

Surface modification of PAN membrane by chemical reaction and
physical coating: comparison between static and pore-flowing
procedures.

Yang Qin, Hu Yang*, Zhenliang Xu, Feng Li

Membrane Research Center, Chemical Engineering Research Institute,
East China University of Science and Technology, Shanghai 200237,
PR China.

Corresponding Author: Hu Yang

Table of content

| | |
|--|----|
| The separation property of ETA modified PAN membranes by static method at different temperature. | S1 |
| Contact angle of ETA modified PAN membrane by static procedure | S2 |
| Mechanical properties of ETA modified PAN membrane by static procedure | S3 |
| BET results and pore size distribution of modified membranes | S4 |
| Pore size distribution | S5 |
| Experimental materials | S6 |
| ETA modification mechanism | S7 |

* Corresponding author, Chemical Engineering Research Center, East China University of Science And Technology, Shanghai, China, Email: hyang@ecust.edu.cn, Tel: 021-64252989

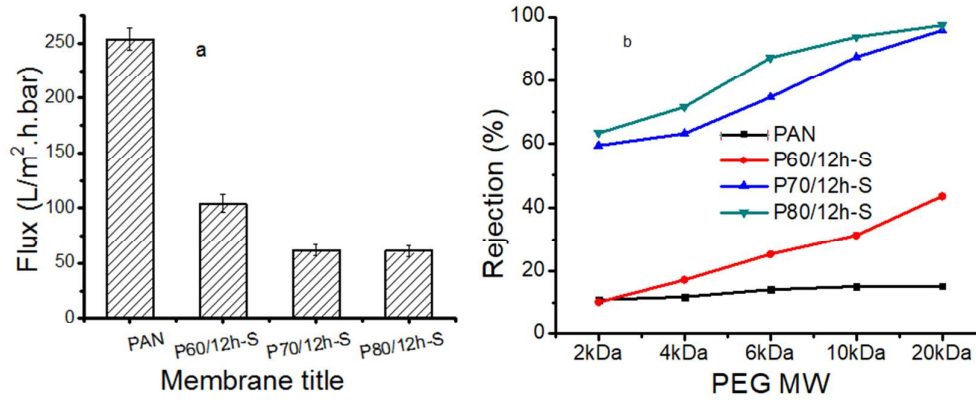


Figure S1. The flux(a) and rejection(b) of ETA modified PAN membranes by static method at different temperature, using 6% ETA aqueous solution.

Form the data, it can be concluded that the flux firstly decreased then increased with the modification time. The flux decrease of membrane was due to the thermal motion of PAN chains. Since polymer has a low thermal-resistance. When treated at high temperature, the free molecular motion of polymer will deform the porous structure of membrane. After modification, the improved affinity to water caused the adsorption of water into polymer membrane, which impeded the shrinkage of the porous structure.

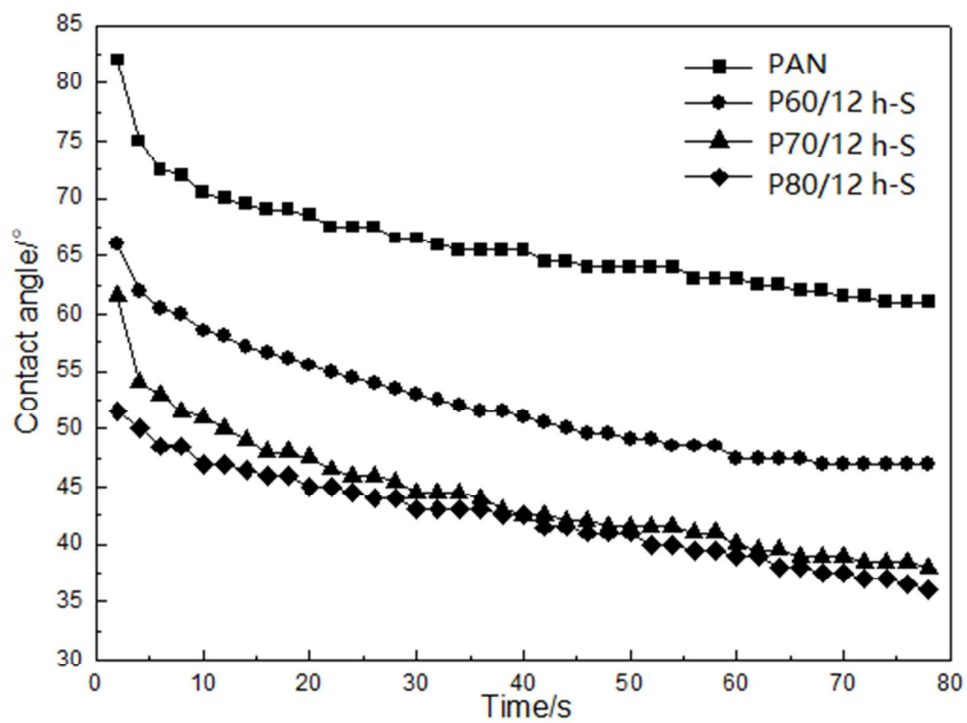


Figure S2. Contact angle of ETA modified PAN membrane by static procedure.

PAN membrane showed a hydrophobic property. After the modification at different temperature, the CA decreased obviously with temperature. Such a decreased CA trend proved the increased modification degree at the high temperature, which means that the higher temperature is favorable for the modification.

The mechanical properties of the membranes were conducted by using Microcomputer Digital Display Integrative Control Testing Machine (QJ210A, Shanghai Qingji Instrument Sciences and Technology Co. Ltd., China) at ambient temperature. The flat sample with the width of 15cm was clamped at both ends and pulled in tension at a constant elongation speed of 50mm/min with an initial length of 25cm. Three measurements was averaged.

