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Method for Preparation of Amidoximated Acrylic Copolymer: Characterizations and other study

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Abstract: *Fabrication of copolymer membrane was done in DMP and then these films were reacted through HA in water solution. In the duration of amidoximation, nitrile group of copolymer films were changed into amidoxime group. The original film and amidoximated acrylic copolymer membranes were characterized by using different types of techniques like FTIR, TGA, X-ray and SEM etc. some noticeable changes in the copolymer characteristics were seen during amidoximation method as thermal behavior, exterior morphology and hydrophilicity etc.*

Keywords: *copolymer; amidoximation; characterization; thermal behavior; exterior morphology*

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I. Introduction

Resistance of Polyacrylonitrile (PAN) is outstanding to various organic solvents for thermal strength and mechanical strength [1]. Polymers normally used in water purification especially in coagulation method from long time [2]. For changing the main properties of useful polymers at commercial scale a well known technique is used which is known as copolymerization. For different industrial uses many copolymers of acrylic esters have been used [3]. The use of PAN in extensive range of purpose is due to the existence of reactive cyano group that can be changed into a meticulous functional group based on definite uses [4, 5]. PAN has been used in various purposes like manufacturing of C-fifers, clinical uses and textile industries etc [6]. Various methods have been used to convert polymer characteristics like copolymerization of monomers. Few chemical methods are also used for this purpose with some reagents [7-11]. Antimicrobial surfaces are frequently planned by absorbing of toxic substances that are released into the surroundings so that microorganisms are killed [12]. Nano-silver is well known for its antimicrobial activity against microorganisms [13, 14]. Time to time it has been reported that antimicrobial efficiency of Nano-silver significantly affected by the shape and size of the different particles, the smaller the particles, the greater the antimicrobial effect [15].

II. Materials and Methods

All the chemicals used like Toluene, Silver nitrate, Polyvinyl alcohol, Acrylonitrile, Acrylic acid, α-Azobisisobutyronitrile, DMF, NaOH, HCl etc. were of AnalaR grade and obtained from Fluka or Sigma Aldrich. These solvents were dried and distilled by using standard procedure before using. All the chemicals were used normally without doing any purification. Some processes have been already published [16] such as Molecular Weight Determination, Polymerization, Hydroxylamine Treatment, Fabrication of Copolymer etc.

III. Instrumentation

Perkin Elmer, 1750X Fourier Transform Infrared spectrometer was used for recording FTIR analysis by using potassium bromide (KBr) pellets, in the range of 4500–450 cm-1 at room temperature. PHILIPS, Holland, Cuka X-ray generator was used for X-ray diffraction studies of the samples. Perkin Elmer, STA 6000 Simultaneous Thermal Analyzer instrument was used for recording TGA. Perkin Elmer- Pyris system was used for DSC analysis in the range of 50-300° C. The EDX and SEM studies were carried out by using STEREOSCAN 360, scanning electron microscope for both original and amidoximated copolymer film. Scanning electron microscope was operated at 10- 20 kV. All copolymer samples were coated in Au/Pd film before analysis.

IV. Results and Discussion

Original Acrylic Copolymer Film

FTIR

"Fig.1" represents FTIR spectra of acrylic copolymer samples with various acrylic acid concentrations. The peak at 3415 cm^{-1}, 2943 cm^{-1}, 2244 cm^{-1} and 1733 cm^{-1} corresponding to O-H of COOH, –CH stretching, -C≡H stretching vibration and –C=O of carboxyl group respectively. By the addition of little quantity of acrylic acid in the process of polymerization, the peak at 1637 cm^{-1} and 1454 cm^{-1} for stretching vibration of COO- group and stretching of –CH$_2$, peak at 1175 cm^{-1} and 1075 cm^{-1} represent –C≡H stretching and bending, respectively. During these observations it was found that with increase in AA concentration, peak at 3415 cm^{-1} regularly broadens and at 15% concentration of AA it approximately over powers for band at 2943 cm^{-1} whereas the band at 2244 cm^{-1} corresponds to nitrile groups of AN steadily decreases because of decreasing nitrile moiety of polyacrylonitrile.

