

## **SYNTHESIS AND CHARACTERIZATION OF ACRYLONITRILE INCORPORATED PVA BASED SEMI-INTER PENETRATING POLYMERIC NETWORKS**

**DESHPANDE D.S.<sup>1\*</sup>, BAJPAI R.<sup>1</sup>, BAJPAI A.K.<sup>2</sup>**

<sup>1</sup>Department of Physics, Rani Durgavati University, Jabalpur, 482001, (MP) India

<sup>2</sup>Bose Memorial Research Laboratory, Department of Chemistry, Government Autonomous Science College, Jabalpur, 482001, MP, India

\*Corresponding author. E-mail: [deeptideshpandey@gmail.com](mailto:deeptideshpandey@gmail.com)

Received: April 15, 2011; Accepted: May 06, 2011

**Abstract-** The ever increasing use of polymers in our day to day life has given rise to quest for developing polymeric materials suitable for various applications. The current work aims to synthesize a novel semi-IPN in the form of hydrogel comprising of polyvinyl alcohol (PVA) and acrylonitrile (AN), in various proportions, by redox polymerization method in the presence of N, N'-methylene-bis-acrylamide (MBA) as a crosslinker and potassium persulphate (KPS) as initiator. Structure formation of the gel matrix has been confirmed by FTIR spectrophotometry. Phase morphology of the semi-IPNs in various proportions has been studied with scanning electron microscopy and X-ray diffraction technique has been utilized to detect the crystalline and amorphous characteristics of the synthesized gels. Water sorption capacity of the specimens have also been studied. IR spectra of the synthesized semi-IPN confirms the formation of a physical gel with polymer chains held to each other via hydrogen bonding. Their SEM images show single phase morphology with a less rough surface indicating a better compatibility of the two polymers. The XRD patterns of synthesized gels indicate that the crystallinity in the membrane is mainly due to PVA and swelling studies proves the approach to be beneficial for various bioengineering and bioindustrial applications.

**Keywords-** Hydrogels, Semi-IPNs, Polyvinyl alcohol (PVA), Water Sorption, Acrylonitrile.

### **Introduction**

Hydrogels are multi-component hydrophilic polymeric networks that imbibe enough water to cause macroscopic changes in the sample dimension. They serve a key role in biomedical field, viz. drug delivery, cell carriers and/or entrapment, wound management and tissue engineering. Synthesis and swelling aspect of the polymeric materials in the form of hydrogel is one of the important features to be investigated, if one aims to adopt the polymer for some specific application. Hydrogels can be prepared starting from monomers, prepolymers or existing hydrophilic polymers. Polyvinyl alcohol (PVA)[1-2] is one of a major non toxic, non-carcinogenic, water soluble, biocompatible synthetic polymer with excellent film forming, emulsifying and adhesive properties. It possesses high tensile strength and flexibility, as well as high oxygen and aroma barrier properties. PVA is fully degradable with melting point of 230°C. It is an atactic material but exhibits crystallinity as the hydroxyl groups are small enough to fit into the lattice without disrupting it. PVA joined to other polymers opens a window of research for altering or tailoring the property of interest. PVA based materials have important biophysical properties and are frequently used as biomaterials in various medical and pharmaceutical applications [3-5]. Another such synthetic polymer of potential importance is poly (acrylonitrile)

(PAN), which is a semicrystalline vinylic homopolymer. Acrylonitrile is also widely used for making membrane and offers quite good resistance and thermal stability. Biocompatibility tests with acrylonitrile[6] have surprisingly proved to be promising. Dental professionals wear medical gloves made from acrylonitrile. Chemical crosslinking of this monomer provides feasible routes for the improvement of thermo-mechanical properties which are pre-requisite for many industrial and biomedical applications. Thus, with an aim to explore the possibility of employing PVA based acrylonitrile incorporated hydrogels for various bioengineering and bioindustrial applications, the proposed research work aims at synthesizing poly (vinyl alcohol-g-acrylonitrile) semi-IPNs by redox polymerization method in the presence of N-N' methylene bis acrylamide (MBA) as a crosslinking agent and investigating their structural, morphological, and water sorption behavior. Crosslinker helps to alter the various physicothermal properties of the polymer to some extent. Various studies have been reported for PVA and acrylonitrile based hydrogels. For instance, Novel PVA membranes were prepared by crosslinking of PVA with heat treated corn-starch suspension[7]. Significant swelling rate of these membranes yielded them as a fine wound dressing materials. In an attempt to improve the dielectric properties of paper, cyanoethylated PVA[8] was

found to be structurally stable with good physical properties and thermal stability. Jain et al.[9] have shown good biocompatibility, mechanical stability and high swelling characteristics for PAN-gelatin cryogel networks. Bajpai et al.[10] have reported enormous swelling rate of PVA hydrogels obtained by graft co-polymerization of acrylamide and styrene on to PVA using N,N' methylene-bis-acrylamide as crosslinker. Sorption dynamics of poly (vinyl alcohol-g-acrylamide) and gelatin-g-acrylonitrile were studied by Bajpai et al [11-12]. Thermal behavior of acrylonitrile copolymers investigated by Bajaj et al[13] shows their quite stable nature.

## Experimental

### Materials

Polyvinyl alcohol (PVA), (98%, hydrolyzed, mol wt 14,000 Da) was obtained from Research Lab Chem Industries, Mumbai, India and used as a pre-formed polymer without any further purification. Acrylonitrile purchased from Research Lab, Mumbai, India was freed from inhibitor by successive washing the monomer thrice with 5% NaOH, 5% H<sub>2</sub> SO<sub>4</sub> and distilled water and finally distilling the washed monomer under vacuum. N, N'-methylene-bis-acrylamide (MBA; Research Lab Mumbai, India) was used as a crosslinking agent, potassium persulphate (KPS; Loba Chemie, Pvt Ltd. Delhi, India) as an initiator and potassium metabisulphite (KMBS; Qualigns Fine Chemicals, Mumbai, India) as an activator, respectively. Double distilled water was used throughout the experiments.

