

DEGRADATION STUDY OF CELLULOSE TRIACETATE HOLLOW FINE FIBER SWRO MEMBRANES*

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ABSTRACT

Cellulose acetate (CA) membranes are prone to chemical attack mainly by operation at improper pH or by chlorine and other oxidizing agents. The chemical attack could lead either to hydrolysis of the pendant acetyl group or to oxidation of polymer backbone leading to chain scission. Hydrolysis can be detected by determining the degree of polymer acetylation, whereas oxidation can be detected by changes in polymer molecular weight as measured directly, for example by the intrinsic viscosity measurement, and/or indirectly by determining polymer tensile strength. In the present study degree of acetylation, intrinsic viscosity and tensile strength measurements, were used for identifying the causes of the poor performance of two cellulose triacetate hollow fine fiber membranes obtained from a commercial SWRO plant after being in operation for 5 years and 2 years, respectively. To establish causes of degradation in the commercial samples, analyses were also performed on fresh virgin fiber, on a second sample exposed to high concentration of chlorine, and a third sample exposed to high pH. By comparison to the virgin sample, it was established that fiber exposure to high concentration of chlorine and to high pH induced decrease in polymer chain molecular weight and in degree of acetylation, respectively. Both the commercial SWRO membranes were found to have undergone both hydrolysis as well as oxidation. However, polymer chain oxidation was established as the major cause for the

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degradation in performance of the commercial sample which was in operation for nearly 5 years, while hydrolysis of the pendant acetyl group was established as the major cause for the degradation in performance of the second commercial membrane sample which was in operation for 2 years. The paper describes the detail of the measurements made and results obtained.

Keywords : Cellulose acetate, RO membranes, Chemical degradation, Degree of acetylation, Intrinsic viscosity and Tensile strength.

1. INTRODUCTION

Cellulose acetate (CA) membranes are widely used in RO desalination industries because of the overall advantages of their properties, cost and ease of use. One of the most outstanding features of CA membrane is their claimed resistance to Cl_2 . However, occasionally the CA membranes exhibited reversible and irreversible deterioration in their performance. Reversible decline, which is usually caused by fouling due to accumulation of scale, suspended solids or microbiological growth, can be restored to some extent by chemical cleaning. However, in cases of irreversible decline, the performance could not be restored and in such cases membrane replacement was required. The irreversible decline is induced either by physical or by chemical membrane damage. Physical damage is caused either by compaction due to creeping, or by scratching or by mechanical causes such as vibration. The major chemical processes of CA membrane deterioration are hydrolysis and/or oxidation. Both hydrolysis and oxidation will lead to poor membrane performance.

CA membranes are most stable at pH 4.7 and the extreme pH, less or above this value, will accelerate the process of hydrolysis of acetyl groups, pendant to the polymer chain. It is reported that deacetylation of cellulose acetate is caused by chlorine at pH 7, in the presence of metal salts. This study [1] revealed that deacetylation was more effective in presence of cobalt and ruthenium, moderately in presence of iron, nickel, rhodium, palladium and silver, and slightly in presence of copper and gold salts. Hydrolysis leads to a reduction in the degree of acetylation, which in turn leads to loss of salt rejection capacity of the RO membranes.

Another major cause for the chemical degradation of CA is oxidation. Oxidation is accelerated at high concentration of oxidizing agents such as chlorine (Cl_2), which is used in RO process as disinfectant [2]. Studies [3,4] indicated that chlorine in presence of heavy metals leads to oxidation as well as sometimes to hydrolysis of CA membranes. Cobalt and copper have a remarkable effect on the deterioration of the CA membranes while iron, manganese and nickel affect membrane performance but to a lesser extent. Also, temperature, pH and chlorine concentration influence CA membrane performance. The effect of oxidation is mainly through the scission of a membrane polymer chain, thus reducing both its molecular weight as well as mechanical strength, resulting in a decline in salt rejection and to an increase in permeate flux of RO membrane. Oxidation can be detected by either mechanical strength measurement and/or by molecular weight determination. Several methods are used to determine the molecular weight of polymers, including intrinsic viscosity, which is directly proportional to the polymer molecular weight.

In this study, because of its simplicity and availability the intrinsic viscosity, the tensile strength measurements and determination of acetyl content were employed to establish the causes of the observed poor performance of two commercial SWRO cellulose triacetate (CTA) hollow fine-fiber (HFF) membranes. For comparison, the performance of a fresh virgin membrane, a known oxidized membrane and a hydrolyzed membrane - each of CTA HFF origin - were also examined by the same three methods.

