

# NOTE

## Aging Effect of Filtered and Unfiltered Casting Solution on the Performances of Membranes

K. C. KHULBE,<sup>1</sup> T. MATSUURA,<sup>1</sup> H. KIM<sup>2</sup>

<sup>1</sup> Industrial Membrane Research Institute, Department of Chemical Engineering, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

<sup>2</sup> National Research Council of Canada, Ottawa, Ontario K1A 6O5, Canada

Received 1 October 1999; accepted 20 October 1999

### INTRODUCTION

Ma et al.<sup>1</sup> drew attention to the aging effect of casting solution on the properties of hollow-fiber membranes. It was reported<sup>1</sup> that the viscosity of the casting solution and the performance of the membranes prepared from the aged casting solution were affected by the storage time. Storage time and filtration treatment of the fiber casting solution had significant effects on the morphology of the resulting membranes. Recently, Khulbe and Matsuura<sup>2</sup> reported that the ultrafiltration (UF) data were erratic when membranes were prepared from casting solutions in their early stage of storage. The data were stabilized after a storage time of 7 days.

In the present communication, we are reporting the data obtained for UF experiments from the membranes prepared by filtered and unfiltered casting solutions at different storage time. We are also reporting the changes in both filtered and unfiltered casting solutions observed by Raman scattering (RS).

### EXPERIMENTAL

Polyether sulfone (PES; Victrex 4100P) supplied by Imperial Chemical Industries (ICI, Billingham, Cleveland, England) was dried at 160°C for 24 h prior to use. A solution of PES (15 wt %) and polyvinyl pyrrolidone (PVP) (15 wt %) in *n*-methyl pyrrolidone (NMP) was prepared. The solution was divided into two parts. One

part of the solution was filtered through a 5- $\mu$ m filter, whereas the other was unfiltered. Both solutions (i.e., filtered and unfiltered) were used as stock solutions. From both solutions, membranes were cast on predetermined days. The details of the techniques for the preparation of the membrane are described elsewhere.<sup>3</sup> The membrane was mounted immediately after the preparation without storage, in a UF cell<sup>4</sup> and compressed under water at 60 psig for at least 20 h before pure water permeation and UF experiments were carried out at 50 psig. The effective area of the membrane was 13.6 cm<sup>2</sup>. The details of UF experiments are described elsewhere.<sup>2</sup> The conditions of the UF experiments were as follows.

Feed (0.1 wt %)	Polyethylene oxide (PEO; Mol. wt. = 100,000) solution
Operating pressure	50 psig
Temperature	Room temperature.

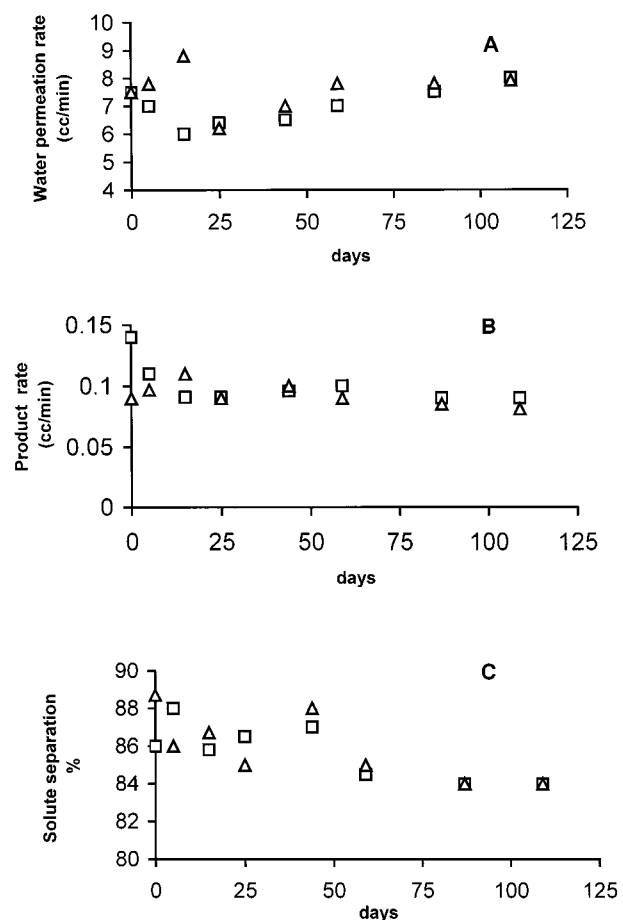
Micro-Raman spectroscopy was used to monitor the change of the polymer solution (casting solution) with time. Raman spectra was excited with a He/Ne laser (Dilor) operated at a power level of 5 mW and a frequency of 615 nm. Polymer solution was placed on a sample stage and a He-laser beam was focused through the whole sample depth (1 cm) (sample was in a small glass container). Each measurement was carried out for exactly 40 s. Raman spectra for filtered and unfiltered polymer solutions were analyzed qualitatively in terms of elapsed time since the beginning of the measurement.

