

Synthesis, Study and Characterization of Amidoximated Acrylic Copolymer

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ABSTRACT

Copolymer membranes were fabricated into DMP and copolymer was treated with HA in aqueous solution at 60-80°C. In the amidoximation process, a part of nitrile groups of copolymer is converted into amidoxime groups. The characterization of virgin and amidoximated acrylic copolymer membranes were carried out by using various techniques as Fourier transform infrared, X-ray diffraction, thermogravimetric analysis, Scanning electron microscope etc. With the amidoximation process various significant changes in the copolymer properties such as functionality, crystallinity, thermal behavior, hydrophilicity, elemental composition and surface morphology were observed.

Keywords— amidoximation; copolymer; crystallinity; thermal behavior; surface morphology

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I. INTRODUCTION

Polyacrylonitrile (PAN) has good resistance to organic solvents is excellent in mechanical strength with high thermal stability [1]. Polymers have been utilized in coagulation processes for water purification for at least four decades [2]. Copolymerization is important techniques adopted in effecting systematic changes in the properties of the commercially significant polymers. The copolymers of acrylic esters have been used for various industrial applications [3]. PAN was introduced in many applications such as in carbon fibers manufacturing for military, sports and aerospace equipment, clinical uses, and synthetic fibers in a modern textile process [4, 5]. A number of methods have been applied to modify polymer properties such as grafting, plasma treatment, adsorption, blending, copolymerization of monomers and chemical treatment such as hydrolysis, reduction and reaction with chemical reagents [6-10]. Polymers which show antimicrobial nature either inherently have this property or they transformed by addition of antimicrobial agents at the time of polymer

processing or by immobilization of these biocidal agents after development of polymer [11-13]. Nanosilver (NS) is known for its broad spectrum antimicrobial activity against bacteria, fungi, protozoa and certain viruses including antibiotic resistant strains [14, 15]. It is consistently reported that antimicrobial efficacy of NS greatly influenced by the dimensions (shape and size) of the particles, the smaller the particles, the greater the antimicrobial effect [16].

II. OBJECTIVES

- Amidoximation of acrylic copolymer membranes.
- Characterization of virgin and amidoximated acrylic copolymer membranes by using various techniques

III. MATERIALS AND METHODS

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 AnalaR 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.

Different processes as Polymerization, Molecular Weight Determination, Fabrication of Copolymer, Hydroxylamine Treatment and Amidoximes Content Evaluations has been already published [17].

IV. INSTRUMENTATION

• FTIR SPECTROSCOPY

Fourier transform infrared (FTIR) analysis was recorded on a Perkin Elmer, 1750X Fourier Transform Infrared spectrometer by using potassium bromide (KBr) pellets in resolution range of 4000–400 cm^{-1} at room temperature. X-ray diffraction studies on the samples were carried on PHILIPS, Holland, Cuka X-ray generator to trace the morphological changes in the material. The thermogravimetric analysis (TGA) was evaluated using Perkin Elmer, STA 6000 Simultaneous Thermal Analyzer instrument (PerkinElmer Inc., Waltham, MA, USA). Differential Scanning Calorimetry (DSC) analysis of samples was carried out Perkin Elmer- Pyris system in the temperature range of 50-300 $^{\circ}$ C. The EDX studies of virgin as well as amidoximated copolymer samples were carried out using STEREOSCAN 360 (Cambridge Scientific Industries Ltd.), scanning electron microscope. Scanning electron microscope (SEM) micrographs were acquired using a STEREOSCAN 360 (Cambridge Scientific Industries Ltd.), scanning electron microscope and were operated at 10 to 20 kV. Samples were coated in Au/Pd film prior to analysis.

