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Desalination and Water Purification Research
and Development Program Report No. 184

Membrane Structural and Transport Fundamentals for Augmenting Traditional Water Supplies



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14. ABSTRACT This project used Penn State's spectroscopic tools to the characterize Dow reverse osmosis (RO) membranes that were fabricated using their pilot-scale processing technology for thin film composite polyamide RO membranes. We analyzed many different sample sets provided by Dow and now have a solid foundation and framework for analyzing the fingerprint region of the spectra as we start to move into further analysis and materials systems.					
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**Prepared for the Bureau of Reclamation Under Agreement No.
R13AC80018**

by

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**U.S. Department of the Interior
Bureau of Reclamation
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Mission Statements

The U.S. Department of the Interior protects America's natural resources and heritage, honors our cultures and tribal communities, and supplies the energy to power our future.

The mission of the Bureau of Reclamation is to manage, develop, and protect water and related resources in an environmentally and economically sound manner in the interest of the American public.

Disclaimer

The views, analysis, recommendations, and conclusions in this report are those of the authors and do not represent official or unofficial policies or opinions of the United States Government, and the United States takes no position with regard to any findings, conclusions, or recommendations made. As such, mention of trade names or commercial products does not constitute their endorsement by the United States Government.

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Acronyms and Abbreviations

°C	degree Celsius
DMF	dimethylformamide
FTIR	Fourier Transform Infrared Spectroscopy
RH-TGA	relative-humidity thermogravimetric analysis
Reclamation	Bureau of Reclamation
RO	reverse osmosis

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1. Goals and Objectives

This project used Penn State's spectroscopic tools to characterize Dow reverse osmosis (RO) membranes that were fabricated using their pilot-scale processing technology for thin film composite polyamide RO membranes. Penn State focused on water hydrogen bonding and water-polymer interactions to explain experimentally observed flux and rejection measurements conducted by Dow. In all, we measured more than 26 samples with systematic variations in composition.

2. Sample Preparation and Measurement Background

The supported active layers of the thin film composite membranes were removed from the nonwoven fabric so that just the polysulfone and polyamide layer remained. The remaining two-layered membrane was placed in a funnel lined with filter paper and washed with sufficient dimethylformamide (DMF) to remove the polysulfone layer. To remove the DMF, the remaining polyamide layer was washed with water and then methanol. The polyamide fibers were placed onto a calcium fluoride crystal and allowed to dry at 50 degrees Celsius ($^{\circ}\text{C}$) under vacuum for 20 hours.

This procedure produces fibrous samples with enough mass to employ our established Fourier Transform Infrared Spectroscopy (FTIR) and gravimetric uptake methods. However, there is a question as to whether or not the fibrous nature of the delaminated samples that have been exposed to DMF truly represents the state of the material. The polyamide active layers are highly crosslinked and thus have a very high T_g that may not be plasticized by solvents such as DMF. However, we have not fully explored the samples' preparation or procedure systematic errors that may be introduced using the delamination and solvent washing technique employed so far in this work.

This project examined how the water uptake values, transport measurements and water-polymer interaction measures relate to one another. Water uptake values were measured using both FTIR and relative-humidity thermogravimetric analysis (RH-TGA) methods discussed in the previous report. Transport measurements include flux and salt passage and were measured by Dow. To measure the water-polymer interacting, the derivative peak was obtained by comparing the fully hydrated sample to the dry sample. The magnitude of the peak yields information about how much water is interacting with that specific polymer peak. This study provided the basis for developing a peak fitting routine can be applied to all spectra is being developed. Peak fitting will allow for a better understanding of the populations of water in each microenvironment.

3. Experiments and Results

The initial FTIR experiments on Samples 1 and Sample 2 are shown in Figure 1. These two samples were used to determine the peak assignments in Table 1. These assignments were used for the remainder of the project.

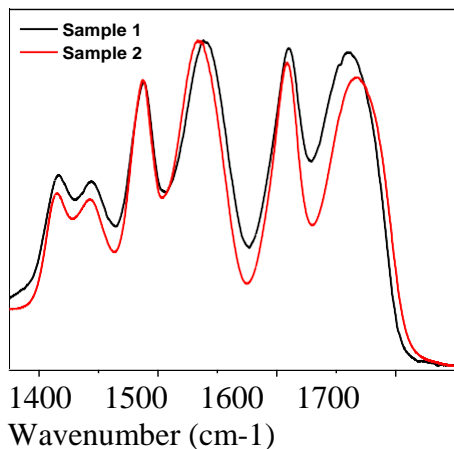


Figure 1.—Original FTIR on samples 1 and 2.