2. EXPERIMENTAL

2.1 *Materials*

The two commercial SWRO CTA HFF membranes with poor performance are brine side membrane elements. After about 5 years in operation, the first one (Mem #1) had permeate conductivity of 13,480 $\mu\text{S}/\text{cm}$. The second one (Mem #2) after about 2 years in operation, had permeate conductivity of 3,920 $\mu\text{S}/\text{cm}$. Virgin membrane fibers and oxidized membrane fibers were obtained from a membrane manufacturer as well as a new membrane module which was used for the hydrolysis. Both the commercial membranes and the hydrolyzed membrane were autopsied and samples were collected from inner, middle and outer portions for detailed analyses.

The hydrolyzed CTA membrane was prepared by continuously operating a new SWRO CTA HFF membrane element (size 5" × 20") for about 375 hours in recirculation mode using non-chlorinated raw seawater feed with a SDI ≈ 4.5. The pH of the feed was maintained at about 9.5 by adding NaOH when required. The temperature was maintained below 33°C at feed pressure of 55 to 60 kg/cm² and at brine flow rate of 5 l/min. The membrane performance (flow and conductivity) was continuously monitored until the performance of the membrane was remarkably reduced. At the end of the experiment, membrane was cleaned with sulfuric acid at pH of 2 to remove any alkaline scales present on the surface of the membrane. After flushing the membrane by dechlorinated potable water, the membrane was removed and autopsied, and samples were collected for further analyses. Before carrying out any analysis all the membranes cut were thoroughly cleaned with distilled water for about 15 hours.

2.2 Degree of Acetylation

Acetylation degree of membranes, which is normally expressed as percentage of an acetyl group in the polymer, was determined using standard ASTM procedure with a slight modification [5]. In this method, a known amount of membrane sample (0.7 g) was first added to 70 ml of acetone in an Erlenmeyer flask and was continuously stirred using a magnetic stirrer for 1 hour, followed by adding 5 ml of methanol. After 30 minutes of additional stirring, 1N NaOH was added in excess (15 ml), to the highly swollen (not completely soluble) membrane sample solution and stirred for another hour. After adding hot (60°C) distilled water for washing down the sides of the flask and continuous stirring for another 10 minutes, the unreacted excess amount of NaOH was titrated against standard sulfuric acid (0.5 N) using phenolphthalein indicator. When the pink color disappeared completely, an excess (0.2 - 0.3ml) of sulfuric acid was added and re-titrated with 0.1 N NaOH. For each sample, a duplicate was also carried out as well as two blank analyses. The acetylation degree was then calculated as the percentage weight of combined acetic acid formed to the total weight of membrane polymer during hydrolysis by the excess NaOH.

2.3 Stress Strain Measurements

Instron Series IX automated Materials Testing System, Series 4200 Interface, was used to measure the tensile properties. Hollow fine-fiber samples of 7 - 8 cm in length were soaked in distilled water prior to the tensile measurement. To prevent the fibers from drying, distilled water was sprayed on to the fiber while running the test. The test conditions were as follows:

Number of test specimens	10
Sample length between the grips	2 cm
Cross head speed	2 cm/min.

Percentage elongation and tensile strength at break were automatically calculated by the computerized Instron for each of the fibers.

2.4 Intrinsic viscosity measurement

The intrinsic viscosity $[\eta]$, which is related to the polymer molecular weight, was determined following the standard procedure [6]. An Ubbelohde - type capillary viscometer was used at a constant temperature of $30 \pm 1^\circ\text{C}$. After determining the efflux time (t_o) for the solvent methylene chloride/ methanol (9/1) mixture, the same (t_i) was determined for the known concentration of the sample. For each concentration of sample, five measurements were made and average of three measurements was taken after discarding both the lowest and highest readings. The measurements were made at different concentrations for each sample by successive dilution using the above solvent. The intrinsic viscosity $[\eta]$ was then obtained as intercept of the plot of η_{sp} / c against c , where c is concentration (g/dl) of membrane sample and η_{sp} is specific viscosity. The specific viscosity can be obtained from relative viscosity (η_{rel}) as $\eta_{rel} - 1$. The η_{rel} can be determined from the efflux time of solvent t_o and sample t_i as $\eta_{rel} = t_i / t_o$.

