Macromolecules **1997,** *30,* 2792−2794

Notes

Formation of Cellulose Acetate Fibers by the Rapid Expansion of Supercritical Methanol Solutions

N. E. Aniedobe and M. C. Thies*

Department of Chemical Engineering, Clemson University, Clemson, South Carolina 29634-0909

Received July 16, 1996
Revised Manuscript Received January 10, 1997

Introduction

The rapid expansion of supercritical solutions (RESS) is an active area of research for the processing of high molecular weight materials, such as polymers.[1,2] In RESS, the polymer of interest is typically dissolved in a compressed solvent that is in the liquid or near critical state. The resulting solution is then heated to the desired operating temperature and expanded from high pressure across a fine-diameter orifice or capillary to ambient pressures, causing the polymer to be rejected from the solution. This rapid expansion process occurs quite rapidly, with residence times in the orifice being on the order of 10^{-5} s, and can lead to unique product morphologies, such as microspheres, dendrites, and fibers.[1−5]

In general, two factors have motivated investigations of RESS processing: (1) the opportunity for producing new and unique product morphologies and (2) the possibility of replacing hazardous solvents with those that are more environmentally benign. In this study we report on the rapid expansion of secondary cellulose acetate (CA) from supercritical methanol solutions. Of particular interest to us was determining whether continuous fibers could be made and to what extent degradation of the CA would occur because of the elevated processing temperatures. No previous rapid expansion experiments with polymers dissolved in methanol (T_c = 239.4 °C, P_c = 81.0 bar) are known. Peterson et al.[3] reported the formation of CA fibers from solutions of supercritical pentane, but no solution concentrations or dissolution temperatures are given.

Experimental Section

The apparatus used for RESS experiments is shown in Figure 1. The main components of the apparatus are (1) high-pressure electronic syringe pumps, for supplying the solvent and pressurizing the system; (2) the view cell, for dissolving the polymer in methanol at subcritical temperatures; (3) the pre-expansion section, for heating the polymer solution to supercritical temperatures; (4) the nozzle through which the supercritical solution is expanded; and (5) a 6 in. o.d. × 10 in. long poly(methyl methacrylate) chamber, for collecting the precipitated solute. Prior to a RESS experiment, the view cell is charged with 0.1−2.5 g of CA. After the view cell is installed in the bath, the cell is filled with liquid methanol using the process-line syringe pump (Isco, Model LC-5000). Next, the view cell is isolated from the system by closing the appropriate valves, the isothermal bath is used to heat the cell to the desired temperature (which is referred to as the dissolution temperature), and the polymer is allowed to completely dissolve in the solvent.

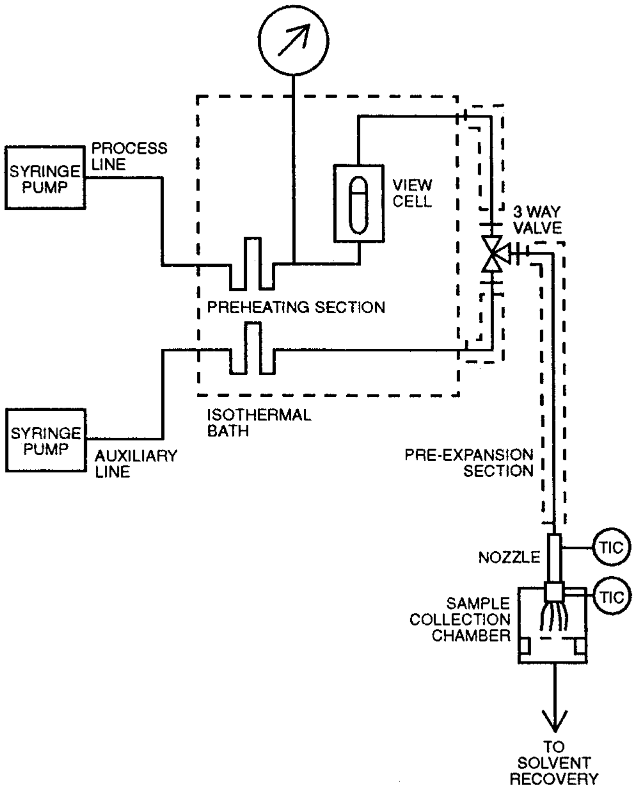

Figure 1. Simplified schematic of the RESS apparatus.