Table 1.—Peak Assignments for Polyamides

Wavenumber (cm ⁻¹)	Assignment
1720	Carboxylate C=O
1661	stretching Amide C=O
1608	Aromatic ring breathing
1537-1415	Amide II, N-H bending and C-N stretching

The samples numbered 3-7 allowed us to extend the scope of the FTIR measurements on a range of new Dow custom-made samples that varied in carboxylate content. Our goal was to compare the Dow commercial samples to these new chemistries and determine how the membrane composition influences the water-polymer interactions. Our major findings showed that there is some effect of membrane chemistry on the OD stretch, but it is subtle and there is overlap with the ND resonance which will require further analysis (Figure 2 as an example). Interestingly, we found that the ND peak is easily observed when the samples are exposed to HOD or D₂O.

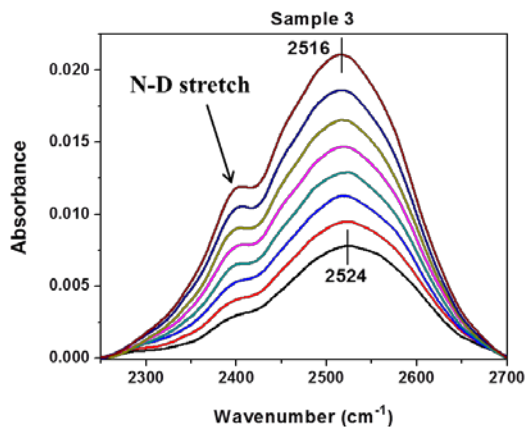


Figure 2.—ND stretch in Sample 3 compared to reference sample.

We have determined that the shoulder at $\sim 2,410\text{ cm}^{-1}$ in the OD region is a result of the deuterium atoms in HOD exchanging with the NH of the amide to form ND. It is well-documented that polyamide membranes will undergo H-D exchange at room temperature when exposed to D_2O vapor, and the exchange appears to occur readily in our experiments. The ND stretch in polyamides appears as a doublet with peaks at $\sim 2,420\text{ cm}^{-1}$ and $\sim 2,470\text{ cm}^{-1}$ and has been used to determine the crystallinity of aliphatic polyamide (nylon) films.

The derivative, or difference spectrum between the wet and dry spectrums, gives insight into how the peaks in the fingerprint region shift when the polymer is hydrated. This information can be used to determine which functional groups on the polymer backbone interact most strongly with water or how backbone interactions change with hydration. These functional group peak shifts can be small, and examining the derivative spectrum can help determine the magnitude of the interaction. The derivative maximum corresponds to an increased interaction of water with the functional group while a derivative minimum corresponds to a decreasing noninteracting functional group. Therefore, the magnitude of the derivative peak can be used as an indicator of the increased interaction between water and various function groups in the polymer.

Derivative peaks were obtained by subtracting spectra of the dry samples from the spectra of the hydrated samples. The magnitude of the derivative peak (maximum to minimum) was obtained by normalizing the derivative magnitude by the absorbance intensity of the OD stretch peak to account for water uptake differences in each sample.

The fingerprint region of the spectra (both wet and dry) for sample 3 is shown in Figure 3. The peak corresponding to the carbonyl of the amide at $1,661\text{ cm}^{-1}$ and the amide II peak at $1,537\text{ cm}^{-1}$ both appear to shift as hydration increases. The derivative spectrum, shown to the right, confirms these shifts. The larger the magnitude, the more water is interacting with the functional groups.

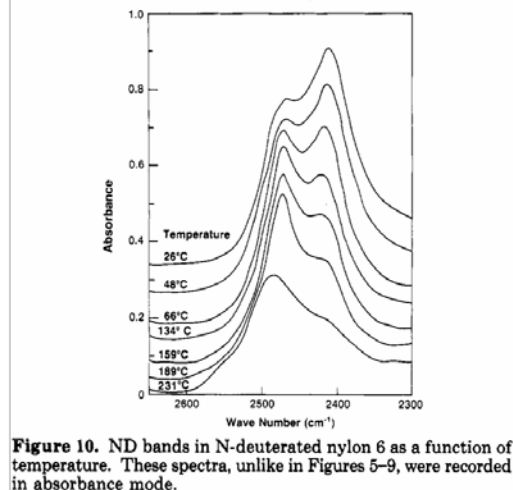


Figure 10. ND bands in N-deuterated nylon 6 as a function of temperature. These spectra, unlike in Figures 5–9, were recorded in absorbance mode.