3. RESULTS & DISCUSSION

3.1 Degree of Acetylation

The degree of acetylation for all the tested membrane samples, i.e., virgin, oxidized, hydrolyzed, and two commercial samples with poor performance, are shown in [Figure 1](#). For all the membrane samples analyzed, the difference between different portions (i.e., inner, middle and outer) of the membrane was found to be not significant as can be

seen from the figure. It is very clear from the figure that the hydrolyzed membrane is definitely having lower degree of acetylation (acetyl content) than that of the virgin or the oxidized membranes, where no hydrolysis is supposed to take place. The commercial membrane (Mem #1) which was in operation for nearly 5 years showed only a slight loss (about 1.4%) in degree of acetylation, whereas the Mem #2, which was in operation for about 2 years, showed a remarkable loss in degree of acetylation (about 5%), indicating a severe degree of the membrane polymer hydrolysis. Thus, it can be said that the hydrolysis was the main reason for the poor performance of Mem #2 and the observed slight hydrolysis of Mem #1 which somewhat contributed to its poor performance.

3.2 Tensile Strength

The membranes tensile strength and percentage elongation at break are shown in [Figures 2 & 3](#). Both the percentage elongation and tensile strength show the same trend in that a reduction in the membrane polymer molecular weight, resulting from polymer chain scission by oxidation is noted for the Mem #1 and Mem #2 samples but not for the virgin or hydrolyzed membrane fibers. The tensile strength of the oxidized fibers could not be evaluated as the fibers were too brittle for the measurement, indicating that the membrane polymer is highly oxidized. A maximum value of tensile strength and percent elongation at break are noted, as expected, for the virgin membrane fibers, and with comparable values for the hydrolyzed membrane. Thus proves that the latter membrane did not undergo any sort of oxidation leading to membrane polymer scission. Hydrolysis removes the pendant acetyl group and is not expected to affect the chain backbone, which is responsible for the polymer strength. By comparison to virgin membrane, the tensile strength and percent elongation of Mem #2 were 48% and 60%, respectively, of that for the virgin fibers, indicating membrane polymer oxidation. The tensile strength and percent elongation of Mem #1 were found to be much lower than those of Mem #2, i.e., only 24% and 10%, respectively, of that of the virgin fibers ([see Figures 2 & 3](#)). Thus, it can be said that both the commercial membranes have undergone oxidation, and that Mem #1, which was in operation for nearly 5 years, was highly oxidized, more so than Mem #2.

3.3 *Intrinsic Viscosity*

Intrinsic viscosity measurement results support the tensile strength results (see Figure. 4). As expected, virgin membrane was found to have the maximum value of intrinsic viscosity (1.24 dl/g) and the oxidized membrane had the lowest value (0.30 dl/g). For hydrolyzed membrane, the intrinsic viscosity was found to be about 1.24 dl/g, indicating that the membrane did not undergo any oxidation, thus confirming the results obtained by tensile measurement. Intrinsic viscosity of Mem #2 could not be measured because the fibers were not soluble in the solvent (methylene chloride/methanol mixture). This was obvious, because it is known that the solubility of cellulose acetate polymers in a particular solvent is strongly influenced by the degree of acetylation [7]. The degree of acetylation measurement results indicated that Mem #2 had a lower degree of acetylation compared to all the other membranes analyzed, thus making it insoluble in the solvent by altering the solubility property of the polymer. The Mem #1 sample showed a remarkable reduction in intrinsic viscosity (0.72 dl/g) indicating that membrane polymer molecular weight was decreased by polymer chain scission due oxidation, thus supporting the tensile study that the membrane was oxidized.

4. CONCLUSION

By comparison to virgin sample, it was established that same CTA HFF membrane exposure to high concentration of chlorine and to high pH induced decreases in polymer chain molecular weight and in degree of acetylation, respectively. It was found that both the commercial membranes, Mem #1 and Mem #2, which were in operation for 5 years and 2 years, respectively, underwent both oxidation as well as hydrolysis. However, polymer chain oxidation was the main cause for the degradation in performance of the Mem #1 commercial sample, whereas hydrolysis of the pendant acetyl group was established as the major cause for the degradation in performance of commercial membrane sample Mem #2.

