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Surface Characterization of Amidoximated Acrylic Copolymer Membrane

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Abstract: This paper shows the studies of wetting ability of polyacrylonitrile (PAN). Amidoximated polyacrylonitrile membranes are being used for the water purification purpose. Copolymerization of acrylonitrile (AN) and acrylic acid (AA) were performed at 65° C under nitrogen gas environment. Prepared membranes were fabricated into DMP and treated with hydroxylamine hydrochloride (HA) in aqueous solution at 60-80° C. The HA concentration was varied from 1-3% (w/v) and the pH of the solution was adjusted to[1]. Surface characterization of amidoximated acrylic copolymer membrane is done by using Fourier transform infrared (FTIR) spectroscopy and contact angle (CA) method. FTIR spectroscopy is used to confirm the copolymerization of poly (AN-*co*-AA) and chemical modification of poly (AN-*co*-AA)[2]. As a result of amidoximation, the noticeable changes are slow disappearance of band at around 2243 cm^{-1} which correspond to nitrile groups of AN. This indicates that CN group fraction decreases during the amidoximation process. Another favorable change is newly formed band belonging to the N-O stretching variation of amidoxime (AO) at around 929 cm^{-1} [3]. Water CA measures surface hydrophilicity by measuring how much a droplet of water spreads on the surface. The amidoximated copolymers were confirmed to be more hydrophilic than the virgin membrane.

Keywords: Contact angle, wettability, hydrophilicity, amidoximation, FTIR.

1. Introduction

Drinking water must not contain harmful chemical substances and pathogenic microorganisms that may be harmful to human health[4]. Membranes emerged as a viable means of water purification in the 1960s

with the development of high performance synthetic membranes[5]. 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 properties[6]. A sharp enhancement in the amidoximation at 80˚C is observed[7]. The membranes containing acrylamide were found to be more hydrophilic and showed higher transmission of fluids and flux recoveries than the virgin acrylonitrile membrane[1]. The cyano group in AN/MA copolymer beads were converted to AO by reaction with HA to remove metal ions in aqueous solution[8]. Amidoximated AN/MA with amidoximation temperature 70˚C and amidoximation time 20 hr h pH 5.0 has a relatively higher adsorption capacity for Ag+ [9]. 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 equation ($\gamma_1 cos\theta = \theta s\gamma\gamma sl$)[10].

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 hydrophobic[11]. Surface providing water CA lower than 60° are considered to be hydrophilic whereas CAs higher than 90° are regarded as hydrophobic and super-hydrophobic with the CA exceeding 120°[12]. It was observed that the oxyflurinated PAN showed less water CA compared to untreated PAN while total surface free energy of PAN membrane increased[13]. Styrene grafted onto PAN shoes greater CA than virgin PAN[14]. Higher hydrophilicity is characterized by the lower values of CA whereas higher values of CA indicate the hydrophobicity of surfaces[15]. Different processes as Polymerization, Molecular Weight Determination, Fabrication of Copolymer, HA and AO Content Evaluations have already published[16]. 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^{o}C and reaction time 3h [3]. 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

Measuring AO content and surface hydrophilicity of acrylic copolymer membranes by using FTIR spectroscopy and CA method.

Materials Instrumentation and Method: Acrylic acid (AA), Acrylonitrile (AN), α-Azobisisobutyronitrile (AIBN),Toluene, Diethylether, Dimethyl-formamide (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.

FTIR spectra was recorded on a Perkin Elmer, 1750X FTIR spectrometer by using potassium bromide (KBr) pellets in resolution range of 4000–400 cm^{-1} (mid IR range) at room temperature. Kruss K100 tensiometer (Hamberg Germany) was used for CA measurements of film using static sessile drop method.

The CA of virgin PAN and amidoximated membranes was done of the membranes with increasing AO content from 0.24 meq/g to ~3.3 meq/g. Water CA measures surface hydrophilicity by measuring how much a droplet of water spreads on the surface and done by static sessile drop method. First copolymer films were mounted on the holder than the angle of water droplet with film surface was measured. The CA of the sample was found from in-built software.

3. Result and Discussion

Analysis of FTIR: FTIR spectra of virgin and amidoximated acrylic copolymers are shown in Fig.1. As a result of amidoximation, the noticeable changes are slow disappearance of band at around 2243 cm^{-1} which correspond to nitrile groups of AN. This indicates that nitrile group fraction decreases during the amidoximation process. Another favorable change is newly formed band belonging to the N-O stretching variation of (AO) at around 929 cm^{-1}. Similar observation has been made for amidoximation of PAN fiber by Weiping[17].

