Reduction of Energy Requirement in Latex Concentration by Ultrafiltration

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This paper discusses the industrial application of ultrafiltration technology for removing water from both the in-process and waste latex streams. Due to the high level of permeate flux attainable with stable latices, the ultrafiltration process for latex concentration is becoming economical and practical on the commercial production scale. Recent product and process developments for latex ultrafiltration are presented, with particular reference to using tubular ultrafiltration membranes. Several technical parameters of interest such as flux characteristics, concentration polarization, latex stability, and membrane cleaning are discussed. Performance data with PVC and SBR latices collected in laboratory and pilot plant studies are presented. Finally, a comparison of operating energy costs among ultrafiltration and evaporative methods for PVC latex dewatering are tabulated. It is shown that the energy cost for the ultrafiltration process is only a fraction of that for the more energy-intensive thermal evaporation processes.

Introduction

The concentration of latex emulsions via ultrafiltration has long been recognized as a possible separation process by the workers in the field. There are two major industrial applications for this process. The first is the concentration of dilute latex from 0.5% to 25% solids or more. It has long been recognized as a possible separation process by the workers in the field. There are two major industrial applications for this process. The first is the concentration of dilute latex from 0.5% to 25% solids or more. It is generally used as a pollution control measure for direct sewage discharge, but frequently for waste latex recovery for reformulation. The principal latices in this category are styrene butadiene rubber (SBR) and poly(vinyl acetate) (PVAc). The second major application is the concentration of in-process latex streams from 30% to above 50%, replacing the evaporator by the ultrafilter. Poly(vinyl chloride) (PVC) is the most important latex in this category.

Under ideal conditions, latex particles in the range of 0.05 to 0.5 µm would be completely rejected by the ultrafiltration membrane, and high permeate fluxes would be obtained. However, efforts to commercialize ultrafiltration systems for industrial latex streams were, to a large extent, frustrated in the early years of ultrafiltration technology. Two major difficulties encountered in this endeavor were latex instability and membrane life.

Latex emulsions must be stable for acceptable flux performance. However, the shear induced by the pumping action required in an ultrafiltration system may deleteriously affect an otherwise stable latex emulsion. The high solids concentration found in the gel layer on the membrane surface due to concentration polarization may also be detrimental to latex stability. When latex emulsions become unstable, coagulation of latex particles takes place and a compact foulant layer is formed on the membrane surface. Consequently, flux will fall off appreciably as the foulant layer offers the limiting hydraulic resistance to permeation. In the severe cases of latex instability and membrane fouling, an entire flow passage in the membrane system may be plugged by the coagulated latex.

Thus, it was necessary to be able to clean and reuse a fouled membrane. The tenacious fouling layer, once formed on the membrane surface, was not easily amenable to ordinary cleaning techniques; however, the early generation ultrafiltration membranes (cellulose acetate type) could not tolerate the harsh chemical environment necessary for effective membrane cleaning. Consequently, no significant progress was made in the commercialization of the ultrafiltration process for industrial latex streams until the emergence of improved ultrafiltration membranes.

Over the past few years, significant product and process developments in latex ultrafiltration have been made to overcome these two difficulties. A chemically inert polymeric (non-cellulose acetate) membrane (designated HFM membrane by Abcor, Inc., Wilmington, MA) was developed. Furthermore, a solvent cleaning technique was devises so that fouled membranes can be effectively cleaned and reused. In this paper, the performance data of HFM membranes with several industrial latex streams are presented. Several technical parameters of interest, such as flux characteristics, latex stability, and membrane cleaning are then discussed. Finally, the operating energy cost of applying ultrafiltration in PVC latex dewatering is estimated and compared to the costs of using the conventional thermal evaporative methods.

Latex Ultrafiltration Performance

In this section, some of the technical parameters of interest in latex ultrafiltration are examined. Some inter-
estimating phenomena, perhaps worthy of further investigation, are found in the flux characteristics and are briefly discussed.

