

## **Novel Water-Borne Coatings via Hybrid Miniemulsion Polymerization**

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As part of a wider effort to develop a new class of water-borne coatings, hybrid miniemulsion polymerization was carried out with acrylic monomers (methyl methacrylate, butyl acrylate and acrylic acid) in the presence of alkyd and oil-modified polyurethane resins. Latexes with different ratios of resin to acrylic monomers were synthesized. The monomer emulsions prepared for hybrid miniemulsion polymerization showed excellent shelf-life stability ( up to 5 months) and the polymerization was run free of coagulation. Solvent extraction indicated that the grafting efficiency of polyacrylics was greater than 20% for all the samples produced.  $^{13}\text{C}$  solution NMR spectrum showed that a substantial fraction of the original carbon double bonds (>60%) in the resin remained after polymerization for film curing. Films obtained from the latexes showed good adhesion and fair hardness properties. Alkyd/acrylate coatings are targeted as a replacement for solvent-based architectural coatings, and oil-modified polyurethane/acrylate coatings may provide a low VOC alternative to solvent-based clear coats.

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## INTRODUCTION

Water-based coatings have become more widely used in the past several decades because they are environmentally friendly, offer easy clean up and, their properties and application performance characteristics have improved. Solvent based systems such as alkyd resins and polyurethanes have remained important for some applications because of superior properties such as gloss and hardness. This is due to curing mechanism of oil-based coatings in which the oils react with atmospheric oxygen to form very hard crosslinked materials. This mechanism is generally lacking in water-based coatings which tend to be soft and pliable, due to the fact that, the coatings are made soft to allow film formation, and, since there is no curing chemistry available, remain soft on drying. This work reports on the graft copolymerization of acrylic monomers in the presence of alkyd and polyurethane resins to develop alternative coatings which have the advantages of water-based systems (low VOC, etc.) with the drying (air cure) properties of solvent-based systems. It has been shown that conventional emulsion polymerization cannot be used to produce these materials; it is necessary to employ a miniemulsion polymerization technique. Alkyd/acrylate coatings are targeted as a replacement for solvent-based architectural coatings, and oil-modified polyurethane (OMPU)/acrylate coatings may provide a low VOC alternative to solvent-based clear coats. Since U.S architectural coating sales in 1995 amounted to 625 million gallons, a conservative estimate of the VOC reduction if all of these coatings were water-based is approximately 500 million pounds of solvent that would not be released into the air.

Emulsion and miniemulsion polymerizations have many similarities, but particle nucleation and monomer transport are very different. Conventional emulsion polymerization is started with a monomer emulsion comprised of relatively large (in the range of 5-10 microns) monomer droplets and significant free or micellar surfactant. Particle nucleation takes place early in the reaction via homogeneous (water phase) polymerization followed by precipitation, or via free radical entry into monomer-swollen micelles. Radicals can enter the monomer droplets, but this phenomenon is generally discounted because of the relatively small droplet surface area. Nucleation stops or slows significantly after the surface area of the particles becomes sufficient to adsorb all of the surfactant from the micelles. The major locus of polymerization thereafter is in the nucleated particles. The monomer must move from the monomer droplets to the reaction sites in the particles by diffusion.

In miniemulsion polymerization, an effective surfactant/hydrophobe system is used to stabilize very small monomer droplets (50–500 nm). In order to break up monomer droplets to such size, high agitation is applied by sonication or homogenization. (1). The hydrophobe (also known as a cosurfactant) is a highly monomer-soluble, highly water-insoluble material added to increase diffusional stability of the emulsion. Usually long-chain alkanes such as hexadecane or long-chain alcohols such as cetyl alcohol are employed as hydrophobes (2,3). Because these hydrophobes cannot diffuse readily through the aqueous phase (due to their extremely low water solubility), removing monomer from a small monomer droplet will cause an increase in the concentration of the hydrophobe, with a resultant increase in the free energy. Therefore, the use of a hydrophobe will significantly retard, or even prevent Ostwald ripening (transfer of monomer from small droplets to large droplets to reduce the total surface energy of the

