

Comparative Study of Swelling Behavior and Contact Angle of Amidoximated Polyacrylonitrile Membranes

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Abstract: Membranes of amidoximated polyacrylonitrile swells in water. Treatment of water through membrane technology is a most common method being used now a days. However physiochemical treatments have their own importance in water quality analyses¹. The microbial infection of water, leads millions of people die worldwide every year causes great concern. Copolymerization of acrylonitrile (AN) and acrylic acid (AA) were performed at 65° C under nitrogen gas environment. Prepared membranes were fabricated into DMP. During amidoximation process, a part of nitrile groups of copolymer is converted into amidoxime groups. FTIR spectroscopy is used to confirm the copolymerization of poly (AN-co-AA) and chemical modification of poly² (AN-coAA). Surface characterization of amidoximated acrylic copolymer membrane is done by contact angle (CA) and swelling behavior. Water CA measures surface hydrophilicity by measuring how much a droplet of water spreads on the surface and swelling behavior. The amidoximated copolymers were confirmed to be more hydrophilic than the virgin membrane. Characterized has also done by various techniques such as FTIR, XRD, TGA, SEM, DSC, EDX etc^{3,4}. In this paper comparative study of swelling behavior and contact angle of virgin as well as amidoximated copolymer is done.

Keywords: Swelling behavior, contact angle, wettability, hydrophilicity.

1. Introduction

Treatment of water resources of all areas needs a serious and immediate attention. Physiochemical treatment as well as microbial treatment both play important role with respect to quality of water. Conductivity and total dissolved solid of water are the two important parameters to measure the salinity level of water¹⁻⁵. In present research work swelling behavior and

contact angle of virgin as well as amidoximated copolymers is shown. Drinking water must not contain harmful chemical substances and pathogenic microorganisms that may be harmful to human health⁶. Membranes emerged as a viable means of water purification in the 1960s with the development of high performance synthetic membranes⁷. AN has been a subject of interest among researchers for many decades. Some disadvantages consist of low moisture absorption, moderate hydrophilicity and poor wettability of PAN membranes, which lies due to hydrophobic nature of nitrile group and compactness of the structure. In this situation, polymer modification appears as an attractive way to obtain polymers with desirable properties⁸. A sharp enhancement in the amidoximation at 80°C is observed⁹. The membranes containing acrylamide were found to be more hydrophilic and showed higher transmission of fluids and flux recoveries than the virgin acrylonitrile membrane¹⁰. The cyano group in AN/MA copolymer beads were converted to AO by reaction with HA to remove metal ions in aqueous solution¹¹. Amidoximated AN/MA with amidoximation temperature 70°C and amidoximation time 20 hr h pH 5.0 has a relatively higher adsorption capacity for¹² Ag⁺. CA measurement has been used in the study of surface energy, wettability and adhesion of low surface energy materials. The most important relation regarding the CA is the Young's equation¹³ ($\gamma_l \cos\theta = \sigma_s - \gamma \sigma_l$). PAN concentrations have a significant effect on the wettability of the nanofiber mats as determined by the CA measurements. The increase in concentration from 6 to 12% of PAN increases the hydrophobicity of the mats rendering them considerably hydrophobic¹⁴. Surface providing water CA lower than 60° are considered to be hydrophilic whereas contact angles higher than 90° are regarded as hydrophobic and super-hydrophobic with the CA exceeding¹⁵ 120°. It was observed that the oxyflurinated PAN showed less water CA compared to untreated PAN while total surface free energy of PAN membrane increased¹⁶. Styrene grafted onto PAN shows greater CA than virgin PAN¹⁷. Higher hydrophilicity is characterized by the lower values of CA whereas higher values of CA indicate the hydrophobicity of surfaces¹⁸. Different processes as Polymerization, Molecular Weight Determination, Fabrication of Copolymer, HA and AO Content Evaluations have already published³. The characterization of virgin and amidoximated acrylic copolymer membranes were carried out by using various techniques such as XRD, FTIR, TGA, SEM, DSC and EDX. The most favorable conditions to get best AO content are HA concentration 3%, acrylic acid concentration 2%, temperature 80°C and reaction time⁴ 3h. CA is the most convenient and surface sensitive analysis to assess the hydrophilic-hydrophobic properties

of polymer surface and provides information based on the interaction of energy between the polymer surface and liquid.

