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CONTINUOUS PROCESS FOR THE PRODUCTION OF VINYL ACETATE-ETHYLENE EMULSION COPOLYMERS

Francis P. Petrocelli* and Cajetan F. Cordeiro
Air Products Polymers, L. P.
7201 Hamilton Blvd.
Allentown, PA 18195, USA

SUMMARY: A lab-scale experimental program was conducted to determine the feasibility of producing vinyl acetate-ethylene (VAE) emulsion copolymers via a continuous reaction process, using poly(vinyl alcohol), or PVOH, as a protective colloid. A process configuration of multiple stirred-tanks in series was utilized. Comparisons were made between continuous and batch processes with regard to final-product properties. As expected, notable differences in the breadths of the particle-size distributions obtained via the two processes were observed. However, these differences did not appreciably alter product performance in tile-mortar applications (as measured by plywood-to-quarry-tile adhesive strengths). Additionally, for the continuous process, in-process and final-product samples were compared to determine how polymer properties varied with conversion.

Introduction

This report summarizes research done in support of evaluating the feasibility of producing vinyl acetate-ethylene copolymer (VAE) emulsions via a continuous process, using poly(vinyl alcohol), or PVOH, as a protective colloid.

Production of emulsion polymers via continuous processes is well-established, as such processes have been used for many years at the commercial scale to produce high-volume elastomers, such as styrene-butadiene rubber (SBR), acrylonitrile-butadiene rubber (ABR), and neoprene [1]. Continuous reaction at elevated pressure to produce VAE emulsion copolymers is known, having been patented by Air Products and others [2,3,4].

We were motivated to revisit the concept of a continuous VAE process in the present work for two reasons:

1. the potential for increasing the productivity of existing batch (or semi-batch) reactor systems.
2. the potential to exploit the inherent differences between batch (or semi-batch) and continuous processes to produce differentiated products having better performance in tile-mortar and adhesive applications.

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As the maximum reaction rate for a given emulsion reactor is typically limited by available heat removal, the total reaction time would be the same for either a batch or a continuous process, if both were run at maximum heat-removal rate throughout. However, the productivity increase mentioned in the first point above results from a significant decrease in the amount of "non-reaction" time (i.e., filling and emptying the reactor vessel) for a continuous process. Of course, this productivity enhancement (see Table 1) comes at the expense of process flexibility, as only a relatively few number of different products can be produced in a continuous reactor system; otherwise, the amount of transitional material generated during product changes becomes prohibitively large.

Table 1: Productivity enhancement resulting from converting two stirred-tank batch reactors into one continuous reactor train

Configuration	**kg/m^3-yr**
Two stirred-tank reactors:	
Two parallel batch processes	7.14×10^5
One continuous process (72 % conversion in first reactor)	1.02×10^6
One continuous process (50 % conversion in first reactor)	1.48×10^6

The second point mentioned above is a recognition from earlier work [2] that, because batch and continuous processes would not produce equivalent polymer properties (i.e., particle-size distribution, molecular-weight distribution, etc.), trying to replicate an existing batch product using a continuous process would be difficult, if not impossible.

Experimental Procedures

A schematic diagram of the lab-scale continuous reactor system used in this study is shown in Figure 1:

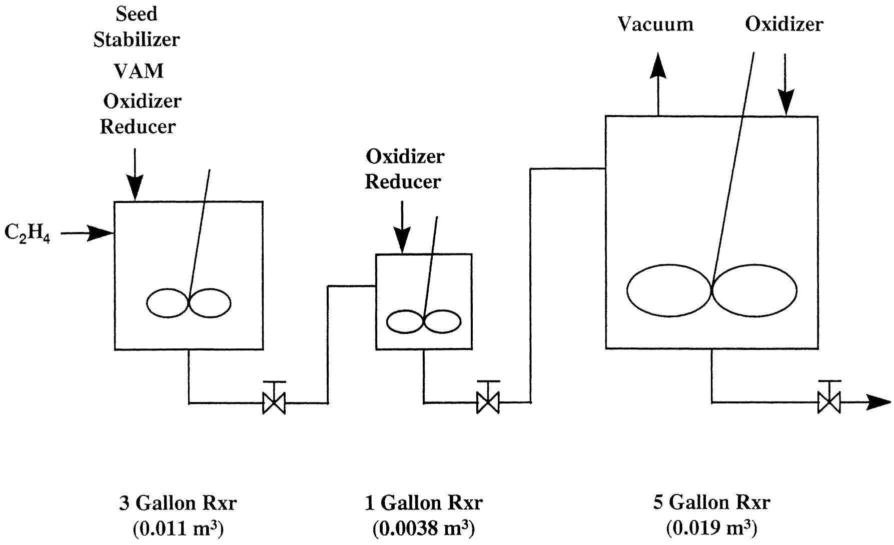

Figure 1: Schematic Diagram of Lab-Scale Continuous Reactor System

A lab-scale reactor train consisting of two stirred-tank pressure vessels (internal volumes of 3.0 and 1.0 gal, or 0.011 and 0.0038 m^3) was used. The two pressure vessels were connected in series; either could be used as the first reactor, but typically the larger reactor was first. Each reactor was equipped with standard 4-blade, 45°-angle, pitched-blade turbine impellers (impeller/vessel diameter ratio of about 0.6). The 0.011 m^3 reactor had three impellers, at vessel levels of 2000, 4500, and 6400 ml; the 0.0038 m^3 reactor had two impellers, at vessel levels of 850 and 1900 ml. Following the two pressure vessels was a "degasser", where vacuum was pulled to remove residual ethylene (internal volume of 5.0 gal, or 0.019 m^3).

Typical reaction temperatures were 50-60 °C in the pressure vessels, and 40 °C in the degasser. Typical residence times were 170-200 min in the 0.011 m^3 reactor, and 50-70 min in the 0.0038 m^3 reactor. Total feed rates were on the order of 40 g/min. Note that the 0.019 m^3 degasser was not run in a continuous mode; rather, product was continuously collected and vacuum continuously drawn in this vessel, but the product was removed only at specified intervals (usually once every 90 min).

During the continuous runs, control of the unreacted monomer concentrations in the 3-gal and 1-gal reactors was achieved through adjusting the respective oxidizer and reducer flowrates (along with an iron catalyst, these components were collectively referred to as the "redox" system). Oxidizers fed to the 3-gal and 1-gal pressure reactors included hydrogen peroxide, t-butyl hydroperoxide (tBHP), and potassium persulfate; the reducer was sodium formaldehyde sulfoxylate. t-Butyl hydroperoxide was the only oxidizer used for "finishing" the reaction in the degasser.

As no condensed material was typically observed in a dry-ice cold trap in the vacuum vent line exiting the degasser, we concluded that the tBHP being fed to the degasser was effective in catalytically finishing the continuous product, and, as a result, the amount of residual vinyl acetate monomer (VAM) being degassed was not significant. To test this, the degasser was operated at atmospheric pressure (i.e., no vacuum) during one experiment; as expected, residual VAM in the final product was unchanged, confirming our conclusion. (At typical degasser conditions, the partial pressure of VAM would be about 0.2 psia.)

In all runs, a steady ethylene (C_2H_4) uptake was observed, indicating that incorporation of ethylene into the latex product was occurring at a regular rate. Introduction of ethylene through sub-surface, as opposed to surface, feed lines and higher agitator rotation speeds (RPM's) both increased the rate of ethylene uptake.

We relied on the pressure differential created by the consumption of ethylene to provide the driving force for transfer between the reactor vessels in the continuous-reactor train. Ethylene content of the polymer (and, thus, the glass-transition temperature, or T_g, of the polymer) was controlled by varying the C_2H_4 pressure in the first reactor (the pressure range in the first reactor was 300-850 psig, or 21.7-59.6 bar, in this study).

The runs were all conducted in an "intermittent continuous" mode (i.e., we would run continuously for 6-8 hrs per day; stop feeds and transfer between vessels, and cool reactors to ambient temperature overnight; heat up and re-initiate reactor contents on a subsequent day). A single “round-the-clock” run was conducted for 96 consecutive hours which demonstrated that the latex properties were equivalent for both the “intermittent continuous” and the “round-the-clock” operating modes.

Two product types (designated A and B) were included in this study. Product chemistry is summarized in Table 2. Relevant comparisons were made to commercial VAE products manufactured by Air Products via a “batch” process (i.e., no delay feed of vinyl acetate monomer, but delay feeds of redox components and ethylene).

Table 2: Composition of continuous products

Copolymer composition (wt % seed / vinyl acetate / ethylene)	**PVOH grade(s)**	**Catalyst type**
A-type product:		
3 / 73-82 / 12-24	low- and medium-MW, partially hydrolyzed	redox
B-type product:		
3 / 68-91 / 6-29	low-MW, partially hydrolyzed	redox

An external seed was used to enhance process stability. Previous studies employing stirred-tank continuous emulsion reactors had pointed to the need to use a seed to avoid process cycling, due to temporal changes in the concentration of free stabilizer in the reactor [1,2]. Due to the desire to have a seed with a small particle size, relative to the final product, the seed used in this work was a surfactant-stabilized commercial VAE product (manufactured by Air Products), with the properties shown in Table 3 (particle-size measurement via capillary hydrodynamic fractionation, or CHDF).