system), and thus keep the small droplets stable during polymerization. For an ideal miniemulsion polymerization, there is no mass transport involved. The large droplet surface area in miniemulsions (because of small droplet size) results in most of the surfactant being adsorbed to the droplets with little free surfactant available to form micelles or stabilize aqueous phase polymerization. Therefore, the predominant nucleation mechanism in miniemulsion polymerization is droplet nucleation. This is exactly what is desired for the current application, since if there is significant micellar or homogeneous nucleation, particles will be formed which contain little or no resin. The total water-insolubility of the resin makes it difficult for diffusion of the resin from the monomer droplets to the particles that are the loci of polymerization. In contrast, in miniemulsion polymerization, polymerization takes place in the (very small) droplets, in the presence of the resin, and without the need for diffusion of the resin across the aqueous phase. If a conventional emulsion polymerization were run in the presence of the water-insoluble resin, the result would be polyacrylic particles in a physical blend with dispersed resin, with very little chance of grafting between the two species. Miniemulsion polymerization in the presence of an additional resin for the purposes of grafting will be termed *hybrid miniemulsion polymerization*.

Wang et al. (4) have reported the grafting of alkyd resin into water-based acrylic coatings. Dong et al. (5) have reported the incorporation of oil modified polyurethane (OMPU) in a similar system. This paper will serve to compare and contrast these two works, and to draw some conclusions about the future of these hybrid materials.

## **EXPERIMENTAL**

### **Materials**

Alkyd resin was supplied by McWhorter Technologies as Durama 2768 which contains 80% durable medium soya-linseed alkyd and 20% solvents, i.e., 6.3% n-butyl acetate, 4.4% xylene, 2.9% solvent naphtha (petroleum), 5.2% trimethylbenzene, and 0.9% ethylbenzene. The solvents were removed by vacuum distillation before use. Oil-modified polyurethane 138-0634 supplied by McWhorter Technologies was used as the OMPU. This resin contains 60% solid linseed modified polyurethane, 20% solvent naphtha (heavy alkylate), 20% naphtha (hydrotreated heavy), 0.07% dibutyl tin oxide and 0.03% triphenyl phosphite. The polyurethane portion was made from TDI (toluene diisocyanate), and no free TDI was left unreacted. The solvents were removed by vacuum evaporation before use. Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), potassium persulfate (KPS) (all from Aldrich), sodium lauryl sulfate (SLS) (Fisher), and benzoyl peroxide (BPO) (Fisher) were used as supplied. The water is deionized.

### **Emulsion Preparation and Polymerization**

The miniemulsions were prepared by dispersing the desired amount of monomer-resin solution in the aqueous SLS solution by mixing with a stirrer at room temperature. The resulting emulsion was sheared further by sonication. The monomer miniemulsion

was transferred to a flask which was equipped with nitrogen inlet-outlet tube, condenser, and mechanical stirrer. The system was purged with nitrogen heated to 60 or 80 °C. Agitation was provided by a paddle stirrer. The polymerization was started by injection of KPS solution. When BPO was present in the monomer mixture the polymerization started during the heating period. The reaction was followed by determining the change in the fraction of volatiles in the emulsion as the (volatile) monomer is converted to (nonvolatile) polymer.

### **Droplet and Particle Size**

Monomer droplet and particle sizes were measured by quasi-elastic light scattering with a Malvern Autosizer IIc. The measurement process for monomer droplets involved dilution of the emulsion with a monomer-saturated solution of 0.1% SLS to about 50:1. Then this diluted emulsion was put into a quartz cuvette and the droplet diameter, distribution and standard deviations were recorded in five minutes. The latex particle size was measured in the same way but the dilution with the 0.1% SLS solution was 100:1.

### **Shelf-life Stability**

Emulsion and latex shelf-life were measured by placing approximately 30 mL of sample in a capped glass vial and observing the time necessary for a visible creaming line to appear. Two drops of a water-soluble red pigment solution were added to each sample to increase the contrast between phases.