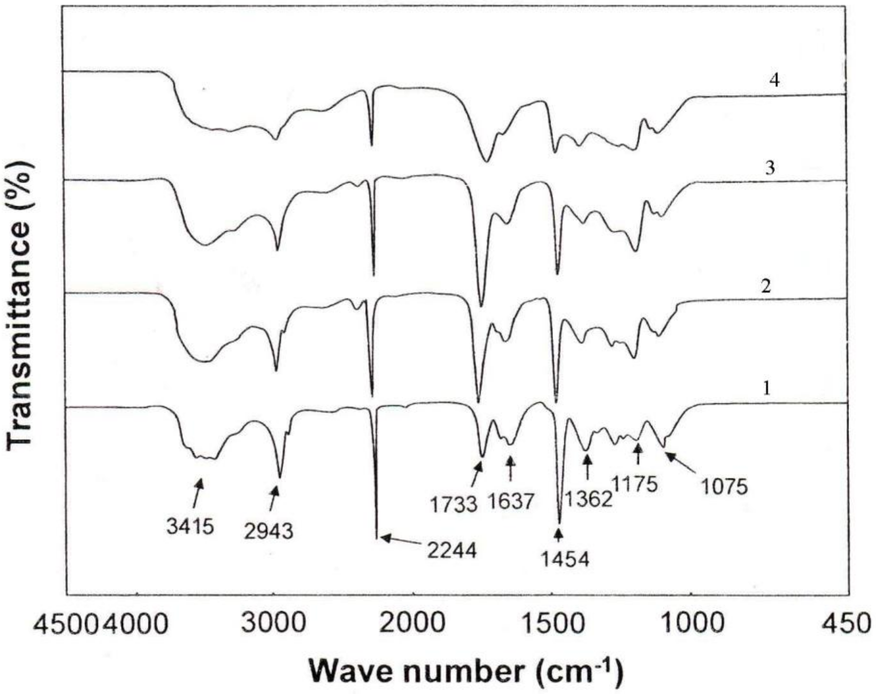


Fig.1. FTIR spectra of copolymer films with various concentrations of acrylic acid as: (1) 3%, (2) 6 %, (3) 12% and (4) 15%.

The progress of the copolymerization process has been explained by the proportion of the peak at 1733 cm^{-1} (carbonyl) and at 2244 cm^{-1} (nitrile) as in figure-1.

X-Ray Diffraction

"Fig.2" represents the X-Ray analysis of original copolymer film with different AA concentration. From the data it is clear that on increasing the concentration of AA the crystalline structure start to change into amorphous form by the process of transforming. Copolymer which contains 15 % AA has been changed just about amorphous form.

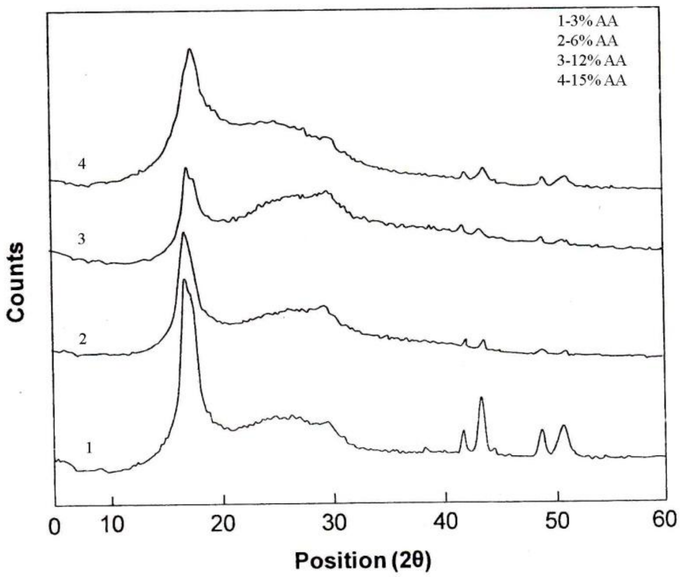


Fig. 2. XRD diffractogram of copolymer films with different acrylic acid concentration.

The crystalline nature was measured as:

$$\text{Crystalline Nature (\%)} = \frac{W_c}{W_o} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Where, Wc and Wo are the weight of crystalline region and total weight of sample, respectively.