### Synthesis of hydrogel

Semi-IPNs of various compositions were prepared by redox polymerization method as reported elsewhere[14]. In a typical experiment, into 10 mL of distilled water were added 1 g of PVA, 3.79 mM of acrylonitrile, 0.43 mM of MBA, and 1 mL each of potassium metabisulphite (0.01 M) and potassium persulphate (0.001 M). The reaction mixture taken in a rectangular glass pellet (50mm×50 mm×10 mm) was kept at 35°C for three days. The semi-IPNs so prepared were taken out carefully and purified by equilibrating them in distilled water so as to ensure complete leaching of unreacted chemicals, prepared monomer and polymers. The purified semi-IPNs were cut into equal sized square pieces, dried at room temperature for a week and stored in air-tight polyethylene bags. The formation of grafted hydrogel is schematically shown in "Fig.1".

## Characterization

### FTIR analysis

FTIR spectrometry is a quantitative approach that helps in understanding the miscibility of the two polymers in the specimen. The prepared semi-IPN was subjected to FTIR spectroscopy using an FTIR spectrophotometer (Paragon 1000 FTIR) in the wavelength range of 4000 to 400 cm<sup>-1</sup>.

### Scanning electron microscopy

The surface morphology of the prepared semi-IPNs was examined by recording their SEM images on a scanning

electron microscope (JSM-S600 LV; Resolution = 3.5 nm, mag.x18 to 3,00,000 in 136 steps; accelerating voltage = 0.5 to 30 KV, 53 steps).

### X – Ray Diffraction

XRD provides the information regarding crystalline and amorphous regions within the polymeric gel. In order to ascertain the crystalline nature of the prepared semi-IPNs, their X-ray diffraction study was carried out on Rigaku Rotating Anode Mode (RU-H3R) (18KW), X-ray powder diffractometer with operating target voltage as 35 KV and tube current as 20 mA. The diffraction data were taken from 10 to 70°, 2θ values with a step size of 0.02° and counting time of 2s/step using a wavelength of 1.54Å. The intensity versus 2θ profile were obtained for all the specimens.

### Water Sorption Measurements

One of the most important properties of hydrogel is the ability to imbibe water. Various mechanical properties, surface properties and the resultant behavior at biological interfaces are all a direct consequence of their water sorption capacity. The progress of water sorption process was monitored gravimetrically. In brief, pre-weighed and completely dried rectangular pieces (1cm x 1cm x 1cm) of semi-IPNs were placed in a water reservoir and allowed to swell till equilibrium. The swollen pieces were then taken out at different time intervals and gently pressed in between two filter papers to remove excess of water and finally weighed on a sensitive electronic balance (No. APX – 203 Denver Instrument, GMBH Germany). The swelling ratio was calculated by the following equation:

$$\text{Swelling Ratio} = \frac{\text{Weight of dry IPNs}}{\text{Weight of dry IPNs}} \quad (1)$$

## Results and Discussion

### FTIR spectral analysis

The IR spectra of native acrylonitrile, native PVA used in this study and of grafted gel are depicted in "Figs.2 (a-c)", respectively. The spectra 2 (c) of the grafted hydrogel clearly marks the presence of PVA and acrylonitrile in the gel as confirmed by the peaks observed at 3468 cm<sup>-1</sup> (O-H stretching of hydroxyl group) and at 2260 cm<sup>-1</sup> (C≡N stretching of nitrile group). Presence of crosslinker (MBA) is confirmed by the peak at 3050 cm<sup>-1</sup> due to N-H stretching of secondary amide group of MBA. In addition to the above mentioned peaks, the peaks appearing in the range 3000 to 2900 cm<sup>-1</sup> shows the presence of -CH<sub>2</sub> group in all the three spectra. Apart from this the other commonly observed peaks in the IPN spectra are 1155 cm<sup>-1</sup> (C-O stretching), 970 cm<sup>-1</sup> (CH<sub>2</sub> twisting) and at 770 cm<sup>-1</sup> (N-H oop bend amide). Thus, based on the above discussion, the structure of the synthesized semi-IPN may be imagined as an entangled macromolecular matrix in which crosslinked PAN chains are held to each other via physical type of forces. It is important to mention here that there is a shifting of nitrile peak from 2231cm<sup>-1</sup> (spectra 'a') to 2258 cm<sup>-1</sup> which suggests for weak interaction between OH of PVA and C≡N of PAN.

### SEM analysis

The SEM micrograph visualizes the phase morphology of the synthesized specimens shown in "Figs. 3-5". The separated domains suggest for phase separation and thus provide a morphological evidence of presence of both, PVA and PAN, in the matrix. The possible cause of phase separation may be that whereas PVA is a linear and hydrophilic polymer, the crosslinked PAN, a hydrophobic polymer, may form clusters of crosslinked chains held to one another via H-bondings between the nitrile and hydroxyl functional of PAN and PVA macromolecules. As the amount of PVA increases ["Figs. 3(a-d)"] the loose and separated hydrophilic domains of PVA and PAN becomes quite compact and porous with an increased homogeneity. The presence of spheres on the surface of films ["Figs. 4 (a-d)"] clearly marks the appearance of hydrophobic domains of PAN and also indicates that two types of PVA may exist, one as crosslinked and the other as linear polymer. For the lowest employed amount of the crosslinker ["Figs. 5 (a-d)"] the SEM images of semi-IPNs shows a mesh type morphology which could be due to the reason that at low crosslink density, the network chains have relatively greater movement and arrange themselves to buildup a mesh type of network. However, as the crosslink density gradually increases, the mesh sizes go on shrinking, thus producing an increasingly compact semi-IPN with a heterogeneous morphology.