### **Double Bond Content Analysis**

The double bond content in the resin-monomer mixtures and in the graft copolymers were measured by  $^{13}\text{C}$ -NMR. Chloroform was used as an internal standard for all NMR spectra.

### **Degree of Grafting and Degree of Crosslinking**

Solvent extraction experiments were performed in a Soxhlet extractor with approximately 0.5 g dried latex. Ethyl ether was applied for 24 hours. All resin and grafted copolymer were assumed to be dissolved completely. Grafting efficiency was calculated from the quantity of polymer extracted. Chloroform, toluene, tetrahydrofuran (THF) and 1,4-dioxane were used sequentially in an exhaustive extraction to determine the percentage of the polymer which was crosslinked. Each solvent was applied for 12 hours. Material which remained after extraction with the four solvents was considered to be crosslinked.

### **Film Hardness and Adhesion**

Film hardness testing was determined by the Pencil Test (ASTM D 3363–74), and film adhesion was measured by the Tape Test (ASTM D 3359–78). These films were cast from latex with 1-5% hydroxyethyl cellulose added as a thickener. The films were dried at room temperature.



## RESULTS AND DISCUSSION

### Droplet and Particle Size

For both systems (alkyd and OMPU), droplet sizes ranged from 90 to 260 nm. Droplet size was influenced by duration and intensity of shear, level of cosurfactant (PMMA), and level of resin (alkyd or OMPU). Increased length and intensity of shear developed smaller particles, as did the inclusion of polymethyl methacrylate (PMMA) as a cosurfactant. The inclusion of PMMA was not entirely necessary, as both resins act as cosurfactants. Droplet size decreased with increasing level of resin.

Polymerized polymer particles size correlated well with monomer droplet size, implying predominant droplet nucleation. Particle size ranged from 110 to 240 nm.

### Shelf-Life Stability

Shelf life stability varied with resin level. With adequate sonication and 60 to 100% (based on total acrylate) resin, shelf lives ranged from one to greater than five months. Shelf life is determined by two factors. The first is Stokes law creaming; small droplets will cream much more slowly, and droplets of approximately 1 to 200 nm diameters will be prevented by Brownian motion from creaming at all. The second is Ostwald ripening. If significant ripening takes place, droplets will grow into the range where Stokes law creaming is significant, and visible creaming will occur. The long shelf lives exhibited by these materials indicate small initial droplet size and effective retardation of Ostwald ripening, allowing the monomer droplets to remain small enough so that droplet nucleation predominates.

### Polymerization

Figures 1 and 2 show the conversion-time curves for the hybrid miniemulsion polymerization of alkyd and OMPU, respectively. Some features are common to both systems. First, complete conversion is not achieved, even at 80 °C. Second, the rate of polymerization goes down as the level of resin is increased. This suggests that the resin might be retarding the polymerization. Both the alkyd and OMPU contain unsaturated vegetable oils containing linolenic, linoleic and oleic fatty acids. During polymerization, grafting can occur by chain transfer from the propagating free radical to double bonds on the fatty acid portion of the resin (6). The resulting fatty acid radical may be substantially less reactive than the acrylic radical, resulting in a reduction in polymerization rate. This resin inhibition can be overcome to some extent by using a high polymerization temperature (80 °C) and mixed (KPS and BPO) initiator.

### Residual Double Bond Content Analysis

The residual double bond content was determined for both hybrid materials. For the alkyd/acrylate hybrid, the residual double bond content was 70 to 80%. For the OMPU hybrid, the residual double bond content was 60 to 70%. This means that in both materials, between 60 and 80% of the original double bonds in the fatty acid components remained after polymerization. This is critical, since these residual double bond are

necessary to participate in the film "drying" reactions. In these reactions, residual double bonds in the fatty acid components react with atmospheric oxygen to form crosslinks. It is these crosslinks that give alkyd or oil-based coatings their desirable hardness.