**Flux vs. Pressure.** Although ultrafiltration is a pressure-driven membrane separation process, pressure generally has a surprisingly small effect on the flux characteristics after concentration polarization effects become dominant. Figure 1 shows flux–pressure curves of a 42% solids PVC latex at two different flow rates. The common unit of flux used in the membrane industry is either lmh (L/m² h) or gfd (gal/ft² day) and both units are used in this paper. The flux data presented are obtained from Abcor’s tubular membranes piped in series where each membrane tube measures 2.54 cm in diameter and approximately 3 m in length for an active membrane area of about 0.2 m². It is immediately apparent that the permeate flux does not increase proportionally with the applied transmembrane pressure at constant operating conditions (flow rate, temperature, feed concentration, etc.). When the applied pressure exceeds 70 kPa or so, the flux gradually levels off and reaches a plateau value. This phenomenon is well known to be caused by concentration polarization; that is, concentration at the membrane surface exceeds the bulk or feed concentration. However, the value of this limiting flux level is dependent on the operating flow rate, as shown in Figure 1. There are basically two postulates to explain the limiting flux associated with concentration polarization. The popular explanation (e.g., Porter, 1972) is the assumption of the formation of a “gel layer” on the membrane surface which offers the controlling hydraulic resistance to permeation. The thickness of the “gel layer” and thus the hydraulic resistance decreases with increasing flow rate past the membrane, and vice versa. However, more recent studies on macromolecular solutions such as bovine serum albumin (e.g., Kozinski and Lightfoot, 1972; Vilker et al., 1981) suggest that an increase in the applied pressure only causes a higher osmotic pressure associated with a more concentrated layer at the membrane surface so that the effective driving pressure across the membrane is not increased. The mechanism of concentration polarization in ultrafiltration is thus essentially the same as the one for reverse osmosis of salt solutions where the osmotic pressure is known to be a significant consideration.

For stable latex streams, it is customary to visualize a “gel layer” formed by discrete particles where spherical PVC particles are a prime example. Shown in Figure 2 is a scanning electron micrograph (5000× magnification) to illustrate the deposition of PVC particles on the membrane surface. The concentration of this gel layer is usually obtained by extrapolating the semilogarithmic plot of flux vs. bulk concentration to zero flux. Based on the data of laboratory testing and field piloting at industrial manufacturers, the “gelling” concentrations of commercial PVC latices so obtained lie in the range of 0.61 to 0.69 weight fraction, or approximately 0.53 to 0.62 volume fraction.

The process flux is then envisioned to be controlled by the mass transfer characteristics associated with the concentration boundary layer formed between the “gelling” concentration at the membrane surface and the bulk concentration in the turbulent core of the flow. However, Wales (1980) has recently suggested that the flux in latex ultrafiltration may also be controlled by an “osmotic” pressure or “disjoining” pressure which is developed from the potential barrier opposing particle approach. The “disjoining” pressure of one electrostatically stabilized latex has been measured by Barclay et al. (1972) to be more than 410 kPa, which is typical of transmembrane pressures in ultrafiltration. It should be noted that the curves in Figure 1 were artificially originated from the point of zero flux at zero pressure. If the “disjoining” or “osmotic” pressure is indeed significant, the permeate flux would remain zero until the applied pressure exceeded the “osmotic” pressure corresponding to the bulk or feed latex concentration. The flux–pressure excursion curves will then be similar to Figure 4 in the work of Wales (1980).

**Flux vs. Flow.** Figure 3 shows the flux vs. flow plots for a typical PVC latex and a polybutadiene latex obtained in laboratory test runs with the tubular membranes. Both latices are stable in-process streams where ultrafiltration is expected to concentrate the feed from 20–30% to 50–55% solids before further drying. Besides the fact that high levels of permeate flux are achievable, thus making the process economically attractive, the most noticeable feature in Figure 3 is the very dependent nature of the flux on flow. The exponent in the relationship between the flux, J, and the flow rate, Q, or the mean velocity, U, for many stable latices lies much above unity.

\[ J \propto U^x; \quad x > 1.0 \]  \hspace{1cm} (1)

while x is known to lie in the neighborhood of 0.8 by the analogy of heat and mass transfer in Michaels’ gel model (1969) for the ultrafiltration process. The value of x is seen in Figure 3 to be about 1.8 and 1.7 for the PVC and polybutadiene latex, respectively. This phenomenon of
sensitive flow dependency for latices and colloidal suspensions has been observed and reported before. The most popular postulation is the one advanced by Porter (1972) as the "tubular pinch effect". The particles are assumed to have a lateral migration tendency toward the center of the tube such that the mass transfer at the concentration boundary layer is augmented, in addition to the back diffusion mechanism assumed in the gel model.

