

Macrovoid growth during polymer membrane casting

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Received 1 February 2002; accepted 15 February, 2002

Abstract

The Solutocapillary Convection (SC) hypothesis contends that macrovoid (MV) growth in dry-cast membranes is governed by a solutal-Marangoni convection-induced force caused by the rapid evaporation of volatile solvent from the liquid/gas interface, a viscous drag force, and a gravity-induced buoyancy force. Two different sets of experiments using the cellulose acetate-acetone-water system were conducted to test the SC hypothesis. Membranes were cast aboard a KC-135 aircraft that enabled short periods of microgravity (~0-g) as well as 2-g conditions. The studied process variables included the solvent/non-solvent (S:NS) ratio, surface tension, and the magnitude of the body force (buoyancy). SEM analysis of the resulting membrane morphologies indicated that the MV morphology was strongly influenced by the S:NS ratio. However, dependence of MV size and number density on the buoyancy force could not be established. In the second set of experiments, videomicroscopy flow-visualization (VMFV) was utilized to measure fluid velocities at the MV/casting-solution interface and in the bulk solution. The magnitude of the solutocapillary convection was controlled via surfactant additions. A comparison of the ratio of the edge to the bulk velocity for MVs made from surfactant-free and surfactant-containing casting solutions did not provide evidence of a statistically significant surfactant effect. However, the presence of the surfactant did affect the MV number density. In addition, the presence of tracer particles inside the MVs indicated that a convective flow enables their transfer from the bulk to the interior of the MV.

Keywords: Macrovoid formation; Solutocapillary convection; Polymer membrane defects; Low-gravity casting

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Presented at the International Congress on Membranes and Membrane Processes (ICOM), Toulouse, France, July 7–12, 2002.

1. Introduction

Polymeric membranes formed using evaporative casting techniques can contain macrovoids (MVs), i.e. large tear-drop pores (size $\sim 10\text{--}50\ \mu\text{m}$) that are generally considered to be undesirable in separation applications. Although a number of different mechanisms have been suggested for MV formation [1–4], they do not provide a complete description of the MV initiation and growth process. Recently, the solutocapillary convection (SC) hypothesis has been advanced [5]; this hypothesis contends that MV growth is governed by three principal forces: a Marangoni force generated by surface-tension gradients along the MV/casting solution interface that facilitate MV growth; a viscous drag force that resists MV growth; and a gravitationally induced body force that can either resist or promote MV growth, depending on its orientation. The basic features of the SC hypothesis of MV growth during dry-casting are shown in Fig. 1 for the cellulose acetate (CA)/acetone/water system. Rapid evaporation of acetone from the gas/liquid interface causes the water fraction to increase, thereby generating a surface-tension gradient. Consequently, the MV/casting solution interface experiences mo-

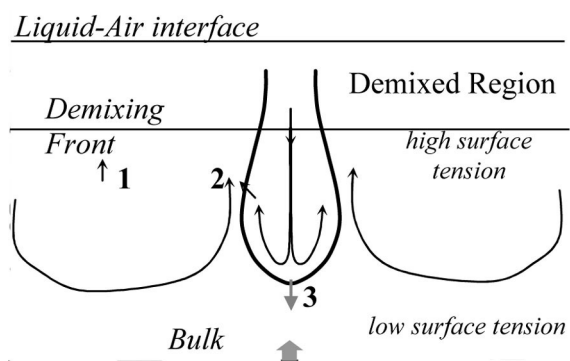


Fig. 1. Schematic describing the SC mechanism for MV growth. The velocities at points 1, 2, and 3 refer to the far-field, MV/solution interface, and the MV velocities, respectively.

tion from the leading edge (low surface tension) to the trailing edge (high surface tension) of the MV. This process, solutal Marangoni (solutocapillary) convection, results in a force on the growing MV that propels it away from the gas/liquid interface and into the underlying bulk solution. Continuity of velocity requirements at the MV/casting solution interface result in the development of convection cells inside the MV. The overall effect is to enhance the mass transfer of non-solvent into the growing MV. However, the solutal-Marangoni convection-induced force is opposed by a viscous drag force as well as a gravitationally-induced buoyancy force.