### **Degree of Grafting and Degree of Crosslinking**

For both materials, the degree of grafting was determined by selective extraction. Degree of grafting is defined as the percent of the polyacrylate which is grafted to alkyd or OMPU. For the alkyd/acrylate hybrid, the degree of grafting ranged from 20 to 70%, with materials containing higher levels of alkyd having higher levels of grafting. For the OMPU/acrylate hybrid, the degree of grafting ranged from 30 to 60%, again with materials containing higher levels of resin having a higher levels of grafting. In all cases, the level of grafting was significant. This is important, since the acrylate and resin may be incompatible. Significant levels of grafting will prevent phase separation into acrylate-rich and resin-rich phases.

Degree of crosslinking is defined as the percentage of total polymer which is insoluble after exhaustive extraction. For both the alkyd/acrylate and OMPU/acrylate hybrid materials, degree of crosslinking was below 5%. This is significant, since a high level of crosslinking during polymerization will result in poor film formation, and poor film properties.

### **Film Hardness and Adhesion**

The alkyd/acrylate materials, when cast into films, were found to be of approximately "B" hardness. Addition of standard metal drying catalysts ("dryers") increased film hardness to "H" or even "2H". The OMPU/acrylate materials also had a "B" hardness. Addition of dryers increased film hardness to "HB." These hardnesses are not particularly high, but represent a starting point for developing the higher hardnesses desired for commercial coatings. Film hardness may be increased by changing the fatty acid component of the resin, adding different levels and types of dryers, and by increasing the glass transition temperature of the acrylate component. Adhesion was good (4-5 on a 1-5 scale) for all materials.

## **CONCLUSIONS**

The hybrid miniemulsion polymerization process has been shown to have a promising role in converting solvent-based coatings into environmentally-friendly water-based coatings. Alkyd/acrylate coatings are targeted as a replacement for solvent-based architectural coatings, and OMPU/acrylate coatings may provide a low VOC alternative to solvent-based clear coats. A wide range of coatings resins might be used in this way, providing they are highly water-insoluble and highly monomer-soluble in order to act as good hydrophobes. There are a number of advantages associated with hybrid miniemulsion polymerization. First, it is a very stable process without coagulation and flocculation. Second, the robust droplet nucleation makes it easier to control the particle number and particle size during the production process. It also enhances the likelihood that the composition of each particle is the same as formulated. Due to the extremely low

water solubility of the resin, and its resultant extremely retarded transport across the aqueous phase, hybrid miniemulsion polymerization provides a means of incorporating resins which could not be incorporated by conventional emulsion polymerization. Finally, by employing resin as both reactant and hydrophobe, higher purity of product can be achieved, since no additional hydrophobe is required.

Films obtained from the acrylic/OMPU latexes show good adhesion and fair hardness. Mixed metal drying agents can enhance the drying rate substantially. Problems remaining to be solved include increasing rate of polymerization and reducing residual monomer content in spite of the inhibitory nature of the alkyd or OMPU resin, and increasing film hardness.

### **ACKNOWLEDGEMENT**

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**Table 1**  
**Recipe for Hybrid Miniemulsion Polymerizations Containing Alkyd**

<b>Run</b>	<b>MMA<sup>1</sup></b>	<b>BA<sup>1</sup></b>	<b>AA<sup>1</sup></b>	<b>Alkyd<sup>2</sup></b>
MA00	45	50	1.0	0.0
MA30	45	50	1.0	30
MA60	45	50	1.0	60
MA100	45	50	1.0	100

SLS: 0.02 mol/L water. KPS: 0.04 mol/L water. Total solids: 29 wt%. BPO: 0.5 wt% based on total acrylate.