Analysis of Copolymer Membranes after Amidoximation

FTIR

"Fig.3" represents the IR spectra of original polymer and amidoximated acrylic copolymers. After amidoximation, the band at 2244 cm^{-1} corresponding to nitrile groups of AN changes slowly. This change represents that nitrile group of AN decreases during amidoximation process. New band at 929 cm^{-1} corosponding to the N-O stretching variation of amidoxime (AO) also indicates these changes. Such types of changes also noticed for amidoximation by "Weiping"[18].

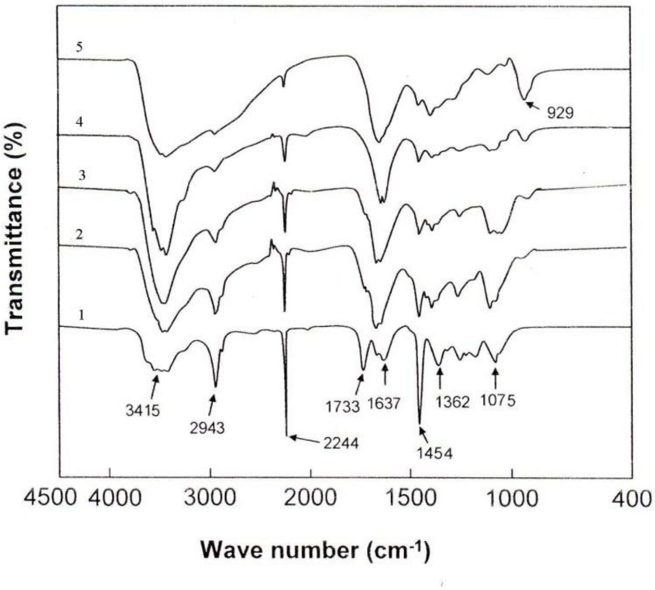


Fig.3. FTIR spectra of 3% acrylic acid copolymer after hydroxylamine treatment (1) original, and membranes, (2) AO, 0.22 meq g^{-1}, (3) AO, 1.11meq g^{-1}, (4) AO, 2.2meq g^{-1}, and (5) AO, 3.5 meq g^{-1}.

In original copolymer film, the peak at 1637 cm^{-1} represents the stretching variation of COO¯ group [19, 20]. A new peak of –C=N- group of amidoxime observed in the same region after the amidoximation process. On increasing the concentration of amidoxime the –C=N- group also increases. Above observations indicates that –C=N- group overcomes the band of –C=O of carboxyl group and COO¯ [21]. The band ratio corresponding to CN at 2244cm^{-1} and CH stretching at 2943 cm^{-1} related to original and amidoximated acrylic copolymers shows variations during this process. With increases in AO content these changes decreases slowly which indicates that the formation of amidoxime group from nitrile group takes place regularly.

X-Ray Diffraction

In Figure- 4 X-ray differection of original film and amidoximated copolymers has been given. According to research work decrease in crystallinity represents that during amidoximation process unusual crystalline changes occurs. The diffraction peaks at 18 and 30o (2θ) becomes wider which shows that crystallization starts to disperse by transforming into an amorphous order. The expansion of peak at 18o shows a decrease in the size of crystal, depending upon amidoxime content.

