Clarification of Viscous Poly Tetramethylene Ether Glycol (PTMEG) Containing Solid Suspension by Dead-End Flow Microfiltration under Constant Pressure

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ABSTRACT: In this study, the microfiltration of polyester fluid containing solid suspension has been investigated under constant pressure. A membrane module, which consists of a microfilter paper of surface area of 19.4 cm^2 and a SS-316 net support (160 mesh), was used. It was found that the homogeneous sodium acetate suspension in polymer can be completely removed by the membrane filter paper to yield a very clear polymer product. The property and rheology of polyester fluid with suspending solids have been studied. The polymer fluid can be viewed as a Newtonian fluid in this work. The filtration behavior in the membrane system was simulated by the blocking filtration law. Satisfactory fit between experimental data and theoretical calculations was demonstrated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2303–2312, 1999

Key words: clarification; poly tetramethylene ether glycol; Newtonian polymer fluid; microfiltration; rheology of polymer

INTRODUCTION

In a typical polymerization process, such as the manufacture of polyester, the synthesized polymer fluid may contain solid suspension, which affects both the color and the turbidity of product. Solids dispersed in polymer fluid are mostly originated from the addition of a catalyst for polymerization. The normal concentrations of catalysts in the process range from 1000 to 3000 ppm.[1] Removal of impurities from the polymer product can be achieved by several methods, such as filtration,[1–5] adsorption by active charcoal,[5,6] or solvent extraction.[4] However, adsorption by active charcoal can only remove coloring impurities, but

is ineffective in removing particulate. As for solvent extraction, most solvents would remove some polymers along with salt impurities, and therefore change its molecular-weight distribution and reduce the yield of the product. Filtration is by far the most effective method to remove impurities as solid suspension and to decrease product turbidity. However, most literature we found[1–5] were patents that offered little description on the details of their filtration behaviors.

In accordance with the Ruth's theory, the total resistance to filtration is the sum of resistance from both a cake and filter medium. During filtration, the medium may become plugged in several different manners, while the cake can be compressed under different pressures. Both the cake and filter medium may, therefore, change their specific resistance at the same time but in different manners. Notebaert et al.,[7] in their study of dewatering characteristics of sewage sludge, noted that the average specific cake resistance changes not only with pressure, but also

with the quantity of filtrate. Shirato and coworkers[8–16] had extended the blocking filtration models to power-law non-Newtonian fluids. They derived equations that included flow index from the power-law fluid as an additional parameter. Rheological properties of suspensions of solid spheres in non-Newtonian fluids were investigated by Kawase and Ulbrecht.[17] Factors affecting cake resistance in non-Newtonian filtration have been presented by Kozicki.[18] Modes of non-Newtonian fluids through a porous medium have been derived by Pascal.[19–21] Flow of Newtonian and non-Newtonian flows through porous medium using a capillary model has been investigated by Kanellopoulos.[22]

In the membrane filtration area, researchers are always concerned about the decline in filtration rate during the operation. Various blocking mechanisms had been proposed,[23,24] which included the concepts of complete blocking, standard blocking, intermediate blocking, and cake filtration (or boundary layer resistance). Numerous corresponding equations were also derived to describe the changes in flow rate vs. time or filtrate volume for each situation. It is possible that the blocking of the flow passage may gradually change from one mechanism to another as the filtration progresses. The real situation will depend upon many parameters such as particle size distribution vs. pore size distribution of the filter medium, possible interaction between particle and filter medium, operating pressure, shear stress on particles, solid concentration in solution, etc. It is a rather complex phenomenon. The researchers, therefore, usually choose only one model to describe their experimental results. However, it is not impossible that the experimental results could be simulated equally as well by different models.

