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# Preparation, characterization and microhardness study of semi interpenetrating polymer networks of polyvinyl alcohol and crosslinked polyacrylamide

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**Abstract** Semi-IPNs based on polyvinyl alcohol (PVA) and crosslinked polyacrylamide (PAM) were prepared and characterized. Various compositions of semi-interpenetrating polymer networks (semi-IPNs) were prepared by varying concentrations of PVA, acrlyamide (AM) and crosslinker N,N′-methylene bis acrylamide (MBA) in the feed mixtures and polymerized using a suitable redox system comprising of potassium persulphate and metabisulphite. The prepared semi-IPNs were characterized by fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and X-ray diffraction (XRD) methods. The prepared semi-IPNs were also investigated for microhardness measurements.

## 1 Introduction

Hydrophilic macromolecular matrices possessing outstanding capacity to accommodate water into their three dimensional structures without undergoing dissolution constitute a versatile class of materials finding a wide spectrum of applications in biomedical and pharmaceutical fields [1–3]. These materials are often known as 'hydrogels' or 'hungry networks' and display a great resemblance to living tissues due to their high water content. This property of water imbibition qualifies them as a potential candidate for artificial implantation in medical science. However, their extraordinary affinity for water also imparts in them a poor mechanical strength and restrict their clinical acceptance in orthopedics and other allied applications where the implanted material has to withstand a constant mechanical stress. Thus, development of hard polymeric material with adequate hydrophilicity is a challenging task.

Polyvinyl alcohol (PVA) is a unique synthetic polymer and credits wide spectrum of biomedical applications such as soft contact lenses [4], implants [5] and artificial organs [6]. This is because of their inherent non-toxicity, non-carcinogenity, good biocompatibility and desirable physical properties such as rubbery or elastic nature and high degree of swelling in aqueous solution. The chemical resistance and physical properties of PVA have led to its broad industrial use. Chemical crosslinking of this linear polymer provides feasible routes for the improvement of the mechanical properties and thermal stability. Chemically crosslinked PVA hydrogels have received increasing attention in biomedical and biochemical applications because of their permeability, biocompatibility and biodegradability [7–10]. Polymers of acrylamide are well known for their hydrophilicity and inertness that make them a material of choice in large number of applications in medical and pharmacy [11].

Reinforced uncrosslinked PVA gels developed by Peppas *et al.* [12] have shown significant interests in the biomedical field. Kobayashi *et al.* [13] explored the possibility of PVA hydrogels as a material for knee injury. Shefee and Naguib [14] studied water sorption behavior of PVA crosslinked with diisocyanate and determined dynamic mechanical properties

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of PVA films. A semi-IPN was prepared by Bajpai *et al.* [15] by crosslink copolymerization of acrylamide, styrene in the presence of PVA. Paul *et al.* [16] described the use of polyacrylonitrile—polyvinyl alcohol membranes for hemodialysis having good mechanical strength to withstand the maximum transmembrane pressure. The foregoing comments regarding the significant use of the PVA has motivated the authors to develop the semi-IPNs of PVA with crosslinked polyacrylamide, which can exhibit good mechanical properties. For better understanding of structure-property relationship of the semi-IPN, the FTIR, XRD and SEM studies have been utilized.

Microhardness measurements have emerged as one of the promising tools for evaluating mechanical performance of a polymeric material [17–19]. In the present investigation also the same technique has been adopted to study the microhardness of various well characterized semi-IPNs of polyvinyl alcohol and crosslinked polyacrylamide.

## 2 Experimental

### 2.1 Materials

Poly(vinyl alcohol) (PVA) (hot processed), mol. wt. 14000 was obtained from Research Lab Chem Industries, Mumbai, India used without further purificiation. Acrylamide (AM) (Research Lab, Pune, India) was crystallized twice in methanol and dried in vacuum over anhydrous silica for a week. 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 (MBS) (Qualigens Fine Chemicals, Mumbai, India) as activator. Bi-distilled water was used throughout the experiments.

### 2.2 Synthesis of IPN

Semi-IPNs were prepared by redox polymerization method reported elsewhere [20]. In a typical experiment, into 25 ml of PVA solution (2.0 g) were added acrylamide (2.0 g), 0.020 g of MBA and 1 ml each of potassium metasulphite (0.01 M) and potassium persulphate (0.001 M). The reaction mixture taken in a rectangular glass pellet (50 mm × 50 mm × 10 mm) was kept at 35°C for a week. The dried IPN was cut into equal sized square pieces and stored in air–tight polyethylene bags.