Due to the sensitive flow-flux empirical relation found for most stable latices, latex ultrafiltration is most advantageously carried out at a high flow velocity, with the allowable pressure drop along a flow path. It is also interesting to note that large diameter tubular membranes are the preferred configuration for latex ultrafiltration on power consumption basis (Shen and Hoffman, 1980).

Flux vs. Temperature. Generally, flux increases with temperature under otherwise constant operating conditions. However, this increasing trend is only seen with a stable feed stream, when the membrane is not fouled rapidly. Figure 4 presents two flux variations with temperature for a dilute waste mixture of poly(vinyl acrylate) and SBR latices to be reclaimed by ultrafiltration. The tests were performed in a small channel flow system with a fresh piece of HFM flat sheet membrane (32 cm$^2$ active membrane area) each time. The triangle data points are for the as-received latex sample; the flux decreased as the sample was heated up. This suggests that the latex was unstable and fouled the membrane. For the second run, when a surfactant was added to the feed to improve latex stability, the normal behavior of increasing flux with increasing temperature was obtained. However, it should be noted that too high a process temperature may reduce latex stability and cause membrane fouling. Thus the upper limits of process temperature for latex ultrafiltration, especially under high concentration conditions, has to be established by observation.

Latex Stability. As illustrated in Figure 4, latex stability has a significant bearing on the ultrafiltration system performance. Zahka and Mir (1977) addressed this subject in some detail. Surfactant addition is usually the most effective way to enhance latex stability as a pretreatment prior to ultrafiltration (Del Pico, 1979). About 0.5% of an anionic surfactant was added to the waste latex sample in Figure 4, lowering its surface tension from 49 dyn/cm to 30 dyn/cm to obtain the increasing flux behavior with temperature.

Experience has shown that the surface tension of a latex sample may be indicative of its stability under ultrafiltration process conditions. Utracki (1973) found his PVC latex sample of 0.2 volume fraction to be shear coagulated in 10-100 s at shear rates of 140-1400 s$^{-1}$ with a couette type apparatus. Considering the shear to be sustained by latices during ultrafiltration where a volume average shear rate is estimated to be about 135 s$^{-1}$ for a 2.54 cm diameter membrane tube, it is prudent to monitor the latex's surface tension to prevent possible rapid membrane fouling.

However, it should be noted that low surface tension does not guarantee favorable latex stability for ultrafil-

**Figure 3.** Flux vs. flow for ultrafiltration of a PVC and a polybutadiene latex.

**Figure 4.** Flux vs. temperature for ultrafiltration of a mixture of poly(vinyl acrylate) and SBR latex.

**Figure 5.** Ultrafiltration performance of an SBR latex with three stabilizing surfactants.
ULTRAFILTRATION OF PVC LATEX
AVERAGE OF FOUR 5' HFM IN SERIES,
\[ P_{IN} = 2.7 \text{ ATM}, P_{OUT} = 14 \text{ ATM}, \]
\[ Q = 7.5 - 8.6 \text{ m}^3/\text{h} \]

- RUN NO. 1 T = 55°C
- RUN NO. 2 T = 43°C
- RUN NO. 3 T = 55°C
- RUN NO. 4 T = 43°C
- RUN NO. 5 T = 55°C

Figure 6. Flux vs. concentration for ultrafiltration of a PVC latex.

tration. Rather, the stability depends on the complete interaction between the particular latex-surfactant combination. Figure 5 presents ultrafiltration results of a 1% SBR latex stabilized with three different surfactants. Each of the three surfactants was able to lower the surface tension of the latex from 50 dyn/cm to 31 dyn/cm. The test was conducted in the small channel flow system (32 cm² membrane area) with the permeate recycled to the feed tank, and new HFM membrane was used for each run. Surfactant no. 1 was anionic type (sodium linear alkylate sulfonate), surfactant no. 2 was nonionic type (condensate of ethylene oxide with hydrophobic bases), and surfactant no. 3 was anionic type (sodium lauryl sulfate). However, the time histories of run no. 1 and 2 clearly indicated membrane fouling as the flux declined with time. In contrast, the flux level was higher and remained stable with time in run no. 3. Thus, only surfactant no. 3 was effective in stabilizing this dilute SBR latex for ultrafiltration, although the use of two other surfactants also resulted in low surface tension.