### Network Parameters

Various network parameters calculated from water uptake potential of hydrogel systems provide a clear view to their biocompatibility, durability and long-term performance. One of the important structural parameters characterizing a crosslinked polymer is the average molecular mass between crosslinks ( $M_c$ ) and crosslink density ( $q$ ). The magnitude of  $M_c$  and  $q$  significantly affects the physical and mechanical properties of crosslinked polymer and its determination has great practical significance. Equilibrium swelling has been widely used to determine network parameters. Flory and Rehner's[15] early research laid the foundation of analysis of equilibrium swelling and proposed the following equation for the perfect network :

$$M_c = \frac{-V_1 \frac{dp}{dV_s} [V_s^{1/3} - (V_s / 2)]}{\ln(1 - V_s) + V_s + \chi V_s^2}$$

and  $q = M_0 / M_c$ . Here  $V_1$  is the molar volume of water ( $\text{mL mol}^{-1}$ ),  $dp$  is the polymer density ( $\text{g mL}^{-1}$ ),  $V_s$  is the volume fraction of the polymer in the swollen IPN approximately equal to  $1 / (1 + \text{swelling ratio})$ ,  $\chi$  is the Flory-Huggins interaction parameter between IPN and solvent (water)[16] and  $M_0$  is the molar mass of repeat unit of polyacrylonitrile. The value of  $\chi$  for polyacrylonitrile was taken from the literature[17]. The density ( $dp$ ) of the semi-IPN was determined to be  $1.2 \text{ g cm}^{-3}$ . The value of  $M_c$  and  $q$  have been calculated for different semi-IPN compositions and summarized in Table-2. It is clear from the data that when the concentration of AN increases from 3.79 mM to 22.31 mM, the average molecular weight between crosslinks ( $M_c$ ) constantly increases whereas the

crosslink density ( $q$ ) decreases. The observed results are quite obvious and may be explained by the reason that with increasing concentration of AN, the number of monomer molecules adding onto growing macroradical also increases which brings about an increase in molecular weight between the crosslinks ( $M_c$ ). It is also clear that due to increase in availability of the monomer, the number of crosslink points will also decrease.

### XRD analysis

When X-ray radiations are directed on a sample they are scattered (diffracted) by electrons present in the material. If the atoms in the material, are arranged in a regular structure, i.e. if the material is crystalline, this scattering results in maxima and minima in the diffracted intensity. The single maxima follow Bragg's law  $n \lambda = 2d \sin \theta$  where  $n$  is an integer,  $\lambda$  is the X-ray wavelength,  $d$  is the distance between crystal lattice planes and  $\theta$  is the diffraction angle.

In an X-ray diffraction pattern the position and intensity of the maxima are characteristic for the crystallographic structure and the atomic composition of the material. In case of a multi-phase composition, the resulting pattern is a combination of the patterns of all structures present. Phase identification can be done by matching the XRD pattern with reference patterns of pure substances. The intensity curve could further, serve as a basis for percentage crystallinity evaluation. Crystallinity is a measure of regularity in arrangement of structural elements. Measurement of area under the intensity curves yields crystallinity. The diffraction intensity scan can be separated into contributions from sharp diffractions and diffused halo. A comparison of relative area under the resolved curve yields crystallinity. Various methods have been developed for measuring the area under various fractions. In the present investigation, crystallinity has been measured on the premise that increasing amorphousness tends to broaden the line width whereas increasing crystallinity increases the intensity, resulting in a sharp peak. The sharp area in the form of triangular region (upper part of intensity curve) in the XRD profile represents the crystalline phase ( $A_c$ ) whereas the broader part (in trapezoidal shape) just below the triangular region represents amorphousness ( $A_a$ ) of the sample. The percent crystallinity ( $X_c$ ) was calculated has been evaluated using following equation[18] :

$$X_c \% = [A_c / (A_a + A_c)] \times 100 \quad (2)$$

where  $A_c$  and  $A_a$  are the area of crystalline and amorphous phases, respectively. Pure PVA is crystallizable, with a typical sharp and narrow peak in its intensity curve[19] with maximum reflection at  $2\theta = 19^\circ$  whereas pure acrylonitrile is non crystallizable, and hence XRD of it's specimen[20] shows a broad peak. The diffraction patterns for the specimens with various weight proportions are shown in "Figs. (6-8)". "Fig. 6" elucidate that as the PVA content in the semi-IPNs increases, sharpness of the peak increases, thus supporting the increasing crystallinity values given in Table 1. When acrylonitrile (semi-crystalline) is used in the concentration range of 3.79 mM to 15.17 mM ["Fig.(7)"] in the semi-

IPNs, PVA crystallizes and the non-crystallizable component is rejected from the crystal region resulting in broad amorphous population, suggesting for the presence of relatively ordered crystalline phase.

On varying the crosslinker (MBA) concentration in the range of 0.43 mM to 1.72 mM [“Fig.(8) ”], the broadening of XRD peaks is observed, which clearly suggests for the reduced crystallinity and crystal size of the semi-IPNs . Reason for the observed findings may be attributed to the fact that with increasing crosslinker content in the semi-IPN the network becomes smaller in dimension which obviously give rise to crystals of lower size. The reduced degree of crystallinity may be explained by the fact that with the higher crosslinker content relatively shorter chains are produced which are less likely to organize into a definite ordered structure. Thus the crystallization process of the synthesized semi-IPNs elucidates that the incorporation of acrylonitrile onto PVA reduces the crystal degree of PVA. Decrease in the crystal degree of PVA with the increase in grafting may be due to decaying regularity of the PVA chains by breaking down the interchain hydrogen bonding along the chain. Further, crystallinity decreases as branching and molecular weight increases.