The purpose of the present study was to investigate microfiltration of solid suspension in polyester fluid using membrane filter paper under constant pressure. In this study, we analyzed the filtration behavior of a polymer fluid with suspending solids using the blocking filtration models. Appropriate equations are proposed to describe the changes in filtration rate with respect to filtrate volume and corresponding parameters estimated through best fitting to the data reported.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental apparatus is schematically shown in Figure 1. Our system was designed to

Figure 1 Experimental apparatus. (1) sample vessel, (2) syringe pump, (3) pump controller, (4) filter modules, (5) thermocouple, (6) temperature indicator, (7) oven, (8) thermal controller, (v) valves.

sustain up to 200°C and 250 atm in operating conditions. Filtration was performed batchwise in this work. Polymer solution containing solid suspension was pumped via a syringe pump (Model 500D, ISCO, USA) into the filter module. Temperature of the module was maintained constant by an oven and a temperature controller. A filter module was tested in this work. Its effective surface area was 19.4 cm^2. A qualitative filter paper (5C, Advance, Japan) supported on a SS-316 net (160 mesh) was used to remove the suspending solids. The surface of the membrane filter paper was observed by a scanning electron microscope (S-2300, Hitachi, Japan), as shown in Figure 2. Particles larger than 1 micron can be retained by this membrane filter paper. However, due to its limited strength, the filter paper might be broken at pressures higher than 100 atm. Besides, this qualitative filter paper exhibited compressible nature, and after an ordinary filtration test its backside would develop a recessed net pattern from the net support. If we change to a porous support for membrane filter paper, filtration can definitely be performed under higher pressures. Nevertheless, the filtration rates were noticeably reduced due to the higher resistance from the porous support than the net.

Poly tetramethylene ether glycol (Dupont, Taiwan), containing units of four carbon atoms, was chosen as our test polymer fluid. Its characteristics measured by instruments is shown in Table I. Sodium acetate (Riedel-de Haën, Germany) was selected as a model suspension solid. Methanol

Figure 2   SEM photograph of membrane filter paper.

Figure 3   Particle size distribution of sodium acetate in polymer fluid.

(Riedel-de Haën, Germany) was used as the solvent to prepare the polymer fluid.

The number-average molecular weight (M_n) and the molecular-weight dispersity (MWD) of the test polymer were determined by gel permeation chromatography system (Waters, USA) using columns such as Stylenegels 0.5 A, 1 A, and 2 A (Waters, USA).

The turbidity of polymer fluid was determined by turbidimeter (RATIO/XR, Hach, USA). Solution viscosity was obtained from viscometer (DV-I, Brookfield, USA) with a spindle LV-1. The shear stress and the shear rate were measured by cone/plate viscometer (DV-II+, Brookfield, USA) with a spindle CP-40. Solution color was determined by colorimeter (MKIV, Lovibond) with a disc NSA ranging from 5–70 mg-Pt/L. The starting polymer fluid, on average, possessed color values (apha) between 10 and 15.

Particle-size distribution of sodium acetate (dispersed in the polymer at around 30°C) was determined by a laser particle analyzer (CIS-1, Galai, Israel).

Sodium acetate of about 0.5 g was first dissolved in 50 g deionized water, and a test polymer of 500 g was dissolved separately in 100 g methanol. The above two solutions were then completely mixed together at 50°C, after which water and methanol were removed by a vacuum evaporator (N-N type, Eyela, Japan) at 100°C. Crystal suspension of sodium acetate was uniformly formed in the polymer and was ready for subsequent microfiltration studies. From the particle-size distribution shown in Figure 3, the average size of the sodium acetate was about 10.88 μm.

THEORETICAL ANALYSIS

The common characteristic equation for different blocking filtration models under constant pressure is given as[25]:

$$\frac{d^2t}{dV^2} = k\left(\frac{dt}{dV}\right)^q \tag{1}$$

Table I   Properties of Polyester Fluid

Formula	$H—(—OCH_2CH_2CH_2CH_2—)_n—OH$
Number average molecular weight (Da)	$2{,}000 \pm 50$
Molecular weight dispersity	2.0 ± 0.05
Density at 40°C (g/cm^3)	0.97
Viscosity at 37°C (cp)	$1{,}650 \pm 50$
Turbidity (NTU)	<0.5
Color (apha)	<5
Melting point (°C)	25–27
Hydroxyl number	56 ± 2

ᵃ 1 apha = 1 mg-Pt/L.

