints and coatings. This trend has been spurred by a growing concern for environmental issues, such as volatile organic solvent emissions and recycling or waste disposal problems [1,2]. This fact has forced the paint industry to develop new alternative formulations [3], such as new water-based paint formulations and high solid systems with low Volatile Organic Compounds (VOCs) [4,5].

Great stability for these latexes should be expected and for this reason the preparation of emulsion via miniemulsion polymerization has been selected. Miniemulsions are classically defined as aqueous dispersions of relatively stable oil droplets within a size range of 50–500 nm prepared by shearing a system containing oil, water, a surfactant, and an osmotic pressure agent [6]. For heterophase polymerization, nucleation of particles comes from three mechanisms: micellar nucleation, homogenous nucleation and droplet nucleation [7]. Miniemulsion is known to be governed by droplet nucleation. To prevent micellar nucleation, the aqueous phase concentration of the surfactant should be below the critical micellar concentration (CMC) after shearing even if, the overall surfactant concentration may be used above or below the CMC [8]. Several types of costabilizer acting as osmotic pressure agent can be selected to suppress degradation by Ostwald ripening [6]. Initiator can be either oil- or water-soluble. In the case of an organo-soluble initiator, it is dissolved in the monomeric phase prior to the miniemulsification stage. Then the reaction starts within the droplets. In the case of a water-soluble initiator, polymerization starts from the continuous aqueous phase, similarly to conventional emulsion polymerization where water-soluble initiators are used usually as they contribute to the charged character of the latex particle [9]. Understanding of the miniemulsion polymerization is required as a mean of reproducibility for the formulation of waterborne paints. Several authors [6,10–17] have already studied different parameters of the miniemulsion such as surfactant, initiator or

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costabilizer amount and type, sonication parameters without studying the link between these factors. The aim of this work was to study the effect of the values of different parameters on particle size that characterizes the polymer obtained by miniemulsion polymerization of methyl methacrylate. A factorial experimental design was used to elucidate the main trends and interactions between variables illustrating the application of these techniques to polymerization studies. Factorial experimental design techniques are extremely useful while using a minimum number of experiments.

A model correlating the experimental conditions and the properties of the polymers by a response surface will be useful to prepare polymer with tailor-made properties.

2. Experimental part

2.1. Chemicals

Methyl methacrylate (MMA purchased from Acros) was freshly distilled under reduced pressure and stored at 4 °C. 2,2'-azobis(2-methylpropionitrile) as initiator (AIBN purchased from Fluka) was recrystallized from ethanol and stored at 4 °C. Hexadecane (HD, from Acros), dodecane (DD, from Aldrich) as costabilizers and sodium dodecyl sulfate (SDS, from Fluka) as surfactant were used as received.

2.2. Synthesis of latex particles

Twenty-five grams of the monomer (0.250 mol), costabilizer and initiator were stirred for 15 min at room temperature and added to a solution of SDS in 81 ml of deionized water previously mixed for 15 min. After stirring for 15 min at room temperature, the miniemulsion was prepared by ultrasonicating the pre-emulsion for different times at fixed amplitude (Sonics Vibracell 750W) at 0 °C in order to prevent the polymerization. Sonication may increase temperature up to 30 °C. Then, the mixture was transferred in a three-neck round bottom flask equipped with a cooler and a gas inlet, bubbled with nitrogen for 20 min, and the temperature was raised to 70 °C within 5 min. Solid content was close to the value of 23.6% wt.

Completion of the reaction was observed after 2 h, as checked by NMR spectrometry by the absence of the ^{1}H NMR peaks assigned to the vinylic protons of the monomer at 5.60 and 6.02 ppm.

2.3. Analysis

The particle sizes (intensity average values) were measured using a Zetananosizer (model S, Malvern Instrument) at a fixed scattering angle of 90°. For sample preparation the original latex was diluted to a 2wt.% solution in deionized water.

The molecular weights of PMMA samples were determined by Size Exclusion Chromatography analysis performed on a Waters 1515 isocratic HPLC pump with a Waters 2414 RI detector and 4 Styragel columns (HR5, HR4, HR3, HR1 from polymer laboratories) in THF with a flow rate of 1 ml/min at 30 °C. The molecular weights were estimated from a calibration curve relative to PMMA standards. For sample preparation, 10 mg of the dried latex was dissolved in 1 ml of THF and filtered through a 0.45 μm Millipore filter.

The average particle size and morphology were determined by Transmission Electron Microscopy (Philips EM 400 electron microscope operating at 200 kV). For sample preparation, the original latex was highly diluted with deionized water until a hardly visible turbidity was reached. Five drops of the diluted sample was placed on a 400 mesh carbon-coated copper grid and left to dry at room temperature. As PMMA usually degrades in the electron beam, particles were protected by a carbon film.

Liquid ^{1}H NMR spectra were recorded with a Bruker Avance 400 using deuterated acetone as solvent.

Percentage solid content (*%SC*) of latex was calculating using expression (Eq. (1)):

$$\%SC = \frac{m}{m_0} \times 100 \quad (1)$$

where m is the weight of the dried latex and m_0 is the initial weight of latex placed in the petri dishes.

2.4. Factorial design of experiments (DOE)

A factorial design of experiments was used in planning experiments that study the effects of five main factors of the miniemulsion polymerization on particle size: (X1) initiator (AIBN) concentration, (X2) costabilizer (hexadecane) concentration, (X3) surfactant (SDS) concentration in a first time, and (X4) sonication time, (X5) sonication amplitude in a second time.

Fixed and design levels for the five factors are given in Table 1.

The five factors have been the object of two factorial designs of experiments for which the domain are represented in Fig. 1. The experiments were run following the design matrix built in Tables 2 and 3.

3. Results and discussion

3.1. General characteristics of miniemulsion polymerization

3.1.1. Spherical particles

Table 4 shows that the particle size of the latex varies over a range of 80–160 nm with a low polydispersity (generally $\sigma < 0.1$). The diameter that is measured in Dynamic Light Scattering (DLS) is called the hydrodynamic diameter and refers to how a particle diffuses within a fluid [18]. The diameter obtained by this technique is that of a sphere that has the same translational diffusion coefficient as the particle being measured (Eq. (2)).

$$d(\mathrm{H}) = \frac{kT}{3\pi\eta D} \quad (2)$$

With d(H) = hydrodynamic diameter (m), k = Boltzmann's constant (J K^{-1}), T = absolute temperature (K), η = viscosity (10^{-6} Pa s), and D = diffusion coefficient (m^2 s^{-1}).

The translational diffusion coefficient will depend not only on the size of the particle "core", but also on any surface