Flux vs. Concentration. Permeate flux decreases with latex concentration. Generally the flux-concentration relation for complete rejection membrane under constant operating conditions follows the logarithmic dependency as predicted in the gel model, i.e.

\[ J \propto \ln \frac{C_s}{C_b} \]

where \( C_s \) is the concentration at which no permeation occurs and is assumed to be the "gelling" concentration at the membrane surface. \( C_b \) is the feed concentration of the turbulent bulk stream.

Equation 2 has been found to describe the flux pattern for a variety of industrial and laboratory streams. It has also been shown to be derivable via a boundary layer integral method for laminar channel ultrafiltration (Probststein et al., 1978). Wales (1980) semiempirically derived a relationship between the flux and concentration which is also of the form in eq 2, based on the shape of the "disjoining" pressure of a stabilized latex reported in Barclay et al. (1972). However, Figure 6 shows some interesting data from five laboratory runs of PVC latex ultrafiltration. First, the flux levels are extremely high in comparison to the performances of other industrial feed streams, typically in the range of 2-50 L/m² h. Secondly, the semilog plot of \( J \) vs. \( C \) did not yield straight lines as suggested by eq 2; rather, distinct curvatures are observed. This interesting phenomenon was possibly caused by the variation of pump discharge flow rate as the latex concentration, and with it the viscosity, increased in a batch run. However, it was also very possibly caused by some other momentum and mass transfer considerations not incorporated in the gel model formulation. For such high flux performances, reference may be made to Thomas' (1973) analysis on reverse osmosis of dynamic membranes. He found his low flux data were in good agreement with Brian's (1966) film theory of concentration polarization in turbulent flows, but progressively worse deviation occurred as the flux level increased. Thomas postulated that high fluxes caused a thinning of the concentration boundary layer. Without going into the details of his eddy
diffusivity model and the arguments on the scales in the
viscous sublayer, his result of concentration polarization
was shown to be of the form
\[ \frac{J}{U}Re^{3/16}Re_w^{-1/2}Sc^{1/4} = \ln \frac{C_w - C_p}{C_b - C_p} \] (3)
where \( Re \) is the Reynolds number, \( Sc \) is the Schmidt
number, \( Re_w \) is the wall Reynolds number based on the
permeate velocity, subscript \( w \) denotes the membrane wall
condition. Equation 3 thus suggests the high flux data of
a complete rejection membrane to be correlated to the
concentration as
\[ J^{1/2} = \ln \frac{C_w}{C_b} \] (4)

The high flux data in Figure 6 are thus replotted and
shown on the right-hand side. It is interesting to note that
straight line correlations appear to result for those high
flux data when plotted as suggested by eq 4. However, eq
3 obviously does not fully describe the flux data in latex
ultrafiltration. For example, the velocity dependency,
as discussed previously, is known to be much greater than
0.813, as indicated in eq 3.

Membrane Cleanability. The ability to effectively
clean and reuse a fouled membrane is crucial to the fea-
sibility of applying ultrafiltration to industrial latices.
Since the advent of the HFM membrane, a solvent
cleaning technique has been devised (Del Pico and
Sternberg, 1976). After a membrane is severely fouled by
PVC latex, for example, the membrane surface cannot be
effectively cleaned by circulating surfactant solution
through the system. The membrane permeability is lim-
ited by the porosity of the foulant layer. One of the ef-
ective cleaning techniques under such conditions involves
the soaking of the membrane surface with methyl ethyl
ketone (MEK) for about 1–2 h, as reported by Zahka and
Mir (1977). The membrane surface is then flushed with
water and the solvent-softened foulant layer is mechani-
cally wiped off. The mechanical wiping action is accom-
plished by forcing spongeballs through the tube where only
a large diameter membrane tube facilitates this operation.

Further experimentation has shown that tetrahydro-
furan (THF) is more effective than MEK in cleaning the
tenacious PVC fouling layer. In a recent extensive field
pilot trial that lasted four months and processed 36 pro-
duction batches of in-process PVC latex, two membrane
solvent cleanings were performed. The first cleaning was
performed after 20 batch runs (about 350 hours of mem-
brane processing time), and the second cleaning was per-
formed after 32 batch runs (about 755 h of membrane
processing time). At each cleaning, membranes were ex-
posed to solvent twice. The solvent exposure may either
be in the soaking mode, where the solvent was simply
pumped into the system and left for one hour or so, or in
the recirculation mode, where the solvent was continu-
ously pumped through the tubular membrane for 1 h. In either
case, necessary steps were taken to assure that the system
was free of excessive water, which is known to reduce THF
effectiveness.