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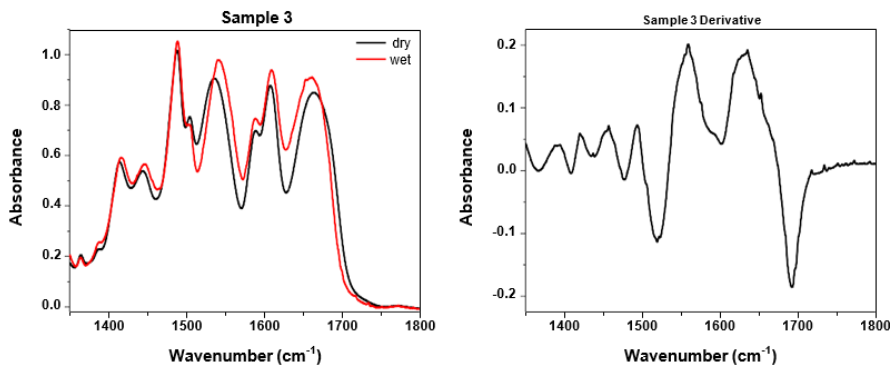


Figure 3.—Sample 3 derivative.

Figure 4 shows how water uptake and the normalized derivative peak are related in all four sets of samples from Dow. In most of the samples sets, there is a trend that the more water the polymer absorbs (higher WU), the less water is interacting with the functional groups on the backbone (lower derivative peak). This result may be an indication of the formation of hydration pockets in the higher water uptake materials and points to heterogeneity between backbone regions and hydrated regions.

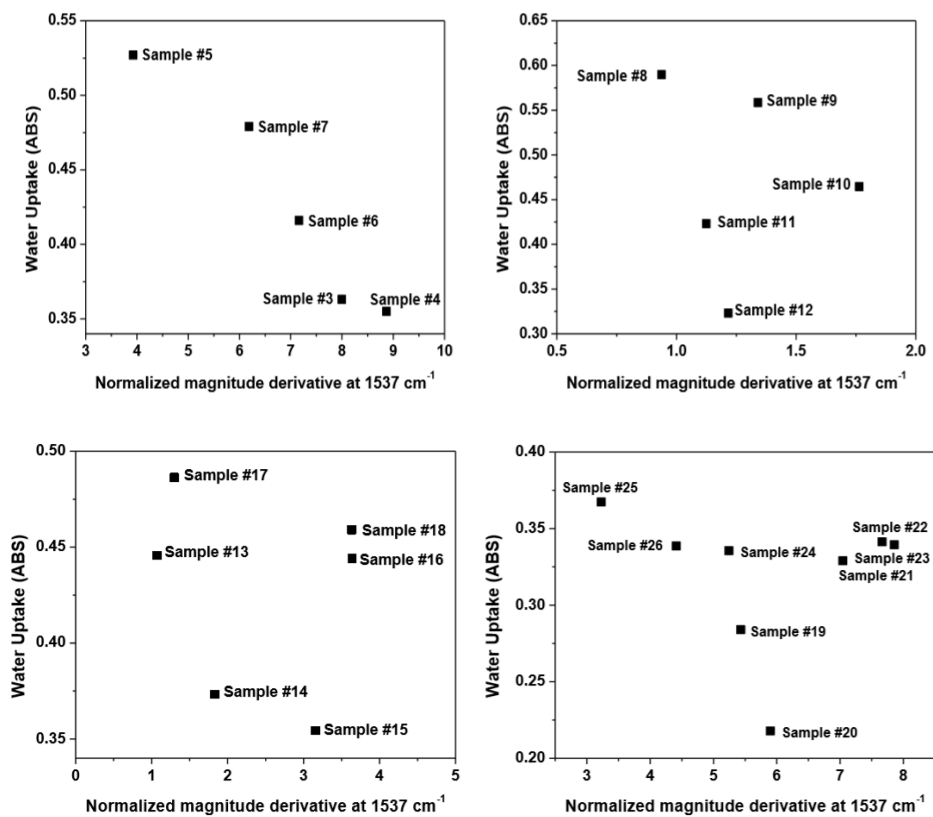


Figure 4.—Normalized magnitude derivatives.

We have seen this type of behavior previously with cation and anion exchange membranes, and we hypothesize that this is related to the existence of water filled cavities instead of water simply hydrating the functional groups, as shown in Figure 5.