Table 3: Properties of external seed polymer used in the continuous experiments

Seed composition (wt % vinyl acetate / ethylene)	**Surfactant / polymer wt ratio**	**D_w (nm)**	**D_n (nm)**
87 / 13	0.05	229	162

Results and Discussion

In Table 4, stabilizer requirements for the continuous runs are compared to those for the analogous commercial batch products; the resulting weight- and number-average particle sizes (measured via disc centrifuge) are also summarized.

Table 4: Seed and stabilizer levels used in the continuous experiments vs. commercial batch processes

Process	**Seed / polymer wt ratio**	**Stabilizer / polymer wt ratio**	**D_w (nm)**	**D_n (nm)**
A-type product:				
batch √	0	0.055	767	514
continuous	0.034	0.037	946	316
continuous √	0.034	0.043-0.048	912	309
B-type product:				
batch √	0	0.058	1349	1020
continuous √	0.030	0.056-0.066	767	234

NOTE: √ indicates a stable process; otherwise, exhibited high grit and/or accelerated sedimentation values

Working with basic translations of the comparable batch recipes, and using an external seed to replace roughly 3 wt % of the monomer content, relatively few process stability issues were encountered with the continuous products. Baseline experiments generated very stable emulsions with low grit (i.e., coagulum) and accelerated-sedimentation rates. The stabilizer levels necessary for achieving process/product stability in the continuous experiments were comparable to those used in the batch-product recipes.

In general, the continuous process produced a much broader particle-size distribution (PSD) than did the comparable batch process, likely due to the broader residence-time distribution that would be obtained from a stirred-tanks-in-series continuous-reactor train vs. a single batch reactor. The broader PSD resulted in a much lower final-product emulsion viscosity at comparable solids, as indicated in Table 5.

Table 5: Relationship between breadth of particle-size distribution and viscosity of final product

Process	**D_w/D_n**	**Solids (wt %)**	**Viscosity (cps)**
A-type product:			
batch	1.49	53.5	2000
continuous	2.95	53.5	480
B-type product:			
batch	1.32	51.2	870
continuous	3.28	53.3	240

As shown in Table 6, the number of external seed particles fed to the first reactor only represented about 10 % of the total number of particles formed, and the net number of new particles formed in each of the two pressure vessels (i.e., Reactor 1 and Reactor 2) was roughly equivalent. Thus, development of the ultimate PSD was not dominated by simple growth of seed particles. Subsequent work with comparable batch systems has shown that the primary particles that are nucleated are no more than 200 nm in diameter, and that agglomeration is an important mechanism for particle growth.

Table 6: Rate of particle entry and exit for each reactor vessel during a continuous experiment

Vessel	Particles / min entering	Particles / min exiting	Δ particles / min
Reactor 1	3.1E+14 (seed)	1.6E+15	+1.3E+15
Reactor 2	1.6E+15	3.1E+15	+1.5E+15
Degasser	3.1E+15	3.4E+15	+3.2E+14

As shown in Figure 2, ethylene content of the polymer (as measured by the C_2H_4/VAM feed ratio) was readily controlled by varying the C_2H_4 pressure in the first reactor.

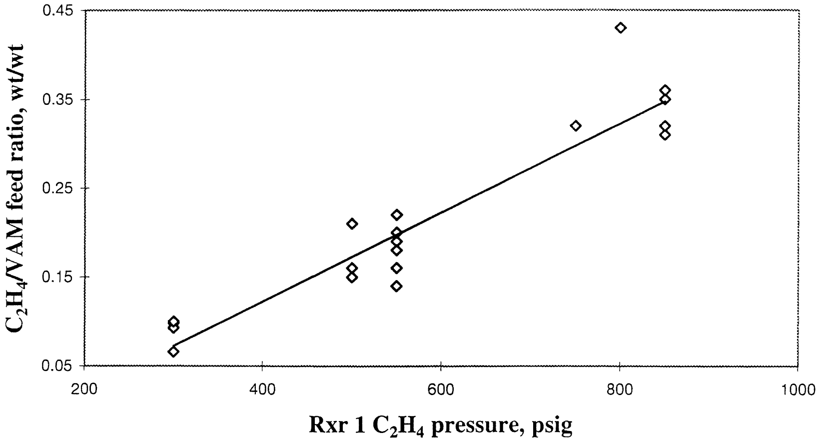

Figure 2: Relationship between pressure in first reactor and ethylene / vinyl acetate feed ratio