2. Objective

- (i) Study of swelling behavior of virgin as well as amidoximated copolymer.
- (ii) Comparative study of swelling behavior and contact angle of virgin as well as amidoximated copolymer.

3. Materials, Instrumentation and Method

Acrylic acid (AA), Acrylonitrile (AN), α Azobisisobutyronitrile (AIBN), Toluene, Diethylether, Dimethylformamide (DMF), Silver nitrate (AgNO_3), NaOH, HCl and Polyvinyl alcohol (PVA). All the chemicals used were of Anala R grade and procured from Sigma Aldrich and Fluka. Solvents were dried and distilled before use according to standard procedure. The chemicals were used without further purification. Some processes like Molecular Weight Determination, Polymerization, Hydroxylamine Treatment, Fabrication of Copolymer etc. have been already published. Kruss K100 tensiometer (Hamburg Germany) was used for CA measurements of film using static sessile drop method. Swelling behavior of AA copolymer membranes is explained by plotting a graph between swelling percentage with increasing percentage of AA with the copolymer membranes having AO content 3.3 meq g^{-1} . Swelling behaviour of copolymer membranes having AO content 3.3 meq g^{-1} was performed with distilled water in water bath. For bulge size, the dry membrane was immersed in water at different temperatures and timings. The excess of water on the membrane surface was removed by filter paper and the puffy sample was again weighted. The degree of bulging was calculated by the following equation:

$$\text{Swelling (\%)} = \frac{W_s - W_0}{W_0} \times 100,$$

Where, W_0 and W_s are the weight of the dry and swollen membrane, respectively¹⁹. However, the drinking water quality parameters are many and different for different sources, as to purify water from pathogens many polymer membranes are being used for many decays²⁰.

3. Results and Discussion

(A) Swelling Behaviour: Variation of swelling with different AA concentration is shown in figure 4.1. From data it is clear that swelling increases faster when AA content increases. Swelling reaches almost 22% for 15 % AA content. We have to develop membranes with very limited swelling so that the dimension should stable after amidoximation process. 2% AA provides maximum AO content with sufficient swelling, hence we have taken membranes of 2% AA content for subsequent studies (fig. 1).

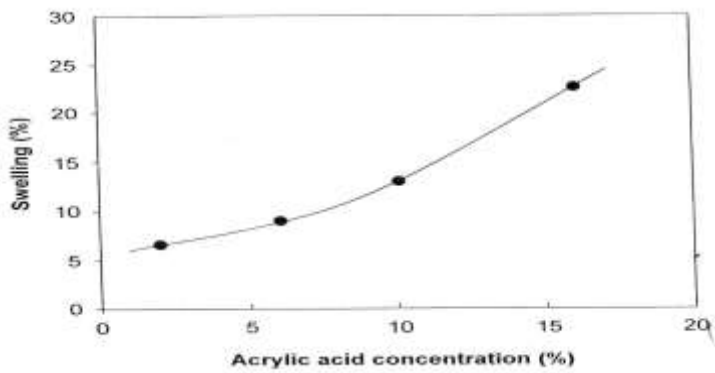


Figure 1. Swelling behavior of copolymer films with different AA concentration

Swelling behavior of membranes was carried out at different temperatures for studying the hydrophilicity in aqueous system (fig. 2). From figure it is clear that swelling increases slowly up to 60°C and on increasing temperature 60-70°C it increases rapidly and when temperature passes 70°C the swelling enhanced quickly up to about 80°C and after it almost level off. Such type of behavior indicates that there is a sudden change in copolymer structure at about 70-80°C.

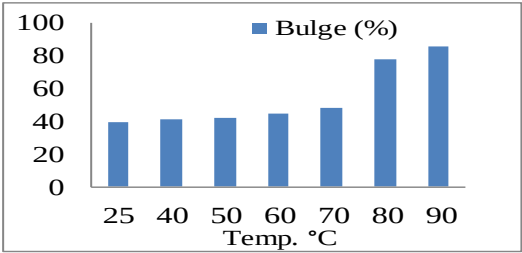


Figure 2. Swelling behaviour of membrane AO 3.3 at different temperatures

Table 1 presents the values of swelling in percent at different temperatures for 6 h.

Table 1. Swelling behaviour of the membrane AO 3.3 at different temperatures

Temperature (°C)	Swelling (%)
30	38
40	40
50	43
60	44
70	47
80	76
90	84

Swelling measurement was carried out at 90°C temperature with respect to time and is given in fig. 3. The bulge linearly increases up to 2 h and then tends to almost saturate (Table 4.2). The results indicated that almost maximum bulge is achieved only in 2 h of time.