### Swelling Measurements

The sorption data can be mechanistically analyzed on the basis of the amount of water absorbed (uptake) as a fraction of time.

### Effect of PVA on swelling

Table 2 demonstrates water absorption tendency expressed in terms of swelling ratio of the semi-IPNs for different composition of PVA, acrylonitrile and MBA. PVA is a hydrophilic polymer and it's increasing amount in gel matrix is expected to enhance hydrophilicity of the network. In order to study the effect of PVA on swelling ratio, the amount of PVA was varied in the range of 1.0 g to 4.0 g . The results surprisingly reveal an initial increase in the swelling rate upto 3.0 g, but a decrease in the swelling ratio is observed for further increase in the PVA content.

The initial results may be attributed to the hydrophilic nature of PVA but with increase in PVA content, the volume fraction of polymer increases, which results in a decrease in water imbibition capacity. Thus, water molecules will have to travel a longer distance through the semi-IPN to make them swell up. Also, with increasing PVA content the number of hydroxyl and methylene groups increases which consequently enhances the hydrogen bonding and hydrophobic interactions within the hydrogel network. This may lead to an initial increase but a final lower water sorption rate. Similar type of results have also been reported elsewhere[21].

### Effect of acrylonitrile on swelling

In order to investigate the effect of hydrophobic monomer (acrylonitrile) on the swelling behavior of semi-IPN, the concentration of AN was varied in the feed mixture in the range 3.79 mM to 15.17 mM .The results in Table 2 clearly reveal that the swelling ratio constantly decreases

with the increasing concentration of AN. The noticed fall in water uptake capacity may be attributed to the hydrophobic and semi-crystalline nature of AN which may result in an enhanced hydrophobic interaction between PAN chains with more compact structure. Thus, the penetration of water molecules and subsequent relaxation of PAN chains are restrained which ultimately results in a suppressed swelling rate of the semi-IPN. Furthermore, with the increasing AN content in the semi-IPN, the increase in number of hydrogen bonds could also be the reason for decreased swelling ratio.

### Effect of MBA

Properties of hydrogels can be easily modified by varying the amount of crosslinker in the semi-IPN. In the present study, the effect of crosslink density on the swelling of the network has been studied by varying the concentration of the crosslinker (MBA) in the range 0.43mM to 1.72mM in the feed mixture of the semi-IPN. The results, as depicted in Table 2, indicates a significant increase in the swelling ratio with increasing concentration of MBA. The reason for the observed increase may be that MBA is a bifunctional monomer with hydrophilic amide and hydrophobic -CH<sub>2</sub> groups. It seems that swelling rate increases due to hydrophilic characteristic of this monomer [22-23].

### Conclusion

The FTIR spectra of semi -IPN not only confirms the presence of PVA and crosslinked PAN but also provides significant information about the nature of the network formed. The peak observed at higher frequency (3601 cm<sup>-1</sup>) due to O-H stretching of PVA suggests for the formation of weak hydrogen bonds between O-H and C≡N of PAN. The separated domains in the SEM images of the semi-IPNs provides a morphological evidence of the presence of both, PVA and crosslinked PAN in the gel matrix. Their XRD patterns indicate that the presence of PVA content in the semi-IPNs give relatively ordered crystalline phase. The presence of acrylonitrile and MBA content reduces the crystallinity of semi-IPNs and it is observed that the crystallinity in the membrane is mainly due to PVA. The interplanar distance 'd' for all the semi-IPNs are almost similar but different from the native PVA. The role of crosslinker (MBA) in the swelling ratio was surprising with high water imbibition property with increasing crosslinker content. These various results obtained from different characterization study very well support the proposed scheme of reaction for the formation of semi-IPNs and suggests their utility in biomedical and other industrial fields.

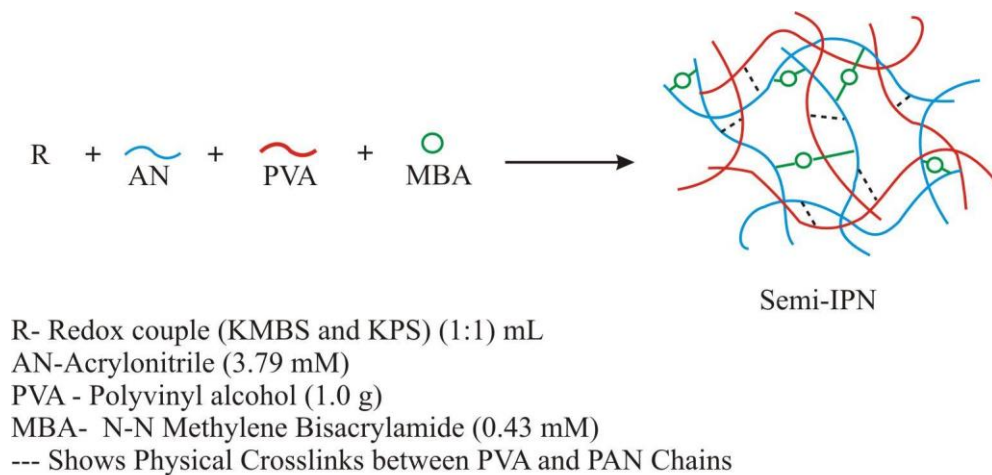
### Acknowledgement

The authors would like to acknowledge IUC-DAE Consortium for Scientific Research, Indore ( M.P.), India for providing SEM and XRD facilities.