5. ACKNOWLEDGEMENT

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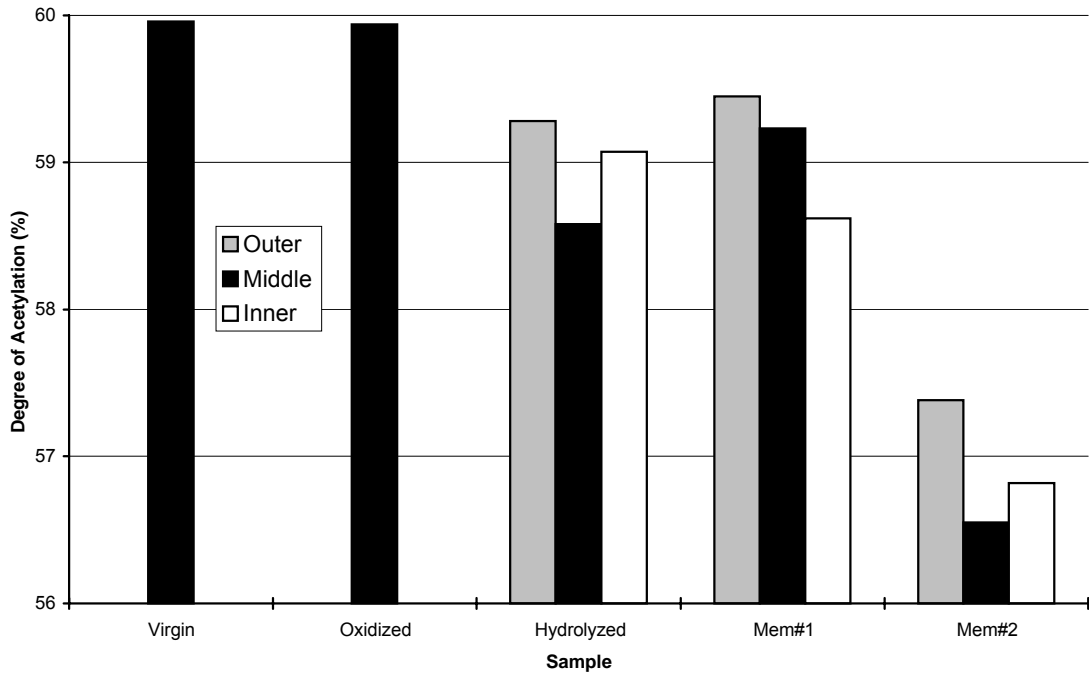