In turn, varying the C_2H_4/VAM feed ratio allowed us to produce continuous products over a range of final-product T_g's. As shown in Figure 3, both the batch and continuous products exhibited the expected decrease in polymer T_g as C_2H_4/VAM feed ratio was increased; the data indicated no significant differences between the batch and continuous processes. Also in Figure 3, the measured T_g's for the continuous samples are compared to T_g's calculated from the C_2H_4/VAM feed ratios. Although agreement is good, the measured T_g at a given C_2H_4/VAM feed ratio is generally slightly higher than the corresponding theoretical prediction; this suggests a small loss of unreacted C_2H_4 from the process (estimated at 3-7 %).

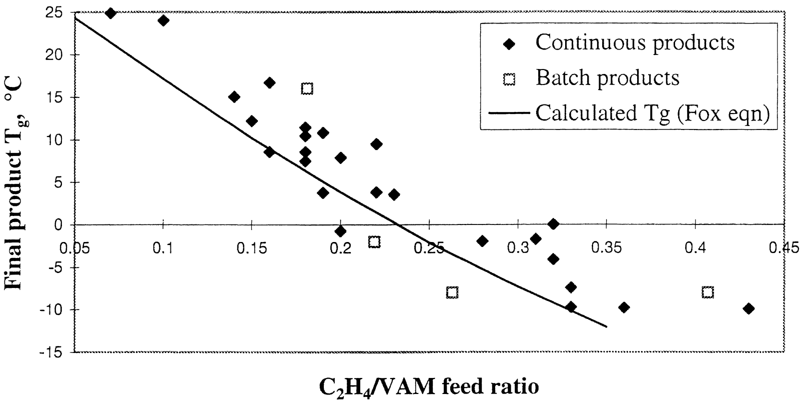

Figure 3: Influence of ethylene / vinyl acetate feed ratio on glass-transition temperature of final product; ◆ = products from continuous experiments, ☐ = products from batch experiments

A comparison of in-process T_g vs. final-product T_g for the continuous experiments (see Figure 4) showed no significant bias, indicating that, at any point in time, the T_g's of the polymer exiting the first (i.e., 3-gal), second (i.e., 1-gal), and final (i.e., degasser) reactor vessels were all the same. Thus, the T_g of the final product was essentially set by the conditions in the first reactor.

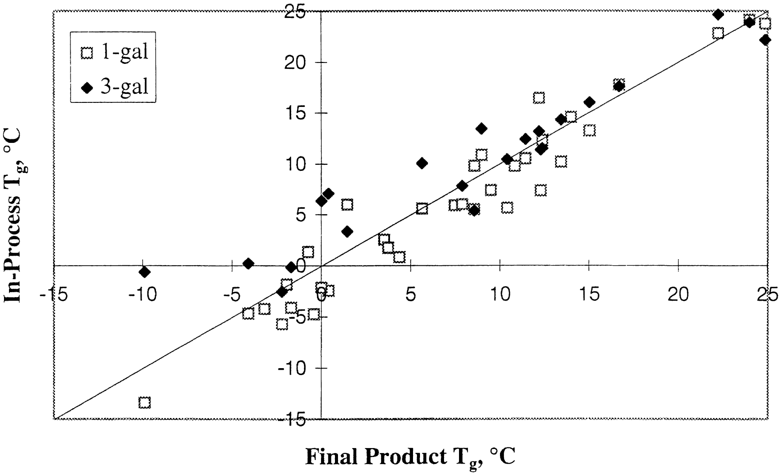

Figure 4: Relationship between final-product and in-process glass-transition temperatures; ◆ = glass-transition temperature for samples taken from the 3-gallon (first) reactor, □ = glass-transition temperature for samples taken from the 1-gallon (second) reactor

When toluene-insoluble percentages (a measure of polymer gel content) were obtained from samples taken simultaneously from the 3-gal, 1-gal, and degasser vessels, the 3-gal values were seen to be consistently lower (see Figure 5). If the toluene-insoluble fraction is considered as a surrogate measure of polymer molecular weight, one would expect the 3-gal values to be higher, not lower, than their 1-gal and final-product counterparts. This expectation is based on the monomer concentration being highest in the 3-gal reactor; thus, the relative rates of chain propagation vs. chain termination (and, thus, polymer chain length and molecular weight) should be highest here as well.