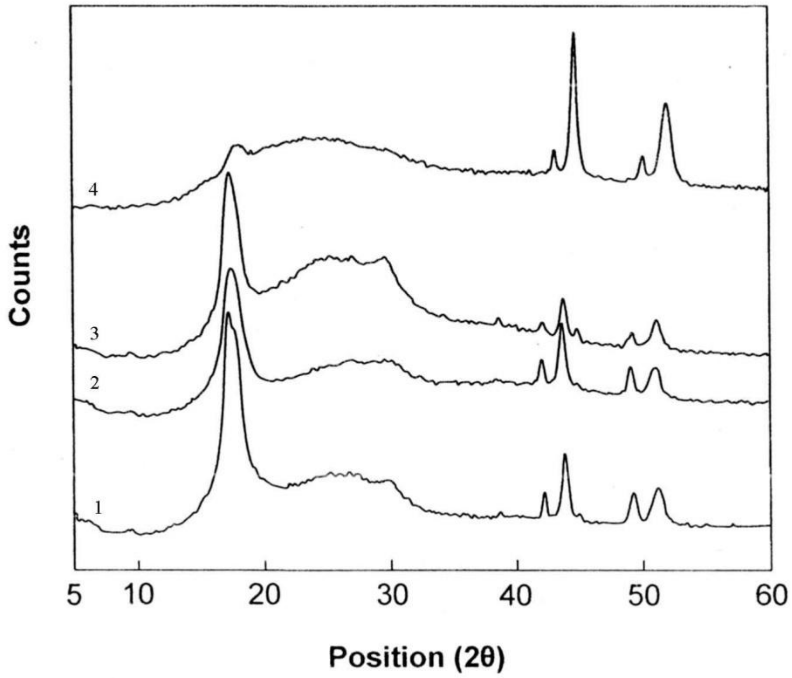


Fig. 4. X- Ray diffraction pattern of copolymer (1) original, and membranes (2) AO, 0.22 meq g^{-1}, (3) AO, 1.11 meq g^{-1}, and (4) AO, 3.5 meq g^{-1} .

The crystallinity of membranes against AO content is calculated by using equation 1 and the results obtained are represented in Table 1. The difference of crystallinity with AO content is represented in “Fig.5”. From the given data it is clear that the crystallinity decreases considerably from 31% (original copolymer) to 15 % (copolymer with AO content 3.5 meq g^{-1}).

TABLE I. Crystallinity of membranes

Amidoxime Content (meq g^{-1})	Crystallinity (%)
Original copolymer	31
0.22	24
1.11	21
3.5	15

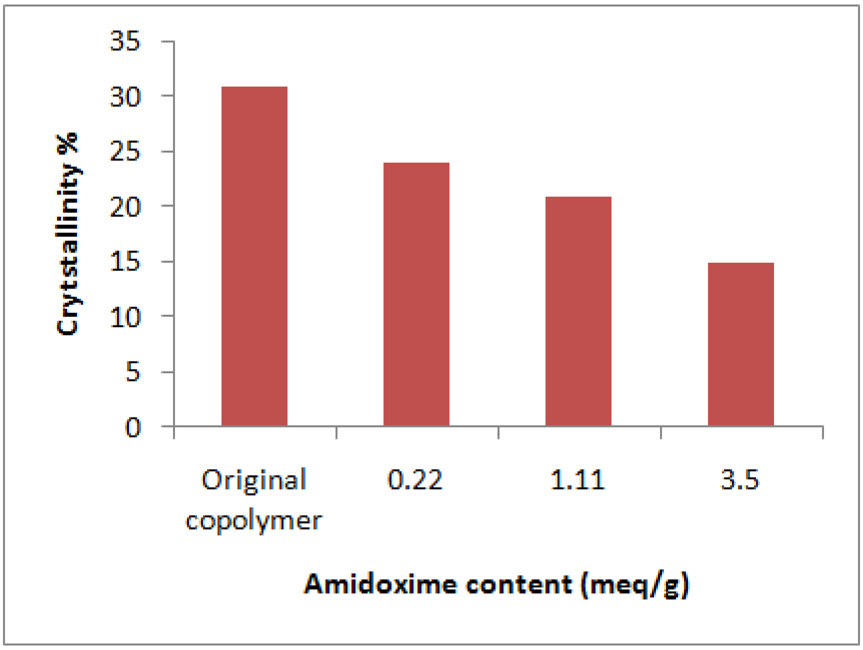


Fig. 5: Variation of crystallinity of membranes with different AO content

TGA

From Thermo gravimetric Analysis it has been observed that pure PAN does not show any weight loss up to 260°C–300°C [22, 23]. Degradation takes place in three steps for original copolymer as in first step original copolymer degrades from 150 – 325°C because of desorbed moisture, evaporation of residual traces noticed up to 180 °C, and decarboxylation of polyacrylic moiety takes place up to 325 °C. It has been noticed, at high temperatures when PAN is heated the intramolecular transformations are clearly attend by intermolecular reactions of groups by means of cross-linking of the polymer [24-26].

DSC

Differential Scanning Calorimetry (DSC) measurements were carried out for virgin and AO 3.5 meq g^{-1} copolymer for the determination of thermograms and glass transition temperature. After analysis of these data, it was noticed that the T_g value for amidoximated copolymer was higher than original copolymer film. The strong interaction among the molecular chains after amidoximation directs to this increase in glass transition temperature.