### RESULTS AND DISCUSSION

Figure 1(A–C) shows pure water permeation rate, product permeation rate when the feed solution contains

Correspondence to: K. C. Khulbe.  
Contract grant sponsor: National Science and Engineering Research Council of Canada.

Journal of Applied Polymer Science, Vol. 76, 1485–1487 (2000)  
© 2000 John Wiley & Sons, Inc.



**Figure 1** Effect of age of the unfiltered ( $\Delta$ ) and filtered ( $\square$ ) casting solution on pure water permeation rate (PWP), product rate (PR), and solute separation.

PEO solute, and solution separation, respectively, versus storage time. As mentioned earlier, membranes were prepared from either filtered or unfiltered polymer solutions. From these results, it seems filtration has no significant effect on the performance of the membrane prepared either by unfiltered or filtered casting solution. It also seems that there is no significant effect of storage time on the performance of the membranes.

Casting polymer solution is a heterogeneous colloidal system in which domains of high and low density exists. The suspended polymer particles tend to link up to form a more extended network of large, loose, and ramifying aggregates in the entire solution region during storage for extended periods. Such ramifying structural aggregation immobilizes much of the solvent and imparts greater rigidity to the colloidal suspension as a whole. However, the degree of ramifying aggregation depends on the concentration of the polymer and the structure of the polymer molecule.<sup>1</sup>

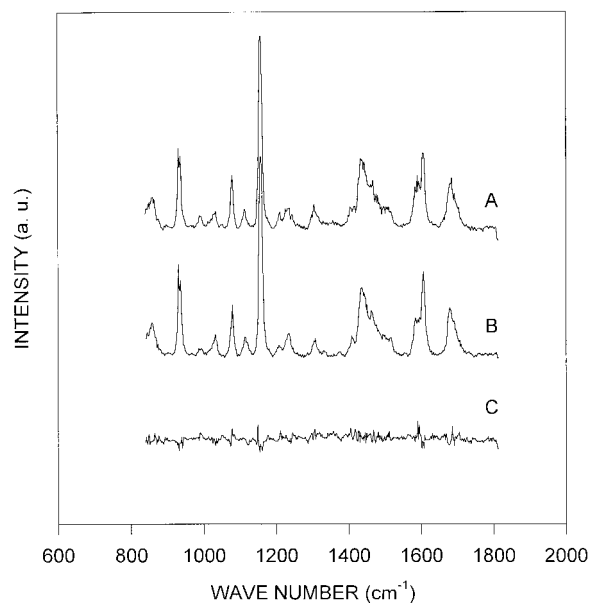
During filtration, the extended structural network of polymer particles created during solution formation

is partly disrupted. Such disruption of the polymer solution structure gives rise to a larger number of discrete polymer aggregates. Ma et al.<sup>1</sup> suggested that an increase in the number of aggregates would yield a larger number of aggregate pores on the skin layer of the resulting membrane and the flux would increase. However, in the present study, no such effect was observed. It could be due to the difference in polymers or the difference in experimental conditions (such as concentration, solvent, property, etc.).

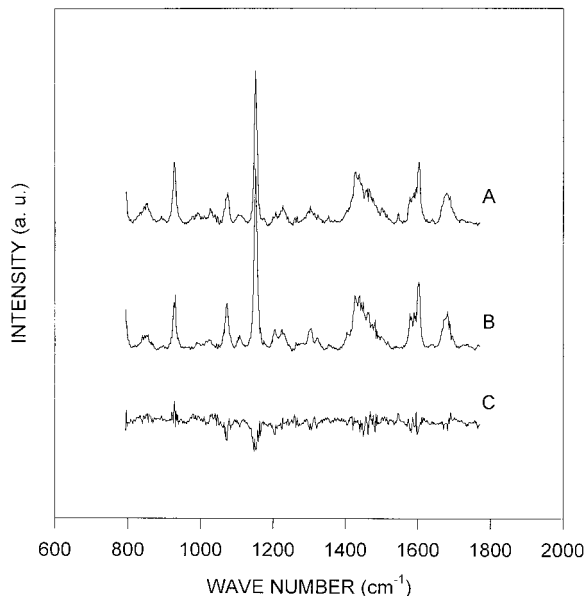
Figure 2 shows the RS spectra of the unfiltered (A) and filtered (B) casting solution at zero storage time and the difference (C) between them. It seems there is no significant difference in the RS between unfiltered and filtered solutions because there are no appreciable (noticeable) signals in (C).