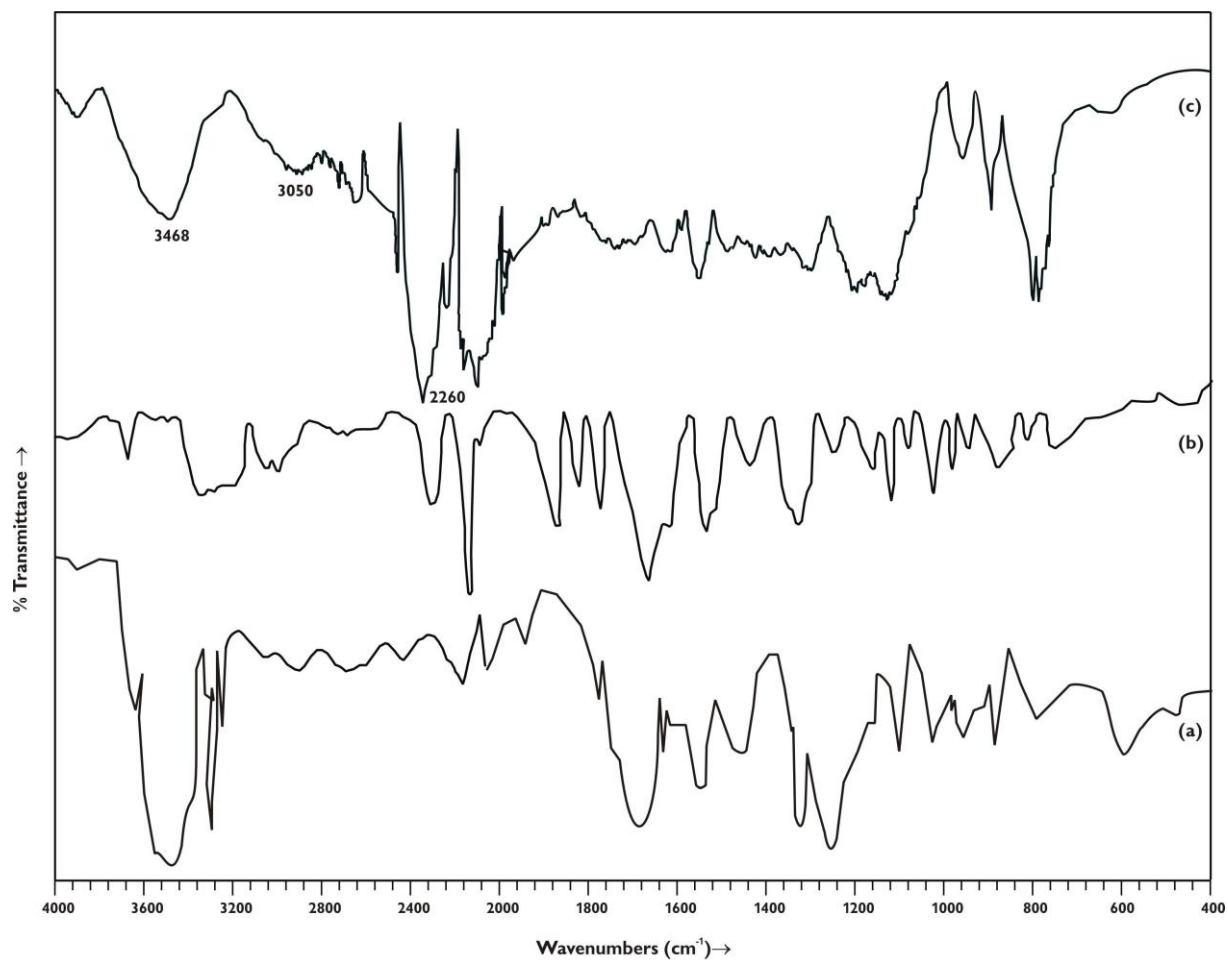
### References

- [1] Lee K.Y. and Mooney D.J. (2001) *Chem. Rev.*, 101, 1869.