V. RESULTS AND DISCUSSION

• FTIR SPECTROSCOPY OF VIRGIN ACRYLIC COPOLYMER

FTIR spectra of acrylic copolymer samples with different acrylic acid (AA) concentration are presented in “Fig.1”. The peak at 3414 cm^{-1} corresponding to O-H of COOH, 2944 cm^{-1} corresponding to -CH stretching, the peak at 2243 cm^{-1} represents -C \equiv H stretching vibration, peak at 1734 cm^{-1} corresponding to stretching of -C=O of carboxyl group due to the addition of small percentage of acrylic acid during the polymerization, peak at 1637 cm^{-1} and 1454 cm^{-1} for stretching vibration of COO $^{-}$ group and stretching of -CH $_2$, peak at 1176 cm^{-1} and 1075 cm^{-1} represent -C \equiv H

stretching and bending, respectively. It is observed that with increase in AA concentration, peak at 3413 cm^{-1} gradually broadens and at 15% AA concentration it almost over powers for band at 2944 cm^{-1} whereas the band at 2243 cm^{-1} corresponds to nitrile groups of AN gradually decreases due to decreasing nitrile moiety of polyacrylonitrile.

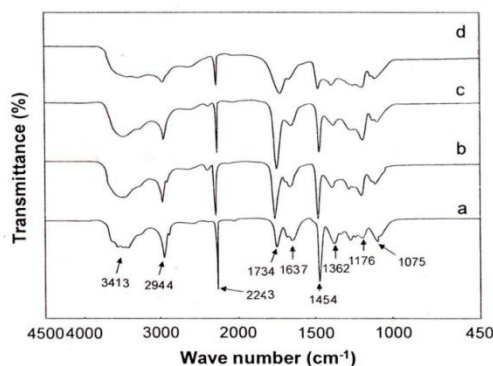


Fig. 1. FTIR spectra of copolymer films with different acrylic acid (AA) concentrations, (a) 2%, (b) 5%, (c) 10% and (d) 15%.

The proportion of the peak at 1734 cm^{-1} for the carbonyl and at 2243 cm^{-1} for nitrile has been taken as the progress of the copolymerization process.

• X-RAY DIFFRACTION OF VIRGIN ACRYLIC COPOLYMER

X-Ray analysis of PANAA copolymer with different AA concentration is presented in “Fig. 2”. It can be noticed that with increases in AA concentration in copolymer the crystalline structure start to dissipate by transforming into amorphous order. It is clear that 15 % AA containing copolymer become approximately amorphous in nature.

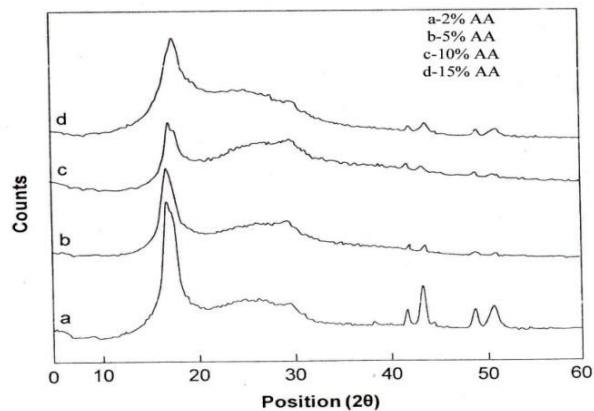


Fig. 2. XRD diffractogram of copolymer films with different acrylic acid concentration.

The crystallinity was measured as:

$$\text{Crystallinity (\%)} = \frac{W_c}{W_o} \times 100 \dots\dots(1)$$

Where, W_c and W_o are the weight of crystalline region and total weight of sample, respectively.

• **ANALYSIS OF AMIDOXIMATED COPOLYMER MEMBRANES**

FTIR

FTIR spectra of virgin and amidoximated acrylic copolymers are shown in “Fig. 3”. 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 amidoxime (AO) at around 929 cm^{-1} . Similar observation has been made for amidoximation of PAN fiber by “Weiping” [18].