In this study, we tested the validity of the SC hypothesis using two different experimental approaches in which the solutal-Marangoni and the body forces were systematically varied: (1) membranes were cast aboard a KC-135 aircraft under short durations of microgravity and 2-g conditions, and (2) videomicroscopy flow visualization (VMFV) was used to measure the velocities near and far from the MV/casting solution interface in solutions containing different surfactant concentrations.

We have previously reported the results of experiments in which membranes were cast aboard the NASA KC-135 aircraft [6]. The KC-135 flies in a series of parabolic maneuvers that give rise to short periods (20–25 s) of microgravity followed by a high-g pullout lasting approximately 90 s. In the previous study, several unforeseen limitations in the membrane casting apparatus (MCA) precluded meaningful statistical analysis. Qualitative observations from that study suggested that (1) MV formation is closely linked to the S:NS ratio in the casting solution and (2) buoyancy hinders MV growth at “low” S:NS ratios. For the present study, a new MCA was designed that incorporated wider wells to obtain larger samples, a different triggering mechanism to minimize sloshing of the casting solution, and finer-machined surfaces to prevent membrane thickness non-uniformities.

VMFV provides a direct means of measuring the interfacial velocities. Recently we reported that VMFV could provide important information regarding the phenomena occurring at the MV interface [7]. In this research, VMFV was further extended to determine the effect of a surfactant on the MV interfacial velocities. Velocities were measured at the edge of the MVs as well as in the casting solution “far” from the MVs; in addition, MV number density values were also obtained.

2. Materials and methods

2.1. Materials

Casting solutions were prepared using CA (molecular weight of 40,000 and an acetyl content of 39.8%), ACS certified grade acetone and deionized water. The surfactant used was Triton X-100 (J. T. Baker Company); Triton X-100 (polyoxyethylene isooctyl phenyl ether) is a nonionic surfactant with a critical micellar concentration (CMC) in water of $\sim 0.22 - 0.24 \times 10^{-3}$ mol/L (~ 135 ppm).

2.2. Experiments aboard the KC-135 aircraft

The new MCA used the same sliding block principle as the earlier design. First, the casting solutions were loaded into chimneys directly over 150- μm -deep casting wells machined into a Delrin[®] sliding block. To initiate membrane formation, the sliding block was manually moved forward until each well was aligned directly under a chimney filled with activated carbon that was suspended on a fine nylon mesh ~ 1 mm above the cast membrane. Solvent and nonsolvent then evaporated, causing phase separation. The MCA had six separate casting cells with a 1 cm diameter; laser probes were mounted on the two central wells to enable monitoring of casting solution demixing.

A full factorial experimental design was used in these experiments in which three variables were studied: gravity-induced buoyancy

force (0-g or 2-g), S:NS mass ratio (2:1, 2.33:1, or 2.75:1), and surface tension (surfactant-free and surfactant-containing solutions). The casting solutions were prepared one day prior to flight and stored in sealed vials. Solutions to be cast onboard the KC-135 were loaded in 1 cc syringes less than 1 h before flight. Shortly after takeoff, the solutions were transferred to and sealed in the MCA. The MCA was activated at the beginning of the relevant 0-g or 2-g interval. In 0-g, the MCA was allowed to free-float. A 1-g control experiment was also planned wherein casting was done aboard the aircraft at 1-g under otherwise similar conditions. All samples were allowed to dry for at least 2 h prior to removal from the MCA. The membrane morphology was analyzed using a scanning electron microscope.

2.3. Videomicroscopy flow visualization

Casting solutions containing 0, 31.4, 300 or 3000 ppm Triton-X surfactant were used for the VMFV experiments. The solutions were stirred vigorously for several hours and removed from the stir plate 30 min prior to casting to allow entrained air bubbles to escape from the solution. A small amount of tracer particulates (200 ppm of TiO_2 particles) was added to the casting solution to facilitate visualization of the microscopic flows. Although the individual TiO_2 particles were only a few nanometers in diameter, they typically formed aggregates as large as 1 micron.