EDX

Energy dispersive X-Ray spectroscopy (EDX) explains the qualitative elemental composition of both original and amidoximated samples. It is clear from the data that with comparison to carbon content of nitrogen and oxygen was increased from approx 8% and 4% respectively and for original copolymer up to 24% and about 38% for nitrogen and oxygen with respect for samples having 3.5 meq/g amidoxime content.

SEM

The surface structure of copolymer samples were recorded by Scanning Electron Microscopy (SEM) and presented in “Fig. 6”.

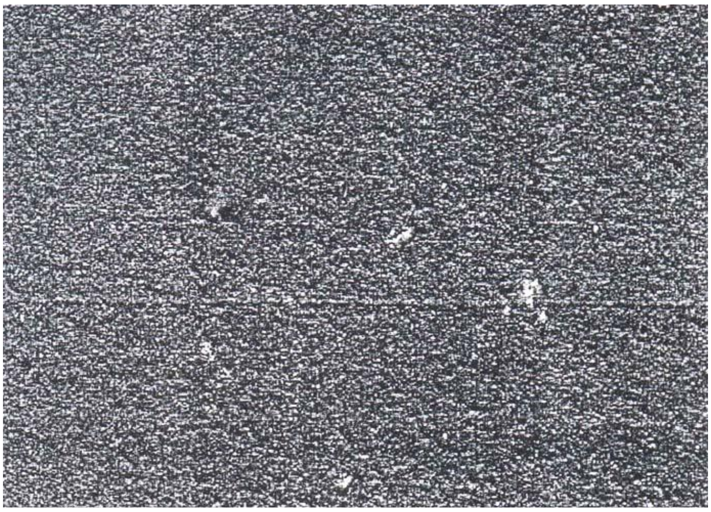
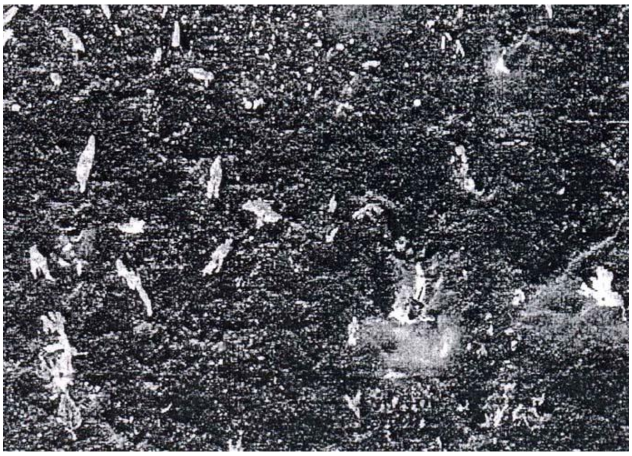


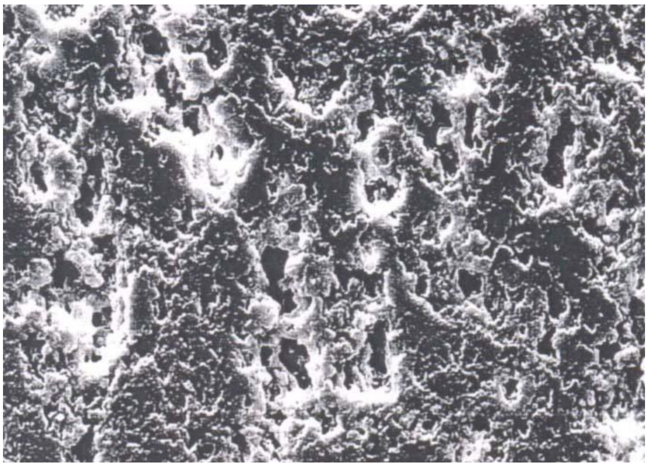
Fig. 6 (a) SEM photograph of acrylic virgin copolymer

In case of acrylic original copolymer smooth surface structure has been found “Fig.6 (a)”. After amidoximation process surface of copolymer becomes rough because of the presence of amidoxime content. Data represents that, the diffusion of hydroxylamine is very fast from solution to copolymer after destruction of paracrystalline region. Due to which amidoximation of nitrile group takes place entirely and becomes the reason of cracking on samples surface “Fig. 11(b,c)”.



(b)

Fig. 1 (b). SEM photograph of acrylic polymer A.O, 0.22 meq/g



(c)

Fig. 11 (c) SEM photograph of acrylic polymer A.O, 3.50 meq/g.

V. 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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