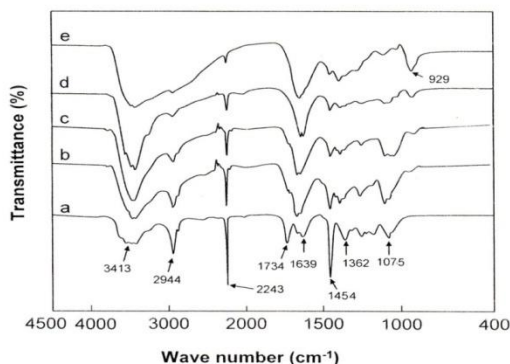


Fig. 3. FTIR spectra of 2% acrylic acid copolymer after hydroxylamine treatment (a) virgin, and membranes, (b) AO, 0.24 meq g^{-1} , (c) AO, 1.12 meq g^{-1} , (d) AO, 2.2 meq g^{-1} , and (e) AO, 3.3 meq g^{-1} .

In virgin copolymer, the peak at 1639 cm^{-1} corresponding to stretching variation of COO^- group [19, 20]. After the amidoximation reaction, a new peak of $-\text{C}=\text{N}-$ group of amidoxime developed in this region. With the increase in amidoxime content, $-\text{C}=\text{N}-$ group of amidoxime increases. This increase is so clear that it overpowers the band of $-\text{C}=\text{O}$ of carboxyl group and COO^- [21]. The variation of band ratio corresponding to CN at 2243 cm^{-1} and CH stretching at 2944 cm^{-1} intensities of virgin and amidoximated acrylic copolymers is shown in “Fig. 4”.

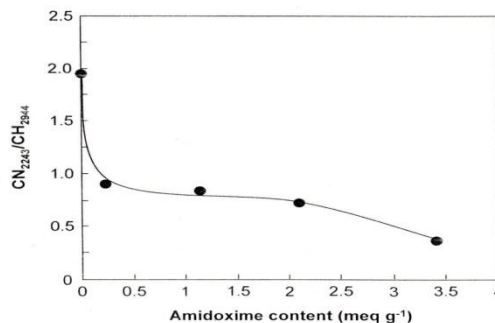


Fig. 4. Variation of the ratio of CN/CH stretching band with different AO content.

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 nitrile groups into amidoxime groups.

X-RAY DIFFRACTION

XRD of amidoximated copolymers and virgin are represented in “Fig. 5”. The data shows a loss in crystalline diffraction with the increases in amidoxime content. The decrease in crystallinity shows that different crystalline changes occur during amidoximation. During this process the diffraction peaks at 18 and 30° (2θ) becomes wider which shows that crystallization starts to disperse by transforming into an amorphous order. The expansion of peak at 18° shows a decrease in the size of crystal, depending upon amidoxime content.

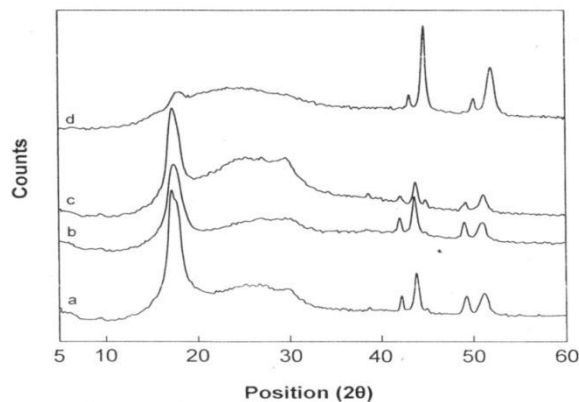


Fig. 5. X- Ray diffraction pattern of copolymer (a) virgin, and membranes (b) AO, 0.24 meq g^{-1} , (c) AO, 1.12 meq g^{-1} , and (d) AO, 3.3 meq g^{-1} .

The crystallinity of membranes against AO content is determined by using expression 1 and the results are in “Table 1”. The difference of crystallinity with AO content is represented in “Fig. 6”. It is clear that the crystallinity decreases considerably from 32% (virgin copolymer) to 14 % (copolymer with AO content 3.3 meq g⁻¹).