The VMFV experimental arrangement is shown in Fig. 2. The casting solution (S:NS = 2.1) was syringe-injected into the space between two horizontal microscope slides separated by a Teflon shim until the solution reached a barrier (pin). The pin isolated the casting solution from air, and also provided a constant diffusion length of 1 cm between the solution/air interface and the leading edge of the microscope slides. Contact between the casting solution and air was initiated by removing the pin. Preferential evaporation of acetone then led to

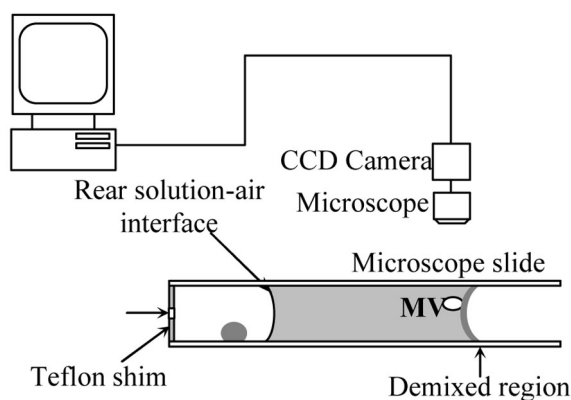


Fig. 2. Schematic of the videomicroscopy set-up. The casting solution is inserted in the space between two horizontal microscope slides separated by a Teflon[®] shim, and phase separation occurs as the solvent evaporates.

solution demixing and membrane formation. The casting solution had both front and rear interfaces with air (Fig. 2). Since evaporation from the rear interface could affect the bulk flow, a drop of acetone was inserted close to the rear interface. The vapor pressure generated by the drop significantly reduced evaporation, and thus stabilized the rear interface.

The demixing front and the MVs were monitored using a video microscope (Nikon EFD-3). A CCD camera (JVC-TK1270) with a view window of 730×550 microns was attached to the video microscope, and images were recorded at 1 s intervals. The PC software Scion Image [8] was used for the flow visualization analysis. Typically, tracer particles close to the MV interface were tracked over five frames to obtain the MV interfacial velocities. Wherever possible, two particles were tracked at the MV edge, and the average of the two velocities was used as the “raw” edge velocity. Similarly, four tracer particles far from the MV but at almost the same distance from the demixing front were chosen and tracked over five frames to obtain the average “raw” bulk velocity. The leading edge of the MV was also tracked during the

same time interval to obtain the MV velocity, which was then subtracted from the raw velocities to obtain the actual edge and bulk velocities. Only those MVs whose size stayed relatively constant during the time interval were evaluated so that the artifacts associated with the growth/shrinkage of the MVs were minimized. The edge velocity ratio (EVR) was calculated by dividing the edge by the bulk velocity. The number of the MVs observed in the viewing frame (MV number density) was also determined.

3. Results

3.1. Microgravity and 2-g experiments

The parabolic maneuvers of the KC-135 aircraft only produce short intervals of 0-g and 2-g, and it was necessary that the entire casting solution demix within this interval. Light reflection measurements using laser probes confirmed that complete demixing did occur within 20 s. Although the membranes prepared in the new MCA were larger and more uniform in thickness compared to the earlier study, some problems were still encountered. As a result, only a limited number of “good” membrane samples were available for analysis.

Since the buoyancy force opposes MV growth, one would expect the MVs formed in 0-g to penetrate deeper into the membrane compared to those formed in 2-g. The surfactant should also have a similar effect, since it reduces the surface tension gradient. However, the limited time interval of 25 s for demixing restricted the initial film thickness. In most cases, the MVs penetrated through the entire membrane thickness. Figs. 3 and 4 show the influence of the buoyancy force and the surfactant (at 2-g) on the MV size (average MV area) at two different S:NS ratios. These data do not indicate a dependence of MV size on the buoyancy force or surfactant concentration, most likely due to the penetration of the MVs through the entire thickness of the cast membrane.