Table II   Equations of the Blocking Filtration Model Under Constant Pressure Drop[25]

Name	q	β	$\dfrac{dV}{dt} = f(V)$	Dimension of α
Cake filtration	0	1	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m + c_s \alpha \dfrac{V}{A}\right)}$	cm/g
	$\frac{1}{4}$	$\frac{4}{3}$	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m^{3/4} + c_s \alpha^{3/4} \dfrac{V}{A}\right)^{4/3}}$	$cm^{5/3}/g^{4/3}$
	$\frac{1}{3}$	$\frac{3}{2}$	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m^{2/3} + c_s \alpha^{2/3} \dfrac{V}{A}\right)^{3/2}}$	$cm^2/g^{3/2}$
Starting filtration	$\frac{1}{2}$	2	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m^{1/2} + c_s \alpha^{1/2} \dfrac{V}{A}\right)^{2}}$	cm^3/g^2
	$\frac{2}{3}$	3	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m^{1/3} + c_s \alpha^{1/3} \dfrac{V}{A}\right)^{3}}$	cm^5/g^3
	$\frac{3}{4}$	4	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu\left(R_m^{1/4} + c_s \alpha^{1/4} \dfrac{V}{A}\right)^{4}}$	cm^7/g^4
Intermediate filtration	1	—	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu R_m} e^{[-\mu c_s \alpha V/\rho_p A^2(-\Delta P)]}$	cm/s
	$\frac{5}{4}$	4	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu}\left(\dfrac{1}{R_m^{1/4}} - \dfrac{c_s \alpha^{1/4}}{\rho_p^{5/4}} \dfrac{V}{A}\right)^{4}$	g/cm^6
	$\frac{4}{3}$	3	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu}\left(\dfrac{1}{R_m^{1/3}} - \dfrac{c_s \alpha^{1/3}}{\rho_p^{5/3}} \dfrac{V}{A}\right)^{3}$	g^2/cm^8
Standard blocking filtration	$\frac{3}{2}$	2	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu}\left(\dfrac{1}{R_m^{1/2}} - \dfrac{c_s \alpha^{1/2}}{\rho_p^{5/2}} \dfrac{V}{A}\right)^{2}$	g^3/cm^{10}
Complete blocking filtration	2	1	$\dfrac{dV}{dt} = \dfrac{A(-\Delta P)}{\mu}\left(\dfrac{1}{R_m} - \dfrac{c_s \alpha}{\rho_p^{6}} \dfrac{V}{A}\right)$	g^5/cm^{15}

Here (d^2t/dV^2) can be considered as the blocking rate, (dt/dV) as the filtration resistance, the value of q defines the mode of filtration occurring, and the value of k for a particular mode of filtration depends on the system, the filter medium, and the conditions of filtration. By assigning different q values, ranging from 0 to 2, various equations representing different filtration models can then be derived. A total of 11 filtration equations with q values equal to 0 (cake filtration model), $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, $\frac{2}{3}$, $\frac{3}{4}$, 1 (intermediate blocking model), $\frac{5}{4}$, $\frac{4}{3}$, $\frac{3}{2}$

(standard blocking model), and 2 (complete blocking model) was summarized in Table II. The q values in a sense represent the rate at which the increase in resistance changes. In other words, when $q = 0$, the rate of increase in filtration resistance is constant. This then corresponds to the situation of an ordinary cake filtration. When $q > 0$, this rate of increase in filtration resistance accelerates with time. After a while, the resistance may become too high to continue the filtration operation. This, then, corresponds to situa-

Table III   Three Types of the Blocking Filtration Model Under Constant Pressure Drop