TABLE I. Percent Crystallinity of membranes with different AO content

Amidoxime Content (meq g ⁻¹)	Crystallinity (%)
Virgin copolymer	32
0.24	23
1.12	20
3.3	14

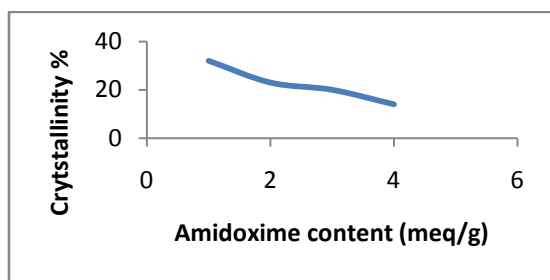


Fig. 6: variation of crystallinity of membranes with different AO content

TGA

Thermogravimetric Analysis (TGA) results are presented in “Fig. 7”. It has been observed that pure PAN does not show any weight loss up to 270°C – 300°C [22, 23]. The presence of acrylic acid moiety lowers the degradation as shown in figure. Degradation occurs in three steps for virgin copolymer. In first step virgin copolymer degrades from 150 – 320°C due to desorbed moisture, evaporation of residual traces up to 180 °C, and decarboxylation of polyacrylic moiety up to 320 °C. It is observed that at high temperatures, when PAN is heated the intramolecular transformations are clearly accompanied by intermolecular reactions of groups, leading to cross-linking of the polymer chain [24-26].

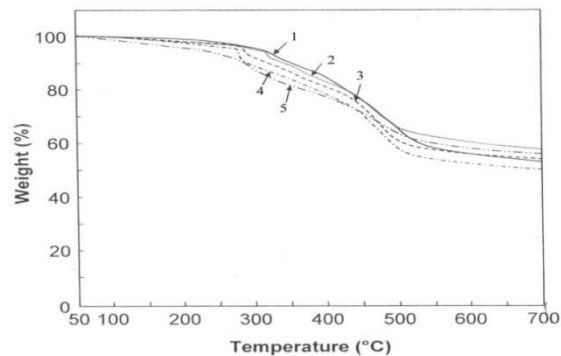


Fig. 7. TGA thermogram of copolymer (1) virgin, and membranes (2) AO, 0.24 meq g⁻¹, (3) AO, 1.12 meq g⁻¹, (4), 2.2, meq g⁻¹ and (5) AO, 3.3 meq g⁻¹.

DSC

Differential Scanning Calorimetry (DSC) measurements “Fig. 8” for virgin and AO 3.3 meq g⁻¹ copolymer were carried out for determination of glass transition temperature and thermograms. After analysis of data, it was observed that the T_g value for amidoximated copolymer was found to be higher as 75°C than virgin copolymer film as 70°C. The strong interaction among the molecular chains after modification leads to this increase in glass transition temperature.

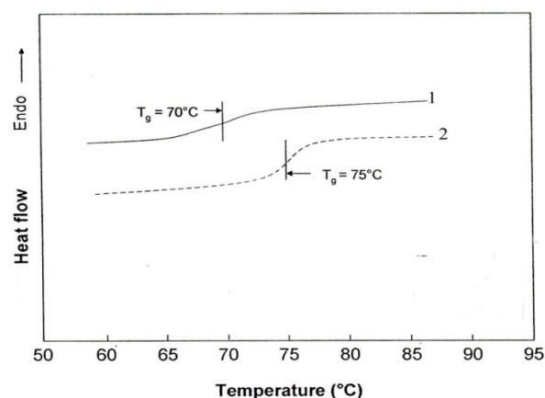


Fig. 8. DSC Thermograms of copolymers showing Tg of virgin(1) and membrane (2), AO 3.3 meq g⁻¹

EDX

The energy dispersive X-Ray spectroscopy (EDX) is presented in “Fig. 9 (a,b)” which explain the qualitative elemental composition of virgin and amidoximated samples.

