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Progress in Organic Coatings 57 (2006) 195–201

PROGRESS IN ORGANIC COATINGS

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Miniemulsion polymerization of vegetable oil macromonomers

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Received 21 June 2005; accepted 9 August 2006

Abstract

The Thames Research Group developed vegetable oil macromonomer (VOMM) technology to combine the advantages of oil-modified polyesters and waterborne systems, and reduce volatile organic compounds in waterborne coatings. VOMMs offer the advantage of temporary plasticization with the potential for crosslinking after film formation. However, incorporating VOMMs into emulsions is challenging because the highly hydrophobic nature of VOMMs restricts their diffusion through the water phase. Miniemulsion polymerization has been used to incorporate highly hydrophobic monomers in waterborne systems. Diffusion limitations are avoided by polymerizing inside the monomer droplets, and to ensure this, droplet stabilization is required. In our study, a soybean oil-based VOMM was used as a copolymerizable hydrophobe in miniemulsion polymerization. Monomer droplets were stabilized prior to polymerization via catastrophic phase inversion to form stable and small droplets (100 nm). Dynamic light scattering analysis was used to confirm miniemulsion stability. A coagulum-free latex was obtained after polymerization. Surface tension studies and light scattering techniques were used to confirm that monomer droplet nucleation was the dominant mechanism. Gel content studies indicated the formation of a highly branched or crosslinked network upon film application. The miniemulsion technique permitted VOMM incorporation as high as 35 wt% into the polymer backbone.

Keywords: Miniemulsions; Vegetable oil macromonomers; VOCs; Waterborne coatings; Soybean oil; Hydrophobicity

1. Introduction

During the last decade, the coatings industry has invested significantly in research to reduce volatile organic compounds (VOC) in coatings. Various strategies employed in waterborne systems include synthesis of core–shell latexes [1], core–shell latexes with a functionalized core (e.g., oil-modified polyester and urethane) [2], latex blends of hard and soft polymers [3,4], and acrylic hybrid latexes [5,6]. The Thames Research Group (TRG) developed vegetable oil macromonomers (VOMM), i.e., long chain acrylated triglyceride derivatives, for use as comonomers in latexes. VOMMs possess unique characteristics such as acrylate groups, alkyl moieties, and unsaturation. The acrylate group facilitates VOMM incorporation into the polymer backbone, the alkyl moieties provide internal plasticization during film formation, and the residual unsaturation provides oxidative cure after application and exposure to air. However, VOMM incorporation in conventional emulsions is challenging because this technique relies on monomer transport from the monomer droplets to the growing particles, and VOMMs possess extremely low water solubility. While special techniques such as high shear and high surfactant concentrations assist with VOMM incorporation into conventional emulsions, randomly incorporating VOMMs at high levels remains a challenge.

Miniemulsion polymerization has been widely used to polymerize highly hydrophobic monomers [7,8]. Diffusion limitations are avoided by polymerizing inside monomer droplets. To ensure droplet nucleation, small monomer droplets (50–500 nm) are formed and protected from diffusional degradation and droplet coagulation by using a water-insoluble compound and an efficient surfactant package. Water-insoluble compounds employed in miniemulsions include hydrophobic, low molecular weight molecules [9], pigments [10], oligomers, or polymers [11–13], and are referred to as cosurfactants or hydrophobes. The low water solubility of the hydrophobes prevents them from diffusing through the water phase, and keeps all other comonomers inside the droplet, thus minimizing the system's free energy. Since most hydrophobes are not covalently bonded to the polymer, they are prone to leaching from the coating or phase separation, prompting research

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doi:10.1016/j.porgcoat.2006.08.011

efforts directed at developing reactive hydrophobes [14–16]. Yet another shortcoming of miniemulsions is the requirement of energetic homogenization systems such as rotor-stators, sonifiers, or high pressure homogenizers to create small droplets [17].