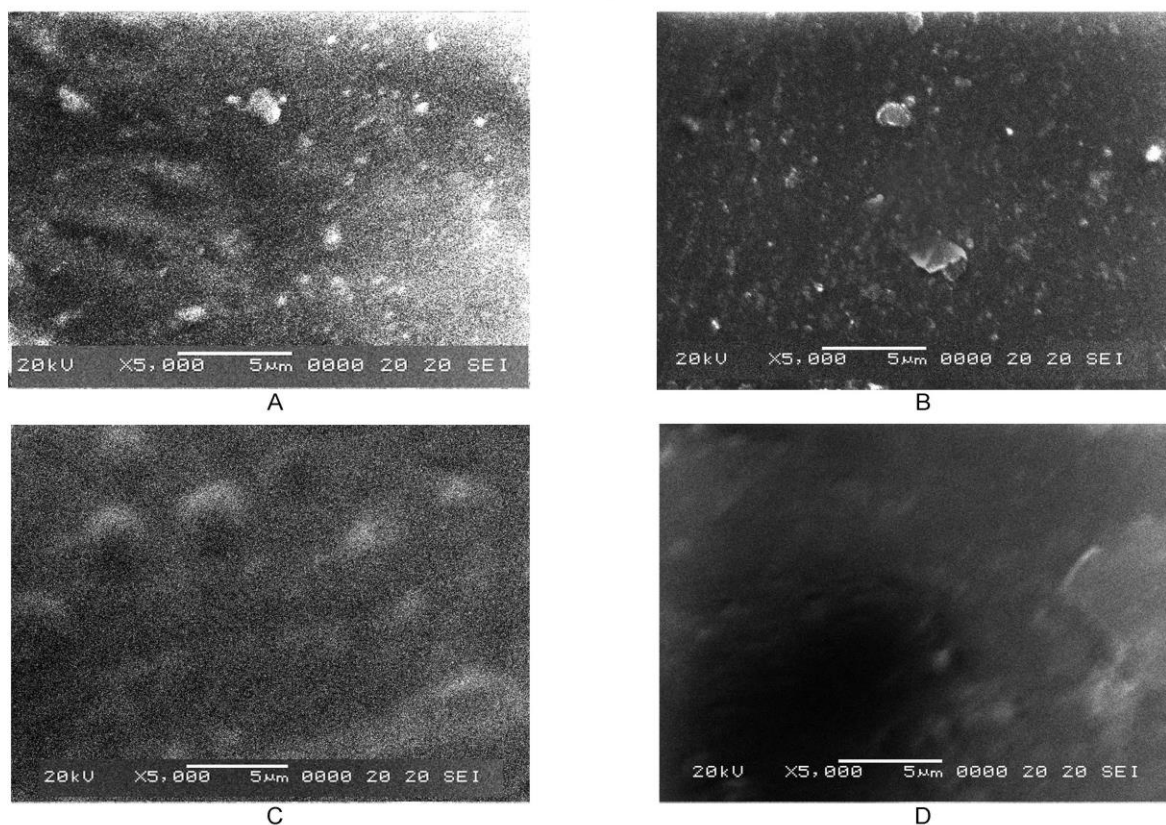
- [2] Hoffman A.S. (2002) *Adv. Drug. Deliv. Rev.*, 43 (3).
- [3] Hung M. and Fang Y. (2005) *Biopolymers Part C, Wiley Periodicals, Inc. Biopolymers*, 81, 160.
- [4] Shah C.P., Mishra B., Kumar M., Priyadarsini K.J. and Bajaj P.N. (2008) *Current Science*, 95, 10.
- [5] Nicholas A. Peppas., Hilt J.Z., Ali K.H. and Langer R. (2006) *Adv. Mater*, 18, 1645.
- [6] Di Martino A., Vaccaro A.R., Lee J.Y., Denaro V. and Lim M.R. (2005) *Spine*, 30(16S): S16-S22.
- [7] Pal K., Banthia A.K. and Majumdar D.K. (2006) *Trends Biomater. Artif. Organs*, 20(1), 59.
- [8] Seo M.S. and Lee H.L. (2003) *Peer reviewed electrical Insulating Papers, Tappi Journal* 4(5).
- [9] Jain E., Srivastava A. and Kumar A. (2009) *J Mater Sci.: Mater Med*, 20(1), 173.
- [10] Bajpai A.K. Shukla S. and Kulkarni R.A. (2004) *J Appl Poly Sci*, 95(5), 11230.
- [11] Bajpai R., Katare R., Bajpai, A.K. and Mishra S. (2006) *J Appl Poly Sci*, 100(3), 2402.
- [12] Bajpai R., Bajpai A.K. and Rajvaidya S. (2004) *In Proceedings of International Seminar on Advance in Polymer Technology*, 16, 64.
- [13] Bajaj P., Sreekumar T.V. and Sen. K. (2001) *Polymer*, 42(4), 1707.
- [14] Bajpai R., Bajpai A.K., and Deshpande D. (2010) *In Proceedings Of 55th DAE Solid State Physics Symposium In American Institute of Physics Conference Proceedings* 1349, 55.
- [15] Finch C.A. (1985) *In Chemistry and Technology of Water Soluble Polymers*, Finch C.A. (Ed.), New York; Plenum Press, 5, 81.
- [16] Ding Z. Y., Akinbis J.J. and Salogev R. (1991) *J Poly Sci Polym Phys*, 20, 1035.
- [17] Brandrup J. and Immergut E.H. (Eds.) (1967) *Polymer Hand Book*, New York : Wiley Interscience.
- [18] Gupta V.B. and Kothari V.K. (1997) *Manufactured Fiber Technology*, V.B. Gupta & V.K. Kothari (Eds), P-225, Chapman and Hall, London.
- [19] Mishra S., Bajpai R., Katare R. and Bajpai A.K. (2005) *J. Mater. Sci.: Mater. Med.*, 17(12), 1305.
- [20] Qiao Z., Xie Y. Zhu Y. and Qian Y. (1999) *J. Mater. Chem.*, 9(4), 1001.
- [21] Shicheng Y. and Kinam P. (2004) *J Bioact Compat Polym*, 19.
- [22] Hekmat A., Barati A., Frahani E.V. and Afraz A. (2009) *World Academy of Science, Engineering and Technology*, 56.
- [23] Gils P.S., Ray D., Mohanta G. P., Manavalan R. and Sahoo P. (2009) *Int J Pharm Sci*, 1(2), 43.