Figure 1. Degree of Acetylation of Various Membrane Samples

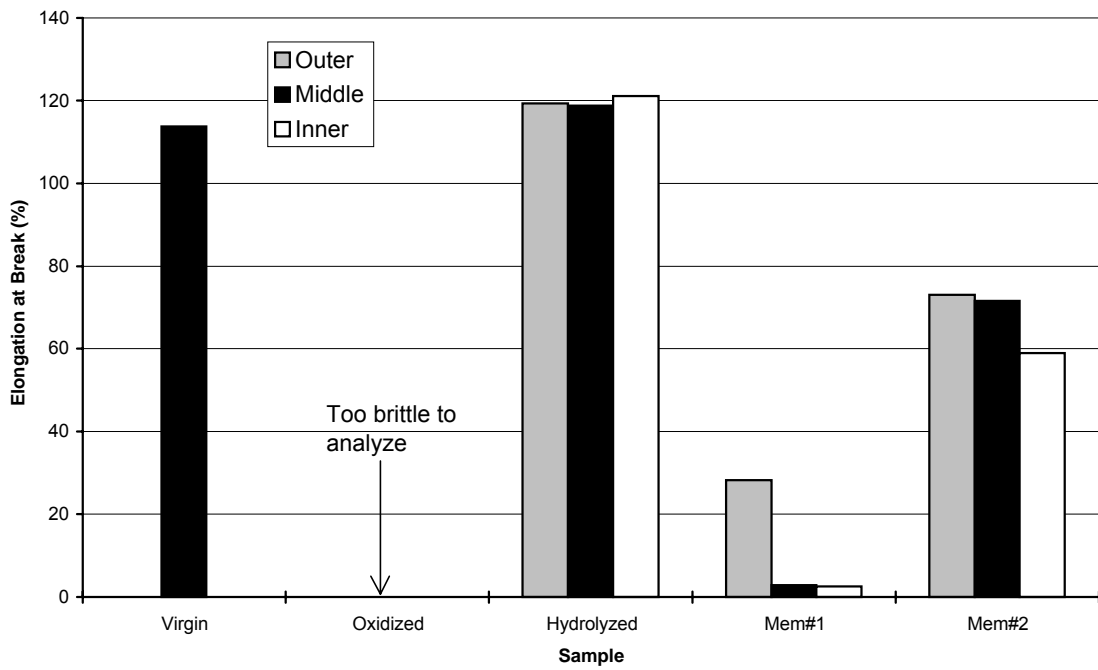


Figure 2. Percentage Elongation at Break for Various Membrane Samples

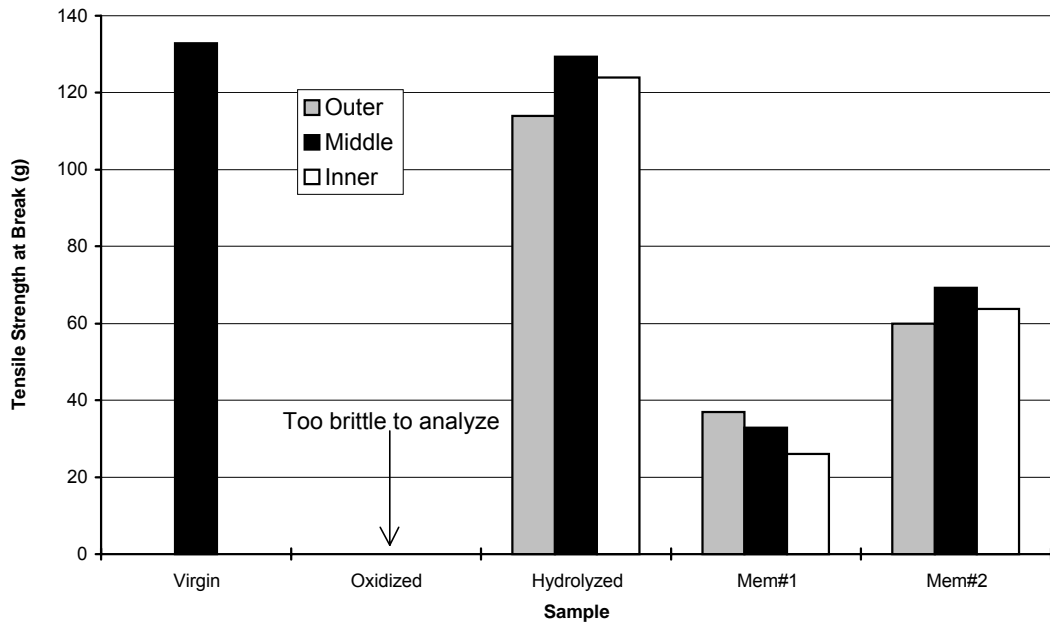


Figure 3. Tensile Strength at Break of Various Membrane Samples

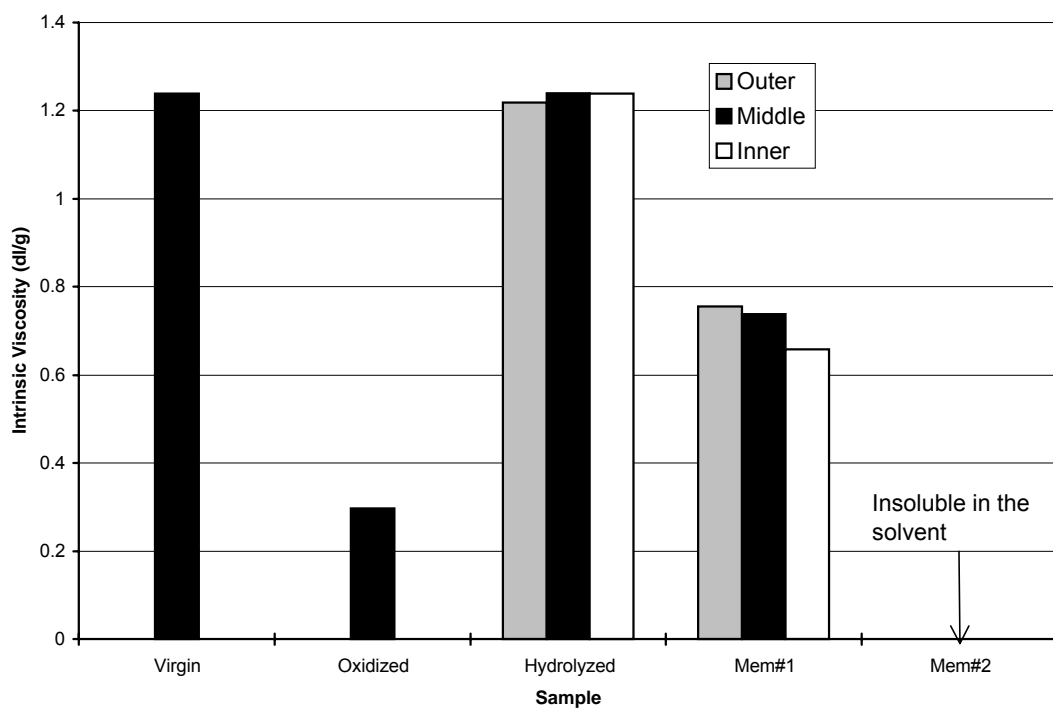


Figure 4. Intrinsic Viscosity of Various Membrane Samples

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