Blocking Formula	$q = f(\beta)$	q	$\dfrac{dt}{AdV} = f\left(\dfrac{V}{A}\right)$
Type I	$q = \dfrac{\beta_1 - 1}{\beta_1}$	$0 \leq q < 1$	$\dfrac{Adt}{dV} = \dfrac{\mu}{(-\Delta P)}(R_m^{1/\beta_1} + c_s\alpha^{1/\beta_1}\frac{V}{A})^{\beta_1}$
Type II	—	$q = 1$	$\dfrac{Adt}{dV} = \dfrac{\mu R_m}{(-\Delta P)}e^{[\mu c_s\alpha V/\rho_p A^2(-\Delta P)]}$
Type III	$q = \dfrac{\beta_2 + 1}{\beta_2}$	$1 < q \leq 2$	$\dfrac{dV}{Adt} = \dfrac{(-\Delta P)}{\mu}\left(\dfrac{1}{R_m^{1/\beta_2}} - \dfrac{c_s\alpha^{1/\beta_2}}{\rho_p^{\beta_3}}\dfrac{V}{A}\right)^{\beta_2}$

tions where various types of blocking mechanisms take place.

After carefully examining the mathematical equations listed in Table II, we can divide these 11 equations into the following three categories, as shown in Table III. The mathematical equations can be rewritten simply as:

type I: $0 \leq q < 1$

$$\frac{Adt}{dV} = \frac{\mu}{(-\Delta P)}\left(R_m^{1/\beta_1} + c_s\alpha^{1/\beta_1}\frac{V}{A}\right)^{\beta_1} \quad (2)$$

where μ is the viscosity, $(-\Delta P)$ is the pressure-drop, R_m is the resistance of the medium, c_s is the concentration of the filtrate, α is the specific cake resistance, V is the volume of the filtrate, A is the area of the medium and β_1 is the power index. The relation between q and β_1 is

$$q = 1 - \frac{1}{\beta_1} \quad (3)$$

When $\beta_1 = 1$, $q = 0$, we then have the cake filtration model.

type II: $q = 1$

$$\frac{Adt}{dV} = \frac{\mu R_m}{(-\Delta P)}e^{[\mu c_s\alpha V/\rho_p A^2(-\Delta P)]} \quad (4)$$

where ρ_p is the density of the solid particles. This corresponds to the intermediate blocking model.

type III: $1 < q \leq 2$

$$\frac{dV}{Adt} = \frac{(-\Delta P)}{\mu}\left(\frac{1}{R_m^{1/\beta_2}} - \frac{c_s\alpha^{1/\beta_2}}{\rho_p^{\beta_3}}\frac{V}{A}\right)^{\beta_2} \quad (5)$$

where

$$q = \frac{1}{\beta_2} + 1 \quad (6)$$

and if $1 < q < 2$, $\beta_3 = 5/\beta_2$; if $q = 2$, $\beta_2 = 1$ and $\beta_3 = 6$. Here, when $\beta_2 = 1$, $\beta_3 = 6$, $q = 2$, we then have the complete blocking model.

RESULTS AND DISCUSSION

Turbidity of Polymer Fluid Containing Suspending Solids

After polymerization and subsequent neutralization processes, impurities may be formed by reaction between homogeneous catalysts and reactants. In Figure 4, we showed the turbidity of polymer fluid as a function of its solid content, i.e., sodium acetate concentration. As can be seen, the turbidity increased parabolically with the concentration of sodium acetate in the polymer. An empirical correlation equation can be fitted as follows:

Figure 4 Turbidity of polymer fluid versus sodium acetate concentration.

Figure 5 Viscosity as a function of temperature for polymer with and without sodium salt.

Turbidity $= 0.84 + 2.00 \times 10^{-2}[\text{CH}_3\text{COONa}]$
$$+ 1.40 \times 10^{-5}[\text{CH}_3\text{COONa}]^2 \quad (7)$$

Here, the turbidity is expressed in NTU and the concentration of sodium acetate as ppm. The correlation coefficient of this equation is 0.995, with a standard deviation of 6.2.