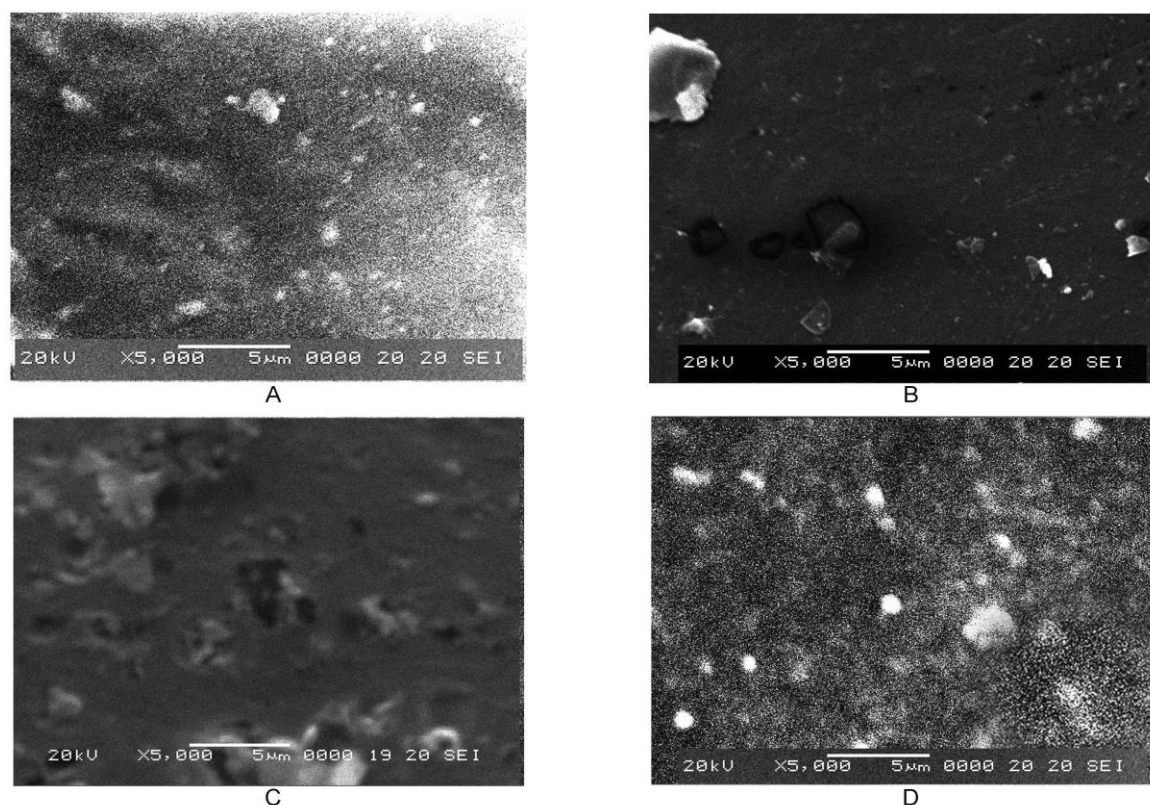
**Fig. 1-** Schematic presentation of formation of semi-IPN



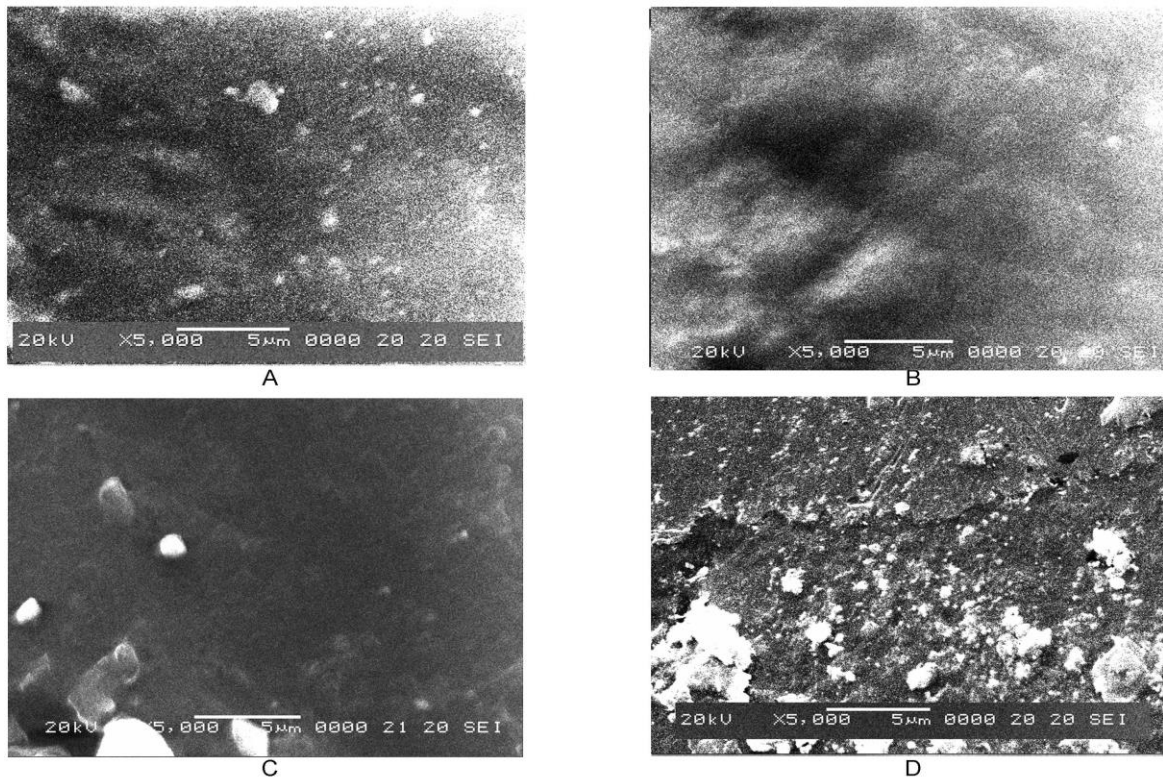
**Fig. 2** -FTIR Spectra of (a) native acrylonitrile, (b) native PVA and (c) PVA-g-acrylonitrile semi-IPN