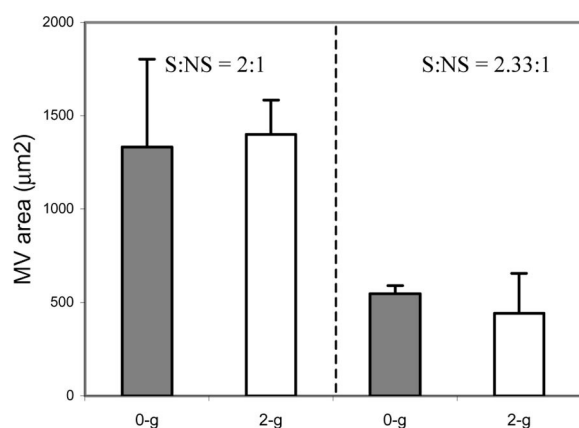


Fig. 3. Influence of buoyancy on the MV size for two different S:NS ratios.

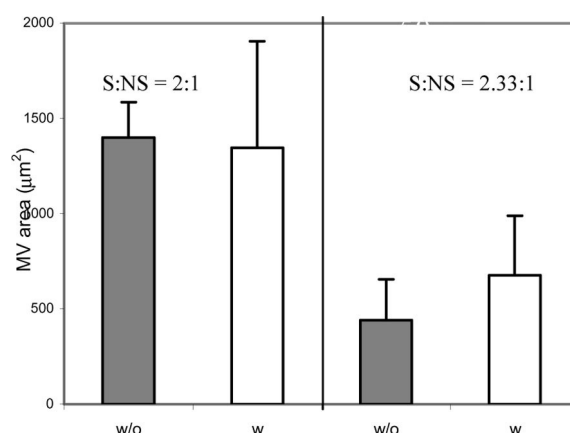


Fig. 4. Influence of surfactant on the MV size at different S:NS ratios under 2-g conditions.

3.2. Videomicroscopy experiments

The viscosities of casting solutions with and without the 200 ppm TiO₂ tracer particulates were measured and found to be statistically identical. Thus, a change in the MV formation hydrodynamics associated with a difference in viscosities was not a concern. Information regarding the effect of the surfactant on the casting solution surface tension would also be valuable, since the surface tension of the ternary solution cannot be predicted on an a-priori basis. However, this measurement is difficult

because of high casting-solution viscosity and rapid acetone evaporation from the solution interface. In addition, the surfactant concentration in the compositions utilized is diluted since water comprises only 30 wt.% of the solution. Consequently, surfactant concentrations that differed by an order of magnitude (30, 300, and 3000 ppm in water) were selected for this study

Figs. 5 and 6 show the effect of surfactant concentration on the EVR and the MV density, respectively. Analysis of the EVR data indicated that there was no statistical difference

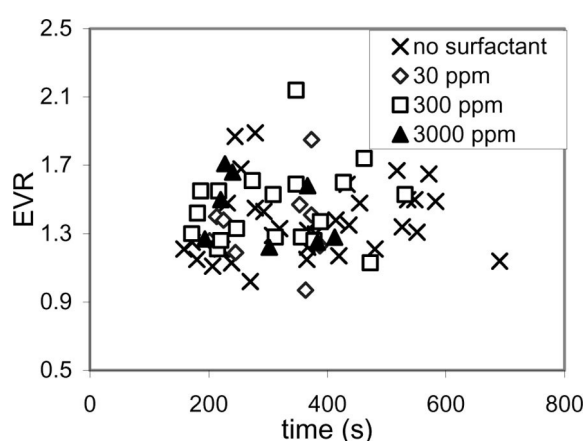


Fig. 5. Influence of surfactant concentration on the EVR. No systematic trends were observed.

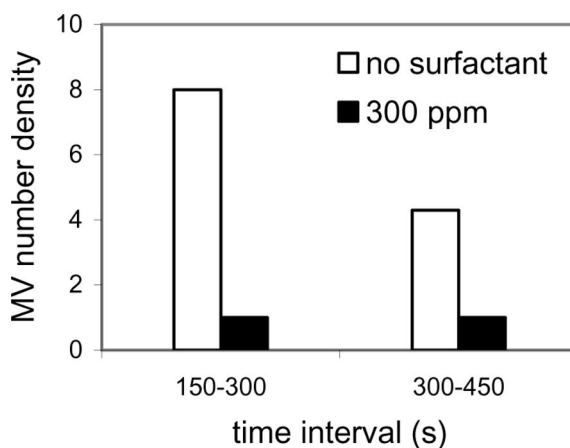


Fig. 6. Influence of surfactant concentration on the MV number density defined as the number of MVs viewed in a single frame.

among the four cases, i.e. 0, 31.4, 300, and 3000 ppm of Triton X-100. On the other hand, analysis of the MV density data indicated that there was a statistically significant difference among the groups. A multiple comparison procedure established that the number density of MVs with a casting solution containing 300 ppm surfactant was distinct from that for a surfactant-free casting solution.