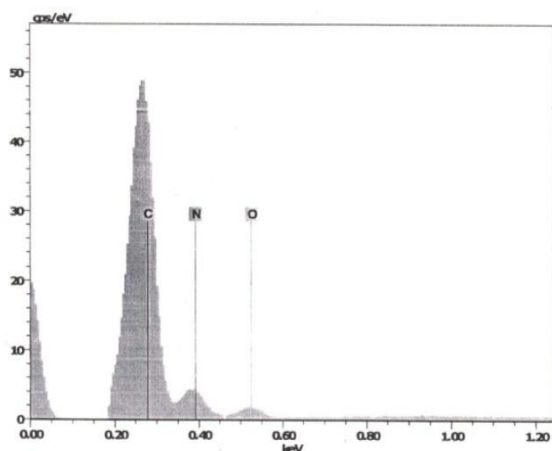


Fig. 9 (a). EDX of acrylic copolymer virgin and membrane

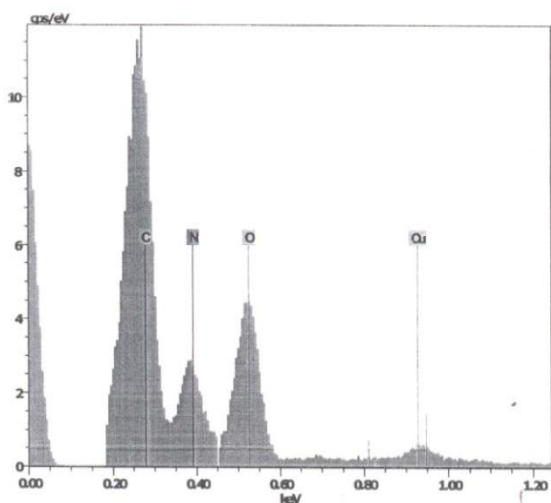


Fig. 9 (b). EDX of acrylic copolymer A.O content 3.3 meq/g

The variation of N/C and O/C % ratio with respect to C as a function of AO content is presented in Fig. 10.

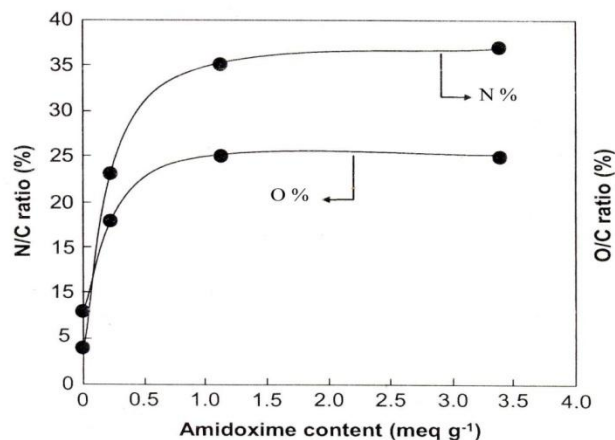


Fig. 10. Determination N (%) and O (%) content by EDX and there variations with respect to Carbon at different A.O content.

It is clear from the graph “Fig.10” that with comparison to carbon content of nitrogen and oxygen was increased from approx 8% and 4% respectively and for virgin copolymer up to 24% and about 38% for nitrogen and for oxygen respect for samples having 3.3 meq/g amidoxime content.

SEM

The surface structure of copolymer samples were determined by Scanning Electron Microscopy (SEM) and presented in “Fig. 11 (i-v)”.