RESS experiments are then initiated. Methanol flow is first established through the nozzle by means of the auxiliary-line syringe pump (Isco, Model 260D), bypassing the polymer solution in the cell. In this way, steady-state conditions of temperature and pressure are established in the pre-expansion section and in the nozzle before solute precipitation is initiated. Temperatures in the pre-expansion section are maintained with three separate heating tapes. A fourth heating tape is wrapped around the 1/4 in. tubing leading to the nozzle orifice and is controlled with an Omega auto-tune temperature controller (Model CN76122). A J thermocouple attached to the middle of the tubing, 4 in. from the nozzle orifice, provides feedback to the controller. The temperature of the nozzle orifice itself (which is reported as the pre-expansion temperature) is controlled with a fifth heating tape and another auto-tune controller. A J thermocouple carefully attached to within 3−5 mm of the nozzle orifice provides feedback. The desired system pressure is maintained by adjusting the flow rate of the methanol to 3−5 mL/min. Flow of pure solvent is continued until temperatures and pressures have stabilized in the pre-expansion section and in the nozzle to within ±1 °C and ±5 psi, respectively, a procedure that normally requires 10−15 min.

After steady state has been established, the process-line pump is set to the same flow rate as the auxiliary-line pump, and the flow of fresh methanol into the view cell is started. When the pressure in the process line equals the auxiliary-line pressure to within ±10 psi, the three-way valve (High Pressure Equipment, Model 15-15AF1) is switched to close the auxiliary-line side and open the process-line side. Using this technique, little or no disturbance to the existing steady-state conditions occurs. The homogeneous polymer solution is then “pushed” out of the cell by the fresh solvent in a plug-flow

S0024-9297(96)01045-5 CCC: $14.00

Table 1. Process Conditions and Product Morphologies for the Rapid Expansion of Supercritical Methanol Solutions

case	initial conc (wt %)	T_{dis} (°C)	T_{pre} (°C)	P (bar)	morphology
1	*a*	110	240	81	a few short fibers, then powders, then thin films
2	*a*	150	260	109	a few fibers, then powders, then films; polymer degradation occurred
3	14	105	240	98	long, continuous fibers, then powders, then films
4	14	125	240	82	long, continuous fibers, then powders, then films
5	15	120	240	82	long, continuous fibers, then powders, then films

[a] Polymer was not initially dissolved in methanol.

manner, heated in the pre-expansion section, and expanded across the nozzle. No mixing of the contents of the cell was employed, so as not to disturb the plug-flow behavior that was observed inside the cell, which helped to maintain a constant CA concentration in the expanding solution. The resulting polymer precipitate, which is insoluble in methanol at ambient temperatures, is collected on microscope slides or filter paper placed in the collection chamber. A cold trap attached to the collection chamber is used to completely condense all expanded methanol.

The nozzle (Advanced Laser Systems) consists of $^1/_4$ in. o.d. × $^1/_{16}$ in. i.d. × 8 in.-long tubing, a 0.010 in. thick flat disk that has been laser-drilled through the center with a 50 μm hole, and an end cap for mounting the disk to the end of the tubing. All nozzle components are of 316 stainless steel. A 0.5 μm filter was installed just upstream of the nozzle and was found to be helpful in preventing plugging of the orifice with nonpolymeric particulate matter. The view cell has an internal volume of 12 cm^3, has windows that extend the entire length of the cell, and contains a horizontally mounted stainless steel screen for holding and observing the polymer as it goes into solution. The isothermal bath has a nitrogen purge for maintaining oxygen concentrations inside the bath below 1 mol %, reducing the risk of explosion or fire should a solvent leak in the preheater lines or cell occur. These items are discussed in detail elsewhere.[6]

Secondary CA, a semicrystalline material with a very low degree of crystallinity and a melting point of ~250 °C, was obtained from Hoechst Celanese Corp. The process used for its manufacture is discussed elsewhere.[7] The number average molecular weight (M_n) and polydispersity (PDI) obtained by GPC were 83 700 and 2.03, respectively. The morphology of the RESS precipitates was determined by scanning electron microscopy (JEOL JSM 848 SEM). Samples were prepared for analysis by gold-sputtering. To determine whether any degradation of CA occurred during processing, FTIR spectroscopy (Bio-Rad, Model FTS-45) was used to analyze precipitates.