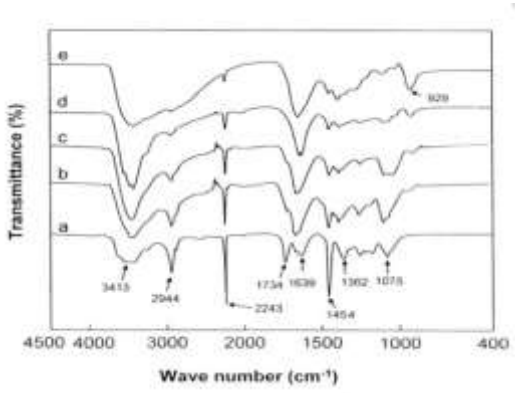

Figure 1. FTIR spectra of 2% acrylic acid copolymer after hydroxylamine treatment (a) virgin and membranes, (b) AO, 0.24 meq g^{-1}, (c) AO, 1.12meq g^{-1}, (d) AO, 2.2meq g^{-1}, and (e) AO, 3.3 meq g^{-1}.

In virgin copolymer, the peak at 1639 cm^{-1} corresponding to stretching variation of COO^{-} group[18,19]. After the amidoximation reaction, a new peak of –C=N- group of AO developed in this region. With the increase in AO content, –C=N- group of AO increases. This increase is so clear that it overpowers the band of –C=O of carboxyl group and COO^{-}[19]. The variation of band ratio corresponding to CN at 2243cm^{-1} and CH stretching at 2944 cm^{-1} intensities of virgin and amidoximated acrylic copolymers is shown in Fig. 2.

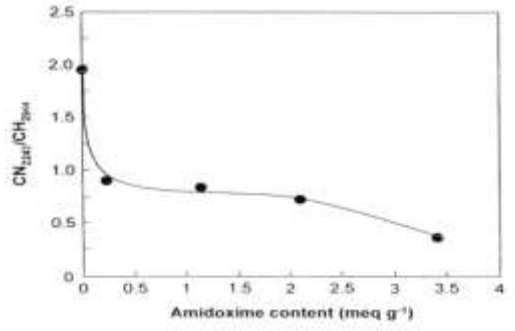

Figure 2. Variation of the ratio of CN/CH stretching band with different AO content.

From the above figure, it is clear that the ratio slowly decreases with increases in AO content which confirmed that with the amidoximation reaction the nitrile content of copolymer gradually decreases due to change of CN groups into AO groups[3]

4. Measurement of CA

CA of Virgin Acrylic Copolymer: The images represent sample with water droplet for CA measurement in Fig. 3.

Figure 3.(a) 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.

CA of Membranes with Different Amidoxime Content:

Figure 3.(b): CA of membranes with amidoxime content AO, 0.24 meq/g.

Figure 3.(c): CA of membranes with amidoxime content AO, 1.12 meq/g.

Figure 3.(d): CA of membranes with amidoxime content AO, 2.2 meq/g.

Figure 3.(e): CA of membranes with amidoxime content AO, 3.3 meq/g.

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

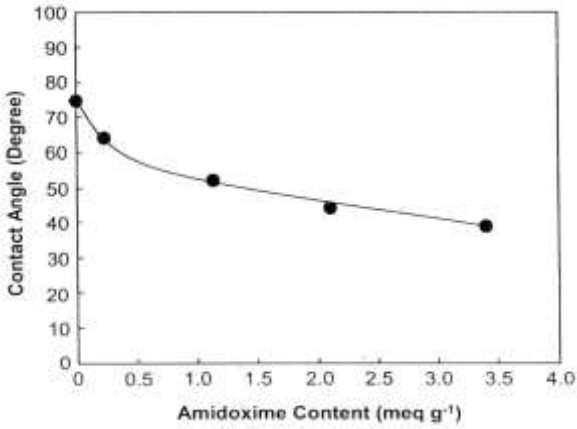

Figure 4. CA of membranes with different AO content.

Variation of CA of membranes with different AO content is shown in Fig. 4. 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 1.

Table 1. 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˚

5. Conclusion

During the transformation of AN into AO groups, FTIR explained different changes in intensities of virgin and amidoximated acrylic copolymer, nitrile group fraction decreases with increase in AO content

which confirmed that as amidoximation takes place, the nitrile content of copolymer regularly decreases due to change of nitrile groups into AO groups. Water CA measures surface hydrophilicity by measuring how much a droplet of water spreads on the surface. The virgin PAN shows CA as 75˚, however with the increase in AO content, CA lowers it shows that the hydrophilic nature is increasing. Thus the amidoximated copolymers were confirmed to be more hydrophilic than the virgin membrane by CA measurement.

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