Rheology of Polymer Fluid

Next, presented in Figure 5 are the viscosity data of the pure polymer and the polymer fluid with 1000 ppm sodium acetate suspension vs. temperature. In this study, the operating temperature varied between 90 and 170°C, and the corresponding viscosity of the polymer fluid was in the range of 40 to 200 cp. At low temperatures, the polymer fluid becomes too viscous for flowing through the membrane and support. By increasing the temperature above 90°C, we can effectively lower the viscosity down to less than 200 cp, which can sustain a reasonable flux through the filtration system.

The existence of suspension solids 1000 ppm in the polymer fluid can lower the viscosity of the polymer fluid and the curve shift to the left. This is possibly due to a reduction of polymeric chain entanglements in the presence of a solid particle.

Using regression analysis, the exponential Arrhenius-type relation for the viscosity to the temperature is given as

$$\mu_{Mn=2,000 \text{ without salt}} = 1.07 \times 10^{-3}e^{4409/T} \quad (8)$$

where the correlation coefficient is 0.999 and the activation energy is 3.67×10^4 J/mol. The units of the viscosity and the temperature are expressed in cp and K.

$$\mu_{Mn=2,000 \text{ with salt}} = 3.67 \times 10^{-3}e^{3952/T} \quad (9)$$

where the correlation coefficient is 0.998 and the activation energy is 3.29×10^4 J/mol.

In general, a polymer fluid as a viscoelastic often behaves as a power-law non-Newtonian fluid, which will affect the filtration behavior somewhat, as suggested by investigators.[5,7–21] The logarithmic plots of shear stress vs. shear rate from rheological measurements at various temperatures are presented in Figure 6. Flow index, N, can then be calculated from the slopes. Our results indicated that N is about 0.97, between 50 and 85°C, and increases toward unity when the temperature increases. This polymer fluid can, therefore, be approximated as a Newtonian fluid for the conditions encountered in this study.

Figure 6 Rheological data of polymer fluid at various temperatures (plot of shear stress vs. shear rate by cone/plate viscometer for polymer fluid).

Flow of Pure Polymer Fluid through Membrane Filter Paper

When pure polymer fluid is passed through the qualitative filter paper, we observe a constant permeating rate for any fixed operating temperature and pressure. The results are shown in Figure 7. At low temperatures, where the viscosity is relatively high, the permeating rate is rather insensitive to a pressure drop across this filter medium. However, as the temperature increases, the slope of the permeating rate vs. the pressure increases accordingly, indicating that the rate is now more sensitive to pressure.

When pure polymer fluid flows through the membrane filter paper with a net support, the flow rate is proportional to the pressure drop. This phenomenon is described by

$$\frac{1}{A}\frac{dV}{dt} = \frac{(-\Delta P)}{\mu R_{m,\text{filter+support}}} \tag{10}$$

where $R_{m,\text{filter+support}}$ is the resistance of the membrane filter paper with a SS-316 net support. The resistance of the SS-316 net support is negligible; due to its pore size it is vary big (i.e., 160 mesh). Calculated values of $R_{m,\text{filter+support}}$ for membrane filters range between 1.57×10^9 cm^{-1} and 1.53×10^{10} cm^{-1}, shown in Figure 8. This

Figure 7 Permeating rate of pure polymer fluid through membrane filter paper vs. pressure drop at various temperatures.

Figure 8 Resistance for the membrane filter paper with support.

Figure 9   Characteristic curve for filtration of polymer with 1,000 ppm sodium acetate through membrane filter paper.

resistance is inversely proportional to temperature. This is probably due to thermal expansion, and at lowered viscosity at a high temperature, polymer fluid can thus permeate into the inside of the fibers of the filter paper prior to the opening up of the pores of the filter papers.