Results and Discussion

Results of our RESS experiments are summarized with the cases shown in Table 1. For all experiments, a constant aspect ratio (L/D) of 5.0 was used. In cases 1 and 2, the view cell was initially charged with nitrogen instead of methanol during heatup. Thus, polymer dissolution only began when the flow of methanol into the view cell via the process line was initiated, and CA concentrations were always low (i.e., <1 wt %). In both cases, swelling and dissolution of the polymer load occurred rapidly at the dissolution temp (T_{dis}). Following pre-expansion, a few short fibers were initially obtained, but the predominant product consisted of agglomerated powders (see Figure 2). In case 2, brownish streaks were observed in the precipitated polymer. FTIR spectra indicated CA degradation.

For subsequent experiments (i.e., cases 3–5), a polymer charge of 1.4 g was used, and the CA and methanol were allowed to form a homogeneous solution in the view cell at T_{dis} before RESS experiments were initiated. These solutions had a strawlike color that is typical of concentrated CA–solvent solutions. The initial concentration of polymer in the cell (i.e., 14–15 wt %) was calculated from the known amounts of polymer and

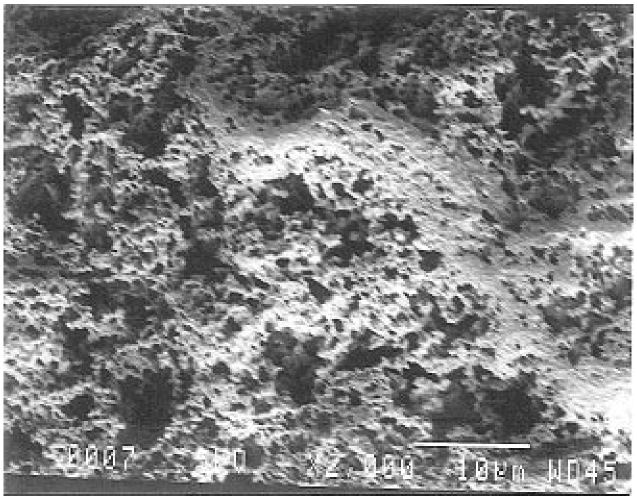

Figure 2. Agglomerated CA powders produced from the rapid expansion of dilute (<1 wt %) CA/methanol solutions at 240 °C and 81 bar.