Figure 3(A, B) shows the RS spectra of unfiltered polymer solution at zero storage time and after 109 days storage, respectively. Figure 3 (C) shows the difference of (A) and (B). Similarly, Figure 4(A, B) is the RS spectra of filtered polymer solution at zero storage time and after storage of 109 days, respectively. Figure 4(C) is the difference. From these figures it seems there are significant differences in the RS spectra between the fresh and the stored casting solutions when the solutions are either unfiltered or filtered. The change in RS spectra during storage is due to the change in the configuration of polymer in the casting solution. The nature of configuration change is, however, not clear.

Figure 5(A, B) is the RS spectra of polymer solutions after 109 days storage, when they are unfiltered and filtered, respectively. Figure 5(C) is the difference be-

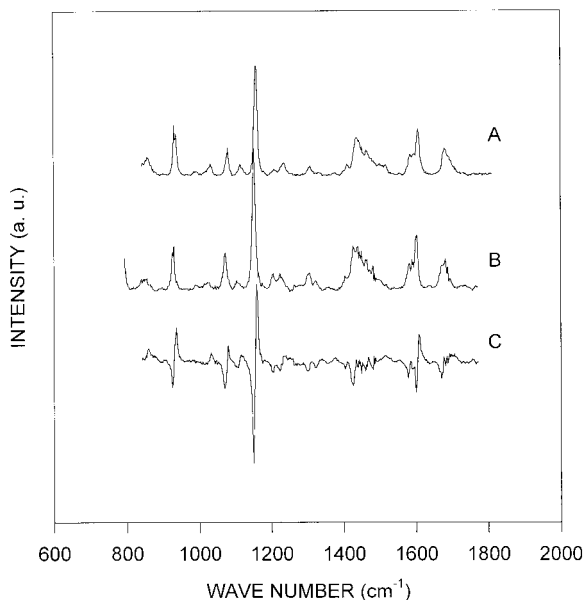


**Figure 2** Raman spectra of polymer solution at storage time zero. (A) Unfiltered; (B) filtered; (C) difference between A and B.

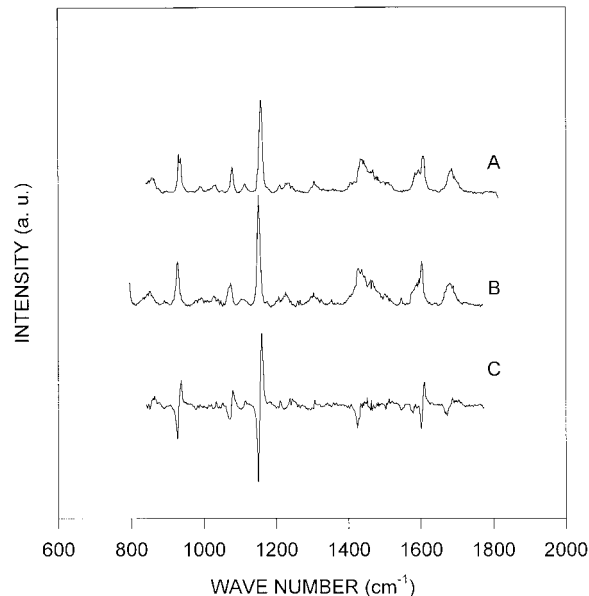


**Figure 3** Raman spectra of unfiltered polymer solution. (A) At zero storage time; (B) after 109 days storage; (C) difference between A and B.

tween (A) and (B). It seems that there is a difference between unfiltered and filtered polymer solution because there are some noticeable peaks in Figure 5(C),



**Figure 4** Raman spectra of filtered polymer solution. (A) At zero storage time; (B) after 109 days storage; (C) difference between A and B.



**Figure 5** Raman spectra of polymer solution after 109 days storage. (A) unfiltered; (B) filtered; (C) difference between A and B.

but the peaks are not as high as in Figures 3(C) and 4(C).

## CONCLUSIONS

From the above experimental results the following conclusions can be drawn. The change in polymer configuration in the casting solution occurs during storage of the casting solution. The change in polymer configuration in the casting solution induced by filtration is not as noticeable as the change during storage. The change in the polymer configuration in the casting solution has no appreciable effect on the UF performance of membranes that are prepared from those casting solutions.

The authors are grateful to the National Science and Engineering Research Council of Canada for their financial support.

## REFERENCES

1. Ma, Xuixiang; Sourirajan, S.; Zhang, H.; Lau, W. Y. *Sep Sci Technol* 1995, 30, 3025.
2. Khulbe, K. C.; Matsuura, T. *J Appl Polm Sci*, to appear.
3. Singh, S.; Khulbe, K. C.; Matsuura, T.; Ramamurthi, P. *J Membr Sci* 1998, 142, 111.
4. Sourirajan, S.; Matsuura, T. National Research Council of Canada No. 24188, 1985, 980.
5. Koenig, J. L. *Chem Technol* 1972, 2, 411.