Figures 7–9 show the temperature-adjusted flux vs. ac-
cumulated operating time at concentrations of 42, 46,
and 50% TS. It is quite clear from these figures that solvent
cleanings performed in the trial showed significant fluxestorecovery capability. Although it was not possible for
cleaned membranes to achieve the same flux performances
Table 1. Operating Energy Cost to Remove 1000 lb/h Water from PVC Latexa

<table>
<thead>
<tr>
<th>spray dryer</th>
<th>evaporatorb</th>
<th>ultrafilterc</th>
</tr>
</thead>
<tbody>
<tr>
<td>energy required</td>
<td>10³ Btu/h</td>
<td>333.3 $10^5$</td>
</tr>
<tr>
<td>energy source</td>
<td>1000 SCF/h</td>
<td>333.3 lb/h</td>
</tr>
<tr>
<td>steam</td>
<td>natural gas</td>
<td>electricity</td>
</tr>
<tr>
<td>energy unit cost</td>
<td>$2.50/10^3$ SCF</td>
<td>$4.00/10^3$ lb</td>
</tr>
<tr>
<td>annual energy cost</td>
<td>$20,000$</td>
<td>$10,656$</td>
</tr>
<tr>
<td>cost 8000 h</td>
<td>P.A.</td>
<td></td>
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</tbody>
</table>

a Dewatering PVC latex from 38% to 50% TS.  
b Assuming a 3-effects evaporator.  
c Assuming 41 gfd average flux and 70% pumping efficiency.

as brand new membranes, it was clearly demonstrated that over 80% process flux recovery could be achieved consistently with periodical solvent cleaning.

Conclusion

It can be concluded that significant progress in product and process development over the past several years in ultrafiltration technology has resulted in the feasibility of concentrating industrial latex streams via large-diameter tubular ultrafiltration systems on a commercial scale. Techniques to enhance latex stability with respect to ultrafiltration processing conditions have been established. Effective cleaning and reuse of fouled tubular membranes by a solvent soaking and mechanical cleaning have been demonstrated. Due to the high flux performance obtainable with stable latex feeds, especially PVC latex emulsions, the tubular ultrafiltration process is also very energy efficient. Table I presents a comparison of operating energy costs using ultrafiltration and two evaporative methods for PVC latex dewatering. Based on some reasonable energy unit costs, it is seen that the annual energy cost of using an ultrafilter is only 13% of that for a spray dryer and approximately one-quarter of that for a three-effects evaporator. Thus, recent advances in ultrafiltration technology have made it a technically viable and economically attractive alternative for industrial latex applications.

Literature Cited

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High Performance Liquid Chromatography. A Reliable Technique for Epoxy Resin Prepreg Analysis

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The application of high performance liquid chromatography (HPLC) techniques for monitoring the chemical compositions of epoxy resin prepregs and for quantitatively analyzing specific resin components is discussed. Case studies are presented which demonstrate the versatility and reliability of HPLC for quality assurance. Using HPLC fingerprinting procedures, variations in the compositions of commercial prepreg materials are detected and related to problems with processability and to the failure of composites manufactured from particular prepreg batches. Examples are given to show how HPLC may be used for trouble-shooting prepreg problems and for developing acceptance criteria for use in prepreg specifications. HPLC is used to investigate the aging and curing behavior of an epoxy resin prepreg.

Introduction

As part of the Army's Materials Testing Technology program, high performance liquid chromatography (HPLC) techniques are being developed and evaluated for monitoring the compositions of epoxy resin prepregs (Hagnauer, 1980; Hagnauer and Dunn, 1980; Hagnauer and Setton, 1978). HPLC quality assurance test procedures are being designed and incorporated into specifications for epoxy resin prepregs used in the production of structural composites. The prepregs consist of glass or graphite fibers impregnated with 30-40 wt % formulated resin. Typically the resin formulations are complex mixtures of epoxy resins, curing agents, diluents, accelerators, etc., and the surfaces of the fibers are "modified" or treated chemically to enhance bonding with the resins during the curing process. Furthermore, the resins are usually "staged" or partially reacted during prepreg manufacture, and since the resins are reactive, prepregs may undergo compositional changes during transport and storage. The processability and properties of epoxy-based composites depend upon the composition of the prepreg materials from which they are manufactured. Therefore, quality assurance methods are required to guarantee that the type, purity, concentration, and distribution of chemical con-