Table S1. Mechanical properties of ETA modified PAN membrane by static procedure.

| Membrane No. | Tensile strength /MPa | elongation /% |
|--------------|--------------------------|------------------|
| PAN | 2.15±0.17 | 15.29±2.2 |
| P60/12h-S | 2.23±0.24 | 13.71±2.1 |
| P70/12h-S | 2.59±0.21 | 6.77±1.5 |
| P80/12h-S | 2.64±0.17 | 9.1±1.8 |
| P70/24h-S | 2.45±0.25 | 13.53±2.8 |
| P80/24h-S | 2.23±0.13 | 12.23±2.1 |

No big difference in the mechanical properties can be observed. If examined in detail, a slightly increase in the tensile strength can be found for modified membranes, which could be due to the shrinkage effect.

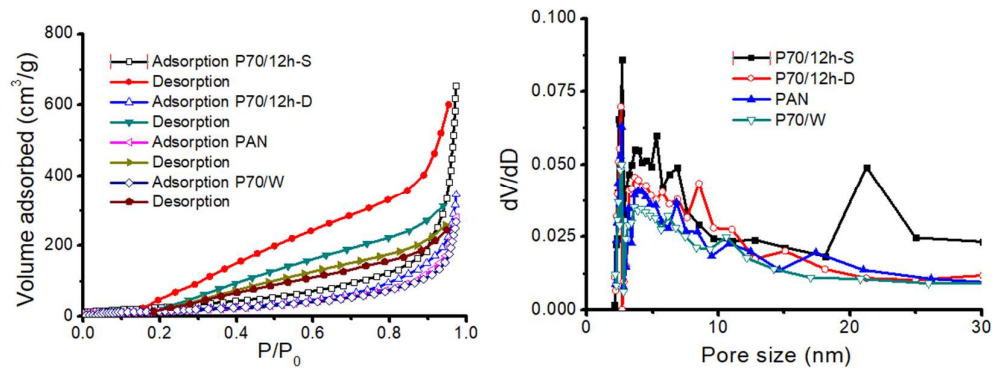


Figure S3. BET results (left) and pore size distribution(right) of pure PAN membrane and modified membranes through different procedures.

Nitrogen adsorption-desorption experiments was carried out by JW-BK122F (Beijing JWGB Sci.&Tech.). The pore structure feature of modified membrane was evaluated by N₂ adsorption/desorption measurement. The surface area are calculated according to the Brunauer, Emmett and Teller (BET) adsorption isotherm equation. Pore size distribution and specific pore volume was calculated by BJH method.

Nitrogen adsorption-desorption experiments could reveal a statistic result, unlike SEM measurement, which is easier to be affected by the sampling process. P70W showed the lowest surface area. P70/12h-S had the largest surface area and an irregular pore size distribution. This result is in agreement with our above discussion since the pore structure is strongly related to the modification process. here, porous structures include those in the cross-section of membrane. During static modification, PAN membrane was in a free state to correspond to the outside conditions. While during pore-flowing process, PAN membrane was influenced by the kinetic property of both the flow and the reaction process. That is why those membranes showed different structure properties.

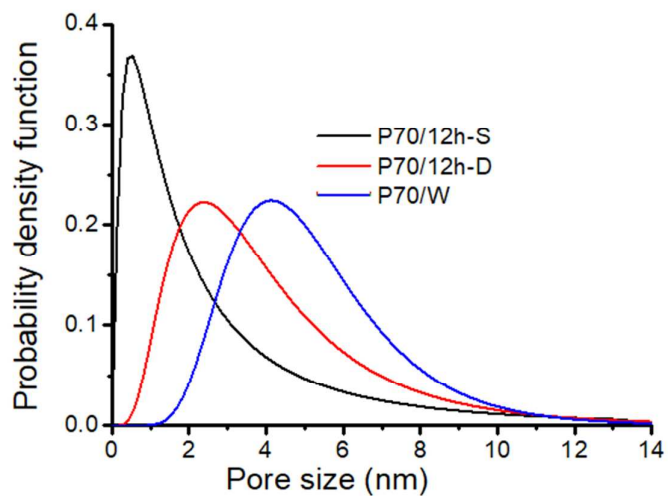


Figure S4, Pore size distribution calculated from the rejection data of membrane.

Pore size distribution was calculated according to the rejection data. It can be concluded that membrane modified by Pore-flowing procedure has the largest surface pore size. This means that treatment procedure has different influence on the structure of the modified membrane. Moreover, they have a broad pore size distribution, the reason is related to the PAN base membrane.

Experimental Materials

PAN (MW: 50 kDa) was supplied from shanghai petrochem. It was dried at 70 °C for 30 min before use,. (DMSO), (purity: >99%) , ethanolamine (ETA) were purchased from Sinopharm Chemical Reagent Co. (SCRC) Company. Polyethyleneglycols (PEG) of different molecular weights (10, 20 and 35 kDa) and bovine serum albumin (BSA, Mw: 67 kDa) were used as received. Polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP)(k17) and chitosan (CS) were purchased from Alladin company.

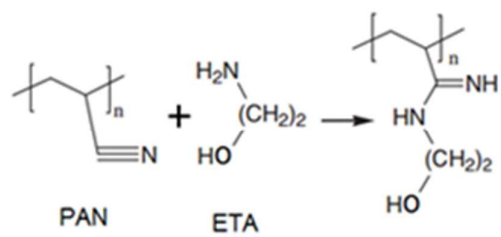


Figure S5. ETA modification mechanism