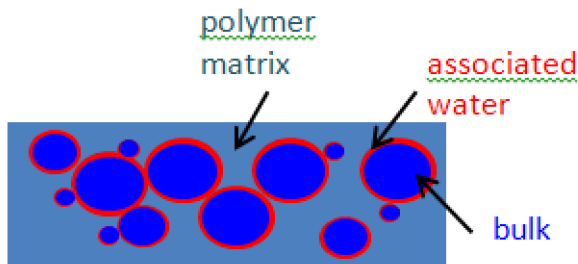


Figure 5.—Schematic of water-filled cavities.

Figure 6 is a sample of the peak fitting routine where we used three peaks to fit the raw data. The blue peak corresponds to signatures from the N-D region. These were included to account for the N-H of the amide exchanges with the deuterium in the water. We observed vibrations from the N-D stretch. The red peak represents bulk water (i.e., water molecules that are interacting with other molecules). The purple peak corresponds to water interacting with the amide functional groups. We expect this peak to be at a higher frequency than the bulk water peak because the hydrogen bond formed between water and the amide should be weaker than the water-water hydrogen bond. The green peak is the cumulative fit, which shows that our routine does not fully capture the N-D side of the raw data, but that the routine does a very good job of fitting the rest of the OD peak.

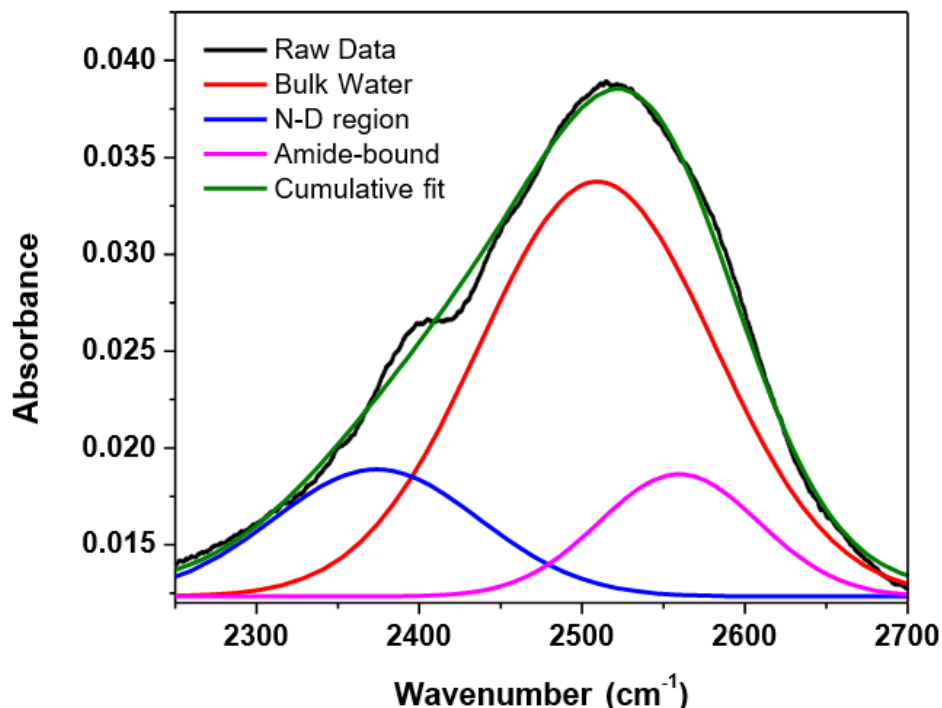


Figure 6.—Sample of the peak fitting routine.

4. Conclusions

In summary, we analyzed many different sample sets provided by Dow and now have a solid foundation and framework for analyzing the fingerprint region of the spectra as we start to move into further analysis and materials systems. Water filled-cavities are the main constant through all the data. When comparing the water uptake values with the normalized derivative peaks, the four sample sets show a general trend that the more water the polymer uptakes, the less water is interacting with the functional groups. This is a huge step in understanding how the water-polymer interactions affect transport properties in the polyamide active layer.

Appendix: Sample Runs

Samples Received and Measured

Low water flux Dow commercial sample, termed “sample 1”

High water flux Dow commercial sample, termed “sample 2”

Sample 3- low IEC Sample 4

Sample 5

Sample 6

Sample 7- high IEC

Sample 8-low IEC, high XL density Sample 9

Sample 10

Sample 11

Sample 12-high IEC, low XL density

Sample 13-high XL density Sample 14

Sample 15

Sample 16

Sample 17-low XL density Jan.– Mar. (Q2) report

Sample 19- Classical chemistry-morphology change to affect flux and rejection

Sample 20

Sample 21

Sample 23

Sample 24

Samples 25

Samples 26