Microfiltration of Polymer with Suspending Solids

Presented in Figure 9 is the permeating volume of the polymer fluid with 1000 ppm suspending sodium acetate particles vs. time at 100°C and various operating pressure drops. It was noticed that the permeating volume actually decreased with increasing pressure. This fact seemed to indicate that the cake formed by sodium acetate is closed packing. Besides, it also suggested that the increase of the filtration driving force caused by the pressure increase is affected by the resistance increase of the cake. At 125 atm, an abrupt increase in permeating volume was observed. We suspect that the qualitative filter paper is broken under this condition. The inverse of the corresponding permeating rate vs. volume is plotted in Figure 10. From this figure, filtration rates are noticed to decrease quite rapidly with volume, especially under high pressures. The polymer filtrate obtained from this operation is quite clear in terms of turbidity. After filtration, many white fine crystals accumulated on the surface of the filter paper.

Next, we used eqs. (2) and (5) to best fit the experimental results and to estimate parameters of R_m, α, and β using the nonlinear regressional technique, as shown in Table V. All correlation coefficients were larger than 0.99. The corresponding q calculated by eqs. (3) and (6) was increased from 0.69 to 1.40 with an increase in the pressure drop. It was noticed that the behavior of microfiltration of the polyester solution containing solid suspension was transferred from type I of the block filtration law to type III with an

Figure 10   Inverse of permeating rate of various pressure drop vs. permeating volume, and the result of blocking filtration modeling for filtration of polymer with 1,000 ppm sodium acetate through membrane filter paper.

Figure 11   Resistance of the membrane filter paper with support from blocking model.

increasing pressure drop. We think that particles from the polymer suspension might still penetrate to some extent into the membrane layer under a high pressure, while also accumulating into a cake at the same time. The resistance of the membrane filter paper is directly proportional to the pressure drop (see Figure 11). It was notice that the membrane filter paper was flexible and with limited pressure strength, for it was made by cellulose; also, it was easily compressed to form smaller pores that would increase filtration resistance. The specific resistance of the sodium acetate cake increased with the driving force, as shown in Table IV. The theoretical curve of dt/dV vs. V based on this set of parameters is also plotted in Figure 10, along with the experimental data. The fit is quite satisfactory.

CONCLUSION

The microfiltration of polyester fluid containing about 1000 ppm sodium acetate suspension through the membrane microfilter under constant pressure was investigated. The rheological properties of the polyester fluid containing solid suspension were measured. The polymer fluid can be viewed as a Newtonian fluid in our work. Our experimental data demonstrated that the homogeneous micrograde sodium acetate suspension in a polymer can be completely removed by the membrane filter paper to yield a very clear polymer product. The system of membrane filter paper with support has a limit for the pressure driving force of 120 atm, and it may deform under a high-pressure force. We have classified the blocking filtration laws into three categories—i.e., types I, II, and III—where these models can be used to describe different behavior of microfiltration. The filtration behavior can be satisfactorily fitted using these blocking law models. Fitted parameters of R_m and α showed a similar relation toward pressure. The blocking behavior of microfiltration of a polyester solution containing solid suspension was changed from type I to type III with an increase in the pressure drop.

Table IV   Parameters β and q of the Blocking Filtration, Resistance of the Filter Paper With Support and Specific Resistance of the Cake for Polymer Fluid with Salt Through Filter Paper

$(-\Delta P)$ (atm)	β (—)	q (—)	$R_{m\,\text{filter+support}}$ (cm^{-1})	α (cm$^{[1+2(\beta_1-1)]}$/g$^{\beta_1}$)	Blocking Formula
50	$\beta_1 = 3.26$	0.69	2.33×10^9	3.41×10^9	type I
75	$\beta_1 = 6.68$	0.85	3.94×10^9	4.41×10^9	type I
100	$\beta_2 = 2.53$	1.40	5.54×10^9	1.07×10^{10}	type III

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