Determining a system's true behavior for miniemulsion polymerization (droplet nucleation) is a daunting task. Particle nucleation in miniemulsion polymerization is not well understood as yet, and conflicting results have led to different theories [17]. While some authors claim that the final particles are a one-to-one copy of the monomer droplets [18], others believe that only a fraction becomes nucleated [19]. However, it is accepted that droplet size and the amount of free surfactant in the aqueous phase are the most important parameters for ensuring monomer droplet nucleation. The difficulty in determining the extent of droplet nucleation is due to the complexity of monomer droplet characterization [17–20]. Techniques such as freeze-fracture/replica using transmission electron microscopy (TEM) [17], cryo-TEM [5], capillary hydrodynamic fractionation (CHDF) [21], small-angle neutron scattering (SANS) [22], soap titration, and light scattering have been implemented to determine monomer droplet size and distribution. However, there is no direct method to measure monomer droplets, due to factors such as possible coalescence of monomer droplets during characterization, sample dilution during analysis, path of fracture which does not necessarily cross the droplet center, and/or that the raw data has to be fitted to a given model. Additional techniques, such as surface tension, conductivity, turbidity, and surfactant titration were adopted to support evidence of particle identity preservation by maintaining the aqueous phase surfactant concentration below the critical micellar concentration (CMC) so that droplet nucleation is the only mechanism present [20,22,23].

In this study, a soybean acrylated macromonomer (SAM) was used as a copolymerizable hydrophobe for miniemulsion polymerization. Unlike other hydrophobes, the acrylate functionality allows the hydrophobe to covalently bond with the polymer while the allylic unsaturation has the potential to crosslink after film formation. The miniemulsion was prepared via an inverse emulsion technique without high energy homogenizers. Dynamic laser light scattering was chosen to determine droplet size and distribution, and was complemented with surface tension measurements to ensure aqueous phase surfactant concentration below the CMC. Even though dynamic laser light scattering does not assure complete droplet nucleation, it is useful to determine the main nucleation locus.

Table 1
Miniemulsion formulation

Materials	Weight (g)
SAM	16.95
Ammonium bicarbonate	0.42
Rhodapex CO-436	1.30
Water	112.24
Butyl acrylate	16.50
Methyl methacrylate	12.65
Ammonium persulfate	0.83

2. Experimental

2.1. Materials

Butyl acrylate (BA), methyl methacrylate (MMA), acrylic acid (AAc), and ammonium bicarbonate were purchased from Fisher Scientific. The ionic surfactant Rhodapex® CO-436 was purchased from Rhodia, and ammonium persulfate was procured from Acros. All reagents were used as received. SAM (Scheme 1) was synthesized in our laboratory [24]. Deionized water was used for latex preparation.

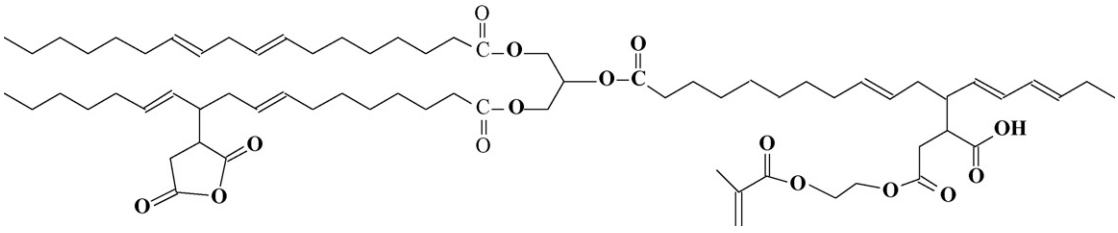
2.2. Miniemulsion preparation

SAM, ammonium bicarbonate, ionic surfactant, and deionized water (3 g) were added to a reaction kettle, and submerged in a 65 °C bath (Table 1). The contents were stirred at 100 rpm for 10 min to form a water-in-oil emulsion. The emulsion was then inverted by adding water (109.86 g) to the kettle. Samples were taken for particle size analysis and 1 month stability tests. The temperature was raised to 80 °C for polymerization. BA and MMA were then added to swell the already formed VOMM droplets in a continuous mode over 20 min, and the system was allowed to equilibrate for another 30 min. A sample was taken for particle size analysis to verify droplet swelling. The miniemulsion was polymerized in a semi-continuous mode by adding ammonium persulfate over a 2 h period.

For comparison, acrylic controls (control 1 (BA/MMA), and control 2 (BA/MMA/AAc)) were synthesized via conventional emulsion polymerization (Table 2). Monomers and initiator were added over a 2 h period.

2.3. Instrumentation

A Microtrac UPA 250 dynamic light scattering analyzer was used to determine size and size distribution of monomer



Scheme 1. Idealized SAM structure.