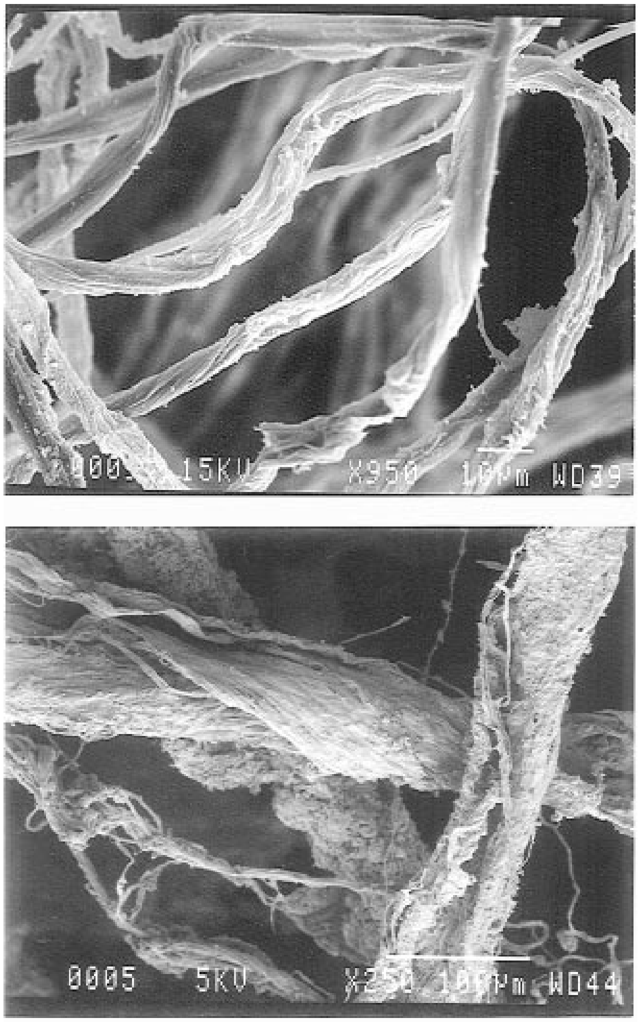

Figure 3. CA fibers produced from the rapid expansion of methanol/CA solutions at 240 °C and 82 bar: (a, top) concentrated (14–15 wt %) CA/methanol solutions; (b, bottom) more dilute CA/methanol solutions.

solvent initially charged to the cell. As can be seen in Figure 3a, increasing the concentration of polymer in solution dramatically changed product morphology, as continuous fibers 2−3 μm in diameter were made. Note that each observed strand actually consists of several entwined fibers. One can also see a few micron- and submicron-sized particles on the surface of these fibers. During the first few minutes of an experiment, the fresh methanol entering the view cell from the bottom "pushed" the CA/methanol solution out the top of the cell in a plug-flow manner, and continuous fibers were formed. Later, the fresh methanol was observed to "break through" and form a visible "path" through the polymer solution in the cell, and the rate of fiber formation decreased. As the concentration of CA decreased further (as could be observed by both the opacity and color change of the solution in the cell), both partially formed fibers and powders began to be produced (Figure 3b). Eventually, fiber formation ceased completely and only powders were formed, and finally thin films, which look very similar to the powders shown in Figure 2, except consisting of smaller particles. For all except case 2, where T_{pre} was 260 °C, no polymer degradation was detected by FTIR.

Our experiments have demonstrated that RESS can be used to produce 2−3 μm CA fibers from the concentrated solutions that would be desirable for a number of commercial applications. In addition, our results indicate that polymer concentration can have a dramatic effect on product morphology. Previous work with RESS has focused on the effect of temperature, pressure, and *L*/*D* on polymer morphology, with solution concentrations generally being well under 1 wt %. Johnston and co-workers[2] have shown that concentration effects are secondary, but we have shown that, if the changes in concentration are large enough, dramatic morphology changes can also be induced solely by concentration changes. However, our results are not inconsistent with the mechanism of Lele and Shine for polymer morphology formation.[1] The polymer-rich phase that is necessary for fiber formation is certainly initially present in the pre-expansion section, whether existing as a single phase or as part of a two-phase mixture. Furthermore, the concentration of CA inevitably falls to the point such that only a solvent-rich phase exists in the pre-expansion section, conditions that result in the formation of the powders and films that were observed.

Acknowledgment. The financial support of Hoechst Celanese Corp. is gratefully acknowledged. We also wish to thank Bernice Feuer for the GPC analysis of the CA, and George Serad and Mike Drews for their helpful discussions.

References and Notes

(1) Lele, A. K.; Shine, A. D. *Ind. Eng. Chem. Res.* **1994**, *33*, 1476.
(2) Mawson, S.; Johnston, K. P.; Combes, J. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3182.
(3) Petersen, R. C.; Matson, D. W.; Smith, R. D. *Polym. Eng. Sci.* **1987**, *27*, 1693.
(4) Lele, A. K.; Shine, A. D. *AIChE J.* **1992**, *38*, 742.
(5) Tom, J. W.; Debenedetti, P. G. *Biotechnol. Prog.* **1991**, *7*, 403.
(6) Aniedobe, N. E. M.S. Thesis, Clemson University, 1994.
(7) Serad, G. A. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1985; Vol. 3, p 200.

MA961045G