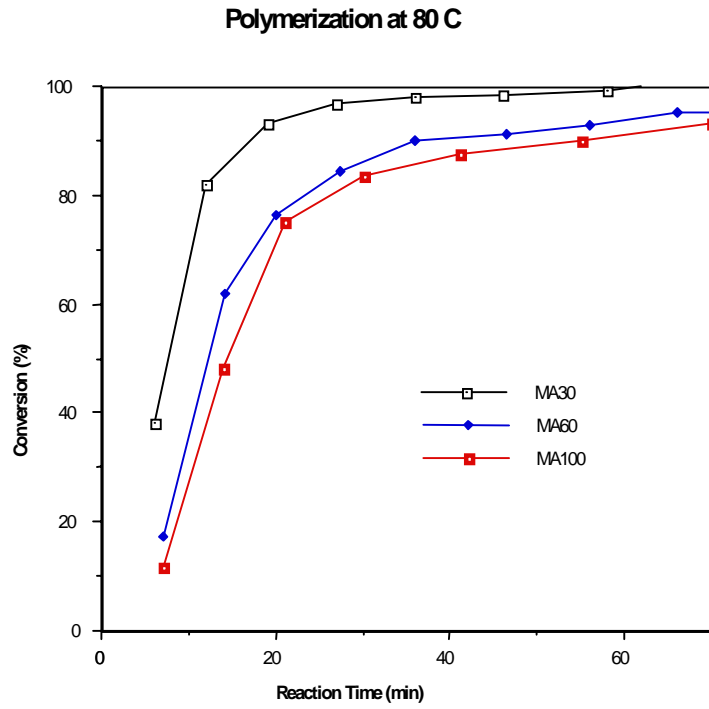
1. %wt of total acrylate, including 4 wt% polymethyl methacrylate (PMMA) used as a cosurfactant.
2. %wt based on total acrylate.

**Table 2**  
**Recipe for Hybrid Miniemulsion Polymerizations Containing Oil Modified Polyurethane**

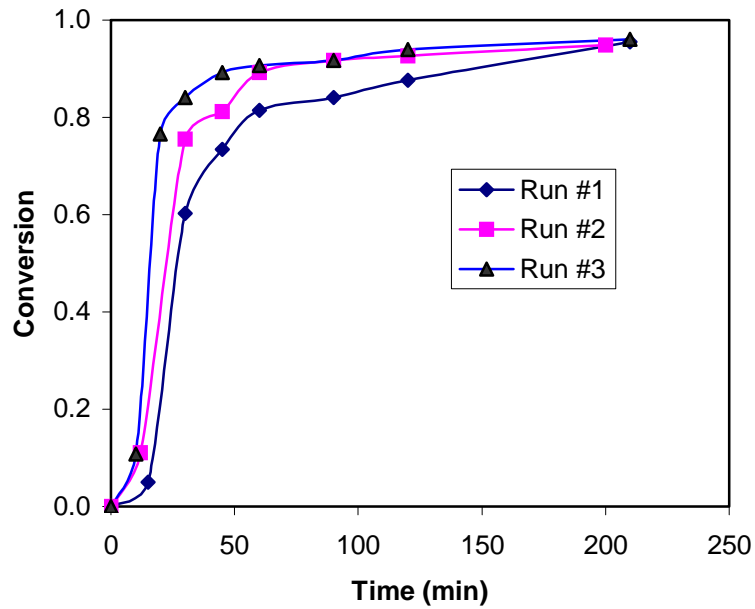
<b>Run</b>	<b>MMA<sup>1</sup></b>	<b>BA<sup>1</sup></b>	<b>AA<sup>1</sup></b>	<b>OMPU<sup>2</sup></b>
1	49	50	1.0	100
2	49	50	1.0	60
3	49	50	1.0	30

SLS: 0.02 mol/L water. KPS: 0.04 mol/L water. Total solids: 33.3 wt%. BPO: 0.5 wt% based on total acrylate.

1. %wt of total acrylate.
2. %wt based on total acrylate.



**Figure 1**  
**Conversion-Time Profiles for**  
**Alkyd/Acrylate Hybrid Miniemulsion Polymerization at 80 °C**



**Figure 2**  
**Conversion-Time Profiles for**  
**OMPU/Acrylate Hybrid Miniemulsion Polymerization at 80 °C**