Observations during the VMFV experiments indicated that in most cases, the MVs grew explosively from the demixing front (within 2–3 s). Over time, tracer particles became visible inside the MVs. This is a particularly significant observation, since the presence of tracer particulate inside the MVs cannot be explained by diffusion, and indicates the presence of a convective flow that transfers the particles from the bulk solution into the MVs.

4. Discussion

In a previous study [6], a scaling analysis compared the magnitudes of the buoyancy and viscous drag forces for a MV approximately 50 microns in diameter and indicated that the buoyancy force is much smaller than the viscous drag force, especially during the initial growth phase. Since the viscous drag force depends upon the velocity of the growing MV, it would diminish to zero in a fully grown MV. Thus, the buoyancy force can become significant in determining the final shape of the MV. However, for the buoyancy effect to be significant, the MV must be sufficiently large (~80–100 μm).

In the present experiments at the lowest S:NS ratios, MVs penetrated through the entire membrane thickness under 0-g as well as 2-g conditions. Hence, the effect of buoyancy or surface tension could not be validated. Our calculations indicate that such validation would require much greater initial casting solution thicknesses (~500 μm).

The VMFV results indicated that the presence of surfactant did have a statistically

significant effect on the MV density, but that the EVR was not significantly altered. Although the dependence of MV number density on surfactant concentration demonstrates the expected result in agreement with the SC hypothesis, the intensity of EVR on surfactant concentration seems to imply that the relationship between solutocapillary convection and MV growth is tenuous. However, several important factors must be considered in interpreting these results. First, the drag forces on the particulate aggregates (assumed negligible) might have been significant and second, not all of the “interfacial particles” were exactly at the MV/solution interface. Hence, these particles might not have accurately tracked the actual edge velocity. Furthermore, velocities were tracked only during the mature phase of the MV growth process in order to avoid the artifacts associated with MV rapid growth/shrinkage. At this point in the MV growth process, the concentration gradients might already have become too small to be of significance. Finally, the overall hydrodynamics in the VMFV arrangement are different from “usual” membrane casting in that the former has a vertical face exposed to air and the demixing front moves horizontally.

Nonetheless, observations during the VMFV experiments yielded important information about MV growth via the observation of tracer particulate inside the MVs. Their presence cannot be explained either by diffusion or by the SC hypothesis, and strongly implies the presence of a convective flow that transports the particles from the bulk solution to the interior of the MVs. This occurrence suggests that multiple mechanisms may be associated with MV growth. This possibility is reinforced by the observation that although the surface tension gradient during the subject CA membrane casting is significant (because of the large difference in the surface tension of water (72 dyne/cm), and acetone (23 dyne/cm)), MVs are also observed in systems where the surface tension difference between the solvent and non-solvent

is not very high [2]. Hence, whereas solutocapillary convection could facilitate MV growth in the CA/acetone/water system, this may not represent the principal mechanism for MV growth.

5. Conclusion

While the KC135 and VMFV experiments have provided new and intriguing data regarding the formation and growth of MVs, the results did not provide complete statistical evidence for the influence of solutocapillary convection on the MV growth process. Indeed, results from both the KC135 and VMFV experiments indicate that MV growth is a complex process and emphasize the need for additional studies that employ more sophisticated approaches. Given the unique potential advantages of the microgravity environment, we believe that the extended periods of low gravity available on the International Space Station would provide an appropriate environment for additional flight and VMFV experiments that could overcome many of the limitations inherent in the present study. Such experiments are planned over the next few years.

Acknowledgements

The authors gratefully acknowledge support of this research by the NASA Microgravity Research Division (NAG8-1475) and the NASA Engineering Fluid Mechanics Division (NAG3-2451), and the University of Colorado Under-

graduate Research Opportunities Program (UROP).

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