However, we also know that the degree of branching affects the toluene-insoluble percentage, with a more-linear chain yielding a lower insolubles value than a more-branched chain of equivalent molecular weight. If one accepts that the conditions in the 3-gal reactor were more conducive to formation of linear polymer, then one can explain the data in Figure 5 as a measure of chain linearity, and not chain length. If the 3-gal reactor conditions of high monomer and low catalyst concentrations did lead to a high propagation rate, a low radical flux, and a low propensity for polymer "backbiting" reactions, then conditions in this vessel were indeed conducive to the formation of more-linear chains (and, hence, a lower toluene-insoluble percentage).

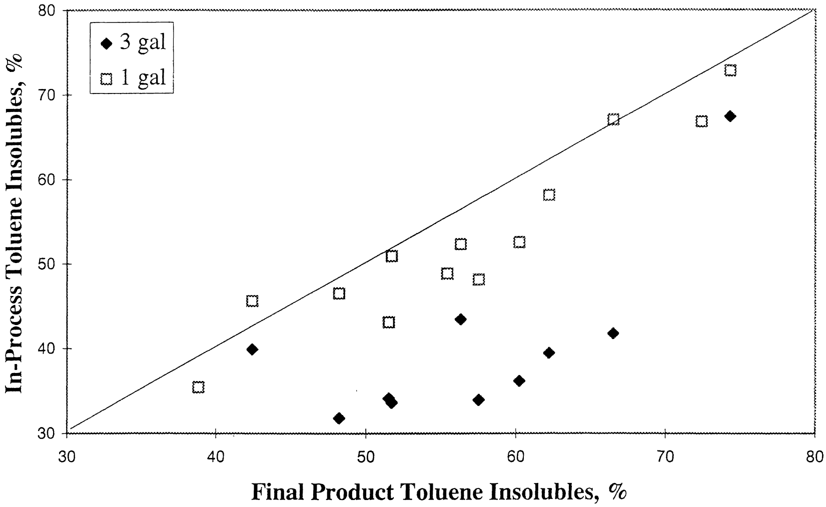

Figure 5: Relationship between final-product and in-process toluene-insoluble percentages; ◆ = toluene-insoluble percentage for samples taken from the 3-gallon (first) reactor, □ = toluene-insoluble percentage for samples taken from the 1-gallon (second) reactor

A comparison of latex performance between products produced from the continuous and batch processes was considered for tile-mortar applications, involving a substrate-substrate combination of plywood to quarry tiles. All test specimens were subjected to constant temperature and humidity (CTH) for seven days prior to testing.

In Figure 6, wood-to-quarry-tile shear strengths of formulated mixtures containing the latexes are shown for the continuous samples, as well as the batch-product controls, as a function of polymer T_g. From these data, we concluded that the performance of the continuous samples was at least equivalent to that of the batch products, with the B-type continuous samples potentially having a modest performance advantage over the A-type continuous samples at moderate T_g's (+5 to +15 °C).

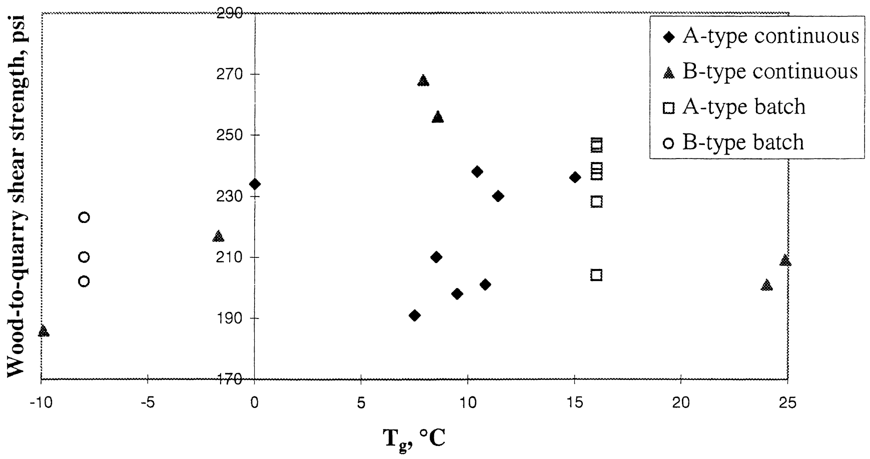

Figure 6: Comparison of application performance (wood-to-quarry-tile shear strengths) between continuous and batch products; ◆ = shear strength (psi) for A-type continuous products, □ = shear strength (psi) for A-type batch products, ▲ = shear strength (psi) for B-type continuous products, o = shear strength (psi) for B-type batch products

References

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