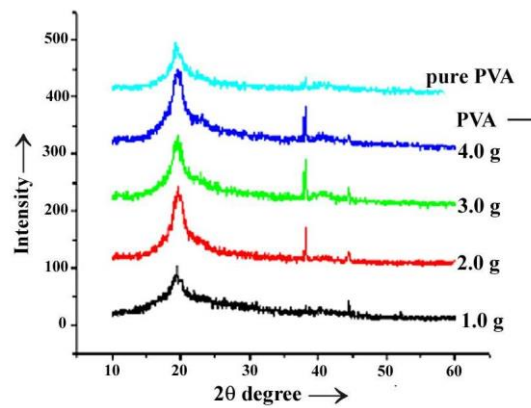
**Fig. 3-** SEM images showing the influence of PVA variation on the morphology of semi- IPN surfaces, PVA = (a)1.0 g, (b) 2.0 g , (c) 3.0 g , (d) 4.0 g for definite concentration of [AN] = 3.79 mM and [MBA] = 0.43 Mm



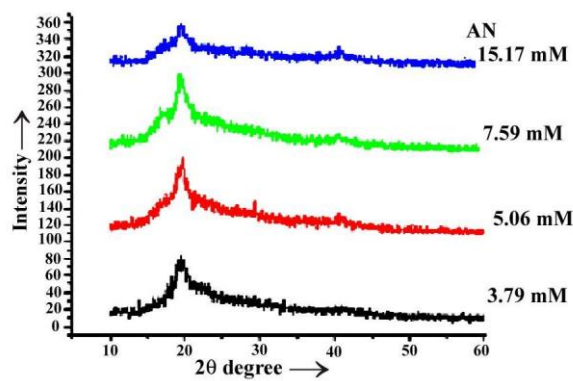
**Fig. 4 -** SEM images depicting the effect of AN variation on the morphology of semi-IPN surfaces, AN = (a) 3.79 mM , (b) 5.06 mM , (c) 7.59 mM , (d) 15.17 mM for definite concentration of (PVA) = 1.0g and [MBA] = 0.43mM



**Fig. 5-** SEM images showing the effect of crosslinking agent on the morphology of semi-IPNs, MBA = (a) 0.43mM , (b) 0.86mM , (c) 1.29mM , (d) 1.72 mM for definite concentration of [PVA] = 1.0g and [AN] =3.79 mM

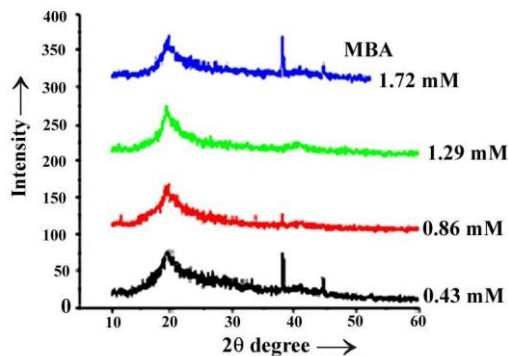


**Fig. 6-** Influence of PVA variation on XRD patterns of Semi-IPNs for definite concentration of AN =3.79 mM and MBA = 0.43mM



**Fig. 7-** Influence of AN variation on XRD patterns of Semi-IPNs for definite concentration of PVA = 1.0 g and MBA = 0.43mM





**Fig. 8-** Influence of MBA variation on XRD patterns of Semi-IPNs for definite concentration of PVA = 1.0 g and AN = 3.79mM

*Table 1-Crystallinity and Interplanar distance 'd' for semi-IPNs of different concentrations*

| S. No. | PVA (g) | AN(mM) | MBA(mM) | Crystallinity(Xc) | Peaks at $2\theta$ (o) | Interplanar distance 'd' (Å) |
|--------|---------|--------|---------|-------------------|------------------------|------------------------------|
| 1      | 1       | -      | -       | 0.63              | 19                     | 4.7                          |
| 2      | 1       | 3.79   | 0.43    | 0.53              | 19.56                  | 4.514                        |
| 3      | 2       | 3.79   | 0.43    | 0.55              | 19.4                   | 4.54                         |
| 4      | 3       | 3.79   | 0.43    | 0.62              | 19.6                   | 4.53                         |
| 5      | 1       | 5.06   | 0.43    | 0.51              | 19.46                  | 4.551                        |
| 6      | 1       | 7.59   | 0.49    | 0.49              | 19.46                  | 4.551                        |
| 7      | 1       | 15.17  | 0.43    | 0.48              | 19.54                  | 4.522                        |
| 8      | 1       | 3.79   | 0.86    | 0.51              | 19.46                  | 4.551                        |
| 9      | 1       | 3.79   | 1.29    | 0.51              | 19.46                  | 4.551                        |
| 10     | 1       | 379    | 1.72    | 0.49              | 19.46                  | 4.551                        |

*Table 2-Swelling Ratios and Network Parameters of the Semi-IPNs of Different Compositions*

| S. No. | PVA (g) | AN(mM) | MBA(mM) | SR   | Mc   | q x 10 <sup>-4</sup> |
|--------|---------|--------|---------|------|------|----------------------|
| 1      | 1       | 3.79   | 0.43    | 4.4  | 2824 | 188                  |
| 2      | 2       | 3.79   | 0.43    | 4.8  | 2967 | 179                  |
| 3      | 3       | 3.79   | 0.43    | 5    | 3206 | 166                  |
| 4      | 4       | 3.79   | 0.43    | 4.78 | 3005 | 177                  |
| 5      | 1       | 5.06   | 0.43    | 4.03 | 2250 | 236                  |
| 6      | 1       | 7.59   | 0.43    | 3.35 | 2675 | 198                  |
| 7      | 1       | 15.17  | 0.43    | 3.09 | 3005 | 177                  |
| 8      | 1       | 3.79   | 0.86    | 4.8  | 3337 | 159                  |
| 9      | 1       | 3.79   | 1.29    | 5.1  | 3430 | 155                  |
| 10     | 1       | 3.79   | 1.72    | 5.43 | 3647 | 145                  |