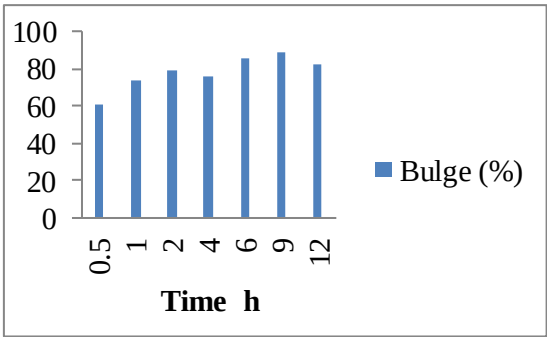


Figure 3. Bulge behaviour of membrane AO 3.3 at 90°C with respect to time.

Table 2. Equilibrium swelling behaviour of membrane AO 3.3 at 90°C with respect to time

Time (min.)	Swelling (%)
30	60
60	73
120	78
240	75
360	85
540	88
720	82

At equilibrium 90°C and from 30 min. to 540 min. there is a increase in swelling and about 720 min. almost level off. Such type of behavior indicates that there is a sudden change in copolymer structure after 9 h. Swelling behaviour shows that on increasing AA% of membranes swelling increases also. Hence it was needed to analyze that how much AA% will provide best results. We have to develop membranes with very limiting swelling, so that the dimension should be stable after amidoximation process

(A) Contact Angle

(i) CA of virgin acrylic copolymer: The images represent sample with water droplet for CA measurement in fig. 4”.



Figure 4. CA of membranes with virgin copolymer membranes

The virgin PAN shows contact angle as 75°, however with the amidoximation process the contact with the increase in AO content, hydrophilic nature of copolymer increases so lowers the angles.

(ii) CA of membranes with different amidoxime content



Figure 5. Amidoxime content 0.24 meq/g.



Figure 6. Amidoxime content 1.12 meq/g.



Figure 7. Amidoxime content 2.2 meq/g.



Figure 8. Amidoxime content 3.3 meq/g.

Thus the amidoximated copolymers were confirmed to be more hydrophilic by CA measurement.

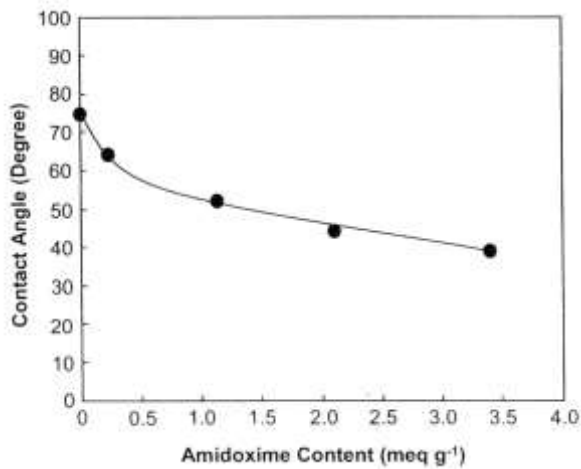


Figure 9. CA of membranes with different AO content

Variation of CA of membranes with different AO content is shown in fig. 9. The above graph clearly shows that on increasing AO content, CA is decreasing. The CA of virgin PAN is 75° decreases till ~43° with the increasing AO content from 0.24 meq/g to 3.3 meq/g respectively table 3.

Table 3. CA measurement at different Amidoxime content

AO content (meq/g)	CA
(virgin PAN) 0.00	75°
0.24	~65°
1.12	~53°
2.2	~49°
3.3	~43°

The above analyses has shown that the membrane with 2% AA and 3.3 meq/g is the best content which gives sufficient swelling and hydrophilicity²¹.

4. Conclusion

Water CA measures surface hydrophilicity by measuring how much a droplet of water spreads on the surface. The virgin PAN shows CA was maximum however with the increase in AO content CA lowers, it shows that the hydrophilic nature is increasing. Thus the amidoximated (3.3 meq/g) copolymers were confirmed to be more hydrophilic than the virgin membrane by CA measurement. Swelling behaviour of membranes is also

related to the wetting ability of membranes. It has analyzed that 2% AA content provides maximum AO content. Hence both parameters show that membranes with 2% AA content and 3.3 meq/g AO content are the best which give sufficient swelling and hydrophilicity.

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