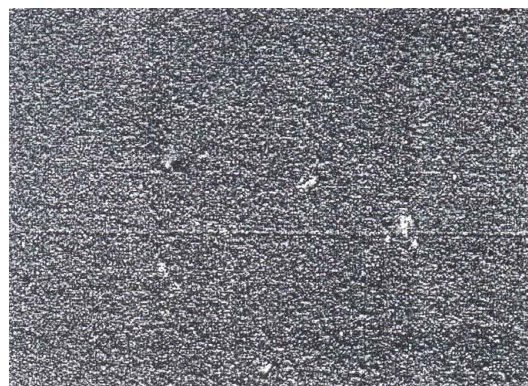


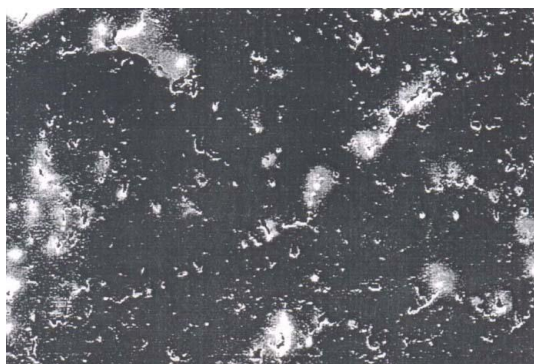
Fig. 11 (i). SEM photograph of acrylic virgin copolymer

In case of acrylic virgin copolymer smooth surface structure has been found “Fig. 15 (i)”. On the other hand after amidoximation process surface becomes rough due to increase amidoxime content. These results show that after damaging of paracrystalline region, the hydroxylamine diffuse very fast from

solution to copolymer. Due to which amidoximation of nitrile group takes place entirely and becomes the reason of cracking on samples surface "Fig. 11(ii-v)".

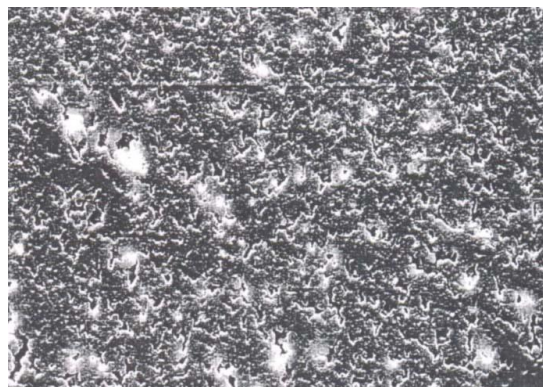


(ii)

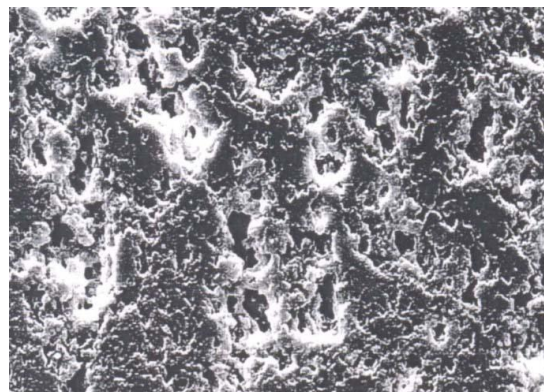


(iii)

Fig. 11 (ii). SEM photograph of acrylic polymer A.O, 0.24 meq/g, (iii). SEM photograph of acrylic polymer A.O, 1.12 meq/g



(iv)



(v)

Fig. 11 (iv). SEM photograph of acrylic polymer A.O, 2.2 meq/g, (v). SEM photograph of acrylic polymer A.O, 3.30 meq/g.

VI. CONCLUSION

Amidoxime content is regulated by the reaction parameters, such as temperature, time and HA concentration previously. FTIR explained different changes in intensities of virgin and amidoximated acrylic copolymer, 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 in to amidoxime groups. XRD data indicated the loss in crystalline diffraction with the increases in amidoxime content. TGA results indicate that as the AO content increases the initial degradation temperature of copolymer decreases. Presence of AA lowers the degradation temperature of virgin copolymer as compared to pure PAN. SEM represented that with the increase in AO content, surface of virgin copolymer becomes rough and the roughness increases with increase in amidoxime content.

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