### 2.3 Microhardness measurements

Since the wet samples were quite poor in mechanical strength, their microhardness study could not be performed. The microhardness of the dry samples were studied with the help of mhp 160 microhardness tester equipped with a Vicker's diamond pyramidal indenter having a square base and 136° pyramidal angle attached to a Carl Zeiss NU2 universal research microscope [21]. The Vickers hardness $H_V$ was calculated by the following relation:

$$H_V = \frac{1.854 \times L}{d^2} \text{kg/mm}^2$$

Where $L$ is the load in kg and $d$ is diagonal of indentation in mm. Indentations at each load were obtained in replicate number and average hardness number was calculated.

## 3 Characterization

The prepared dry samples of semi-IPNS were characterized by the methods discussed below. However, it is worth to mention here that the analysis could be performed with dry semi-IPNs only, because the wet (swollen) samples were somewhat poor in mechanical strength and therefore could not be handled for analysis.

### 3.1 FTIR analysis

The structural characterization of the semi-IPN was performed by recording transmission IR spectra of a thin film of the end-polymer on a Perkin-Elmer spectrophotometer (Paragon 1000 FTIR).

### 3.2 Scanning electron microscopy

The SEM of the prepared semi-IPNs were recorded without sectioned and coating the samples on a scanning electron micrograph (JSM-5600 LV).

### 3.3 X-Ray diffraction (XRD)

The X-ray diffraction studies of the prepared semi-IPNs were carried out on Rigaku Rotating anode mode RU-H3R (18 KW), X-ray powder diffractometer. The intensity versus $2\theta$ profiles was obtained. Crystallinity is a measure of regularity in arrangement of structural elements. The intensity curve could serve as a basis for quantitative crystallinity evaluation. The diffraction intensity scan can be separated into contribution from sharp diffractions and diffused halo. A comparison of the relative areas under the resolved curves yields crystallinty. Various methods have been developed for measuring the area under various fractions. Here, the crystallinity has been measured on the premise that increasing amorphousness tends to broaden the line width whereas increasing crystallinity increases the intensity. The height (CrH) of the main peak above its adjacent minimum represents the crystallinity of the sample and the width (AmW) of the peak at this adjacent minimum is considered to represent the amorphousness of the sample [22–23]. The crystallinity CrI, is calculated from the relation

$$\mathrm{CrI} = 1 - \mathrm{t} \times \frac{\mathrm{AmW}}{\mathrm{CrH}}$$

Where t is the scale factor relating the height of CrH to full scale (total blackness).

From the diffraction patterns of the various poly blends, the interplaner distance d was computed for different peaks. Bragg's equation was used to determine the distance between two successive planes from which the X-ray were diffracted:

$$2\mathrm{d}\sin\theta = \mathrm{n}\lambda$$

Where λ is the X-ray wavelength, $\theta$ is Bragg's angle, and n is the order of diffraction [24]. d was calculated from the first order for various peaks obtained in the diffraction patterns:

$$\mathrm{d} = \frac{\lambda}{2\sin\theta}$$

## 4 Results and discussion

### 4.1 IR spectra

The IR spectra of pure PVA, pure PAM and semi-IPN are depicted in Figs. 1(a–c), respectively. A broad band appeared in the spectra (c) at 3485 $\mathrm{cm}^{-1}$ clearly marks the presence of hydrogen bonding and hydrophilic nature of IPN. It also shows the presence of OH and $NH_2$ groups, which appear at 3439 $\mathrm{cm}^{-1}$ in spectra (a) and 3424 $\mathrm{cm}^{-1}$ in spectra (b), respectively. In addition to the above mentioned peaks, the peaks appeared in the range 3000 $\mathrm{cm}^{-1}$–2900 $\mathrm{cm}^{-1}$, which show the presence of $CH_2$, groups in all the three spectra. In the spectra (c), a sharp adsorption peak at 1698 $\mathrm{cm}^{-1}$ shows C=O stretching which confirms the presence of crosslinked polyacrylamide chains in the semi-IPN. It is of significance to note that the absorption band for C=O stretching of the semi-IPN is much sharper than that for native PVA and PAM, shown in Fig. 1(a and b) respectively. The occurrence of sharp peak may be explained by the fact that some of the hydroxyls at the PVA get oxidized to carbonyl groups (C=O) in the IPN which clearly results in a sharp absorption band.

### 4.2 Morphological study

A material to be employed as a human organ substitute must meet certain well accepted physiological criteria which have been often coined as 'biocompatibility'. The surfaces of biomaterials are believed to play a key role in determining the biocompatible nature of the material. It is largely reported that blood compatibility is affected by the various properties of the material surface, for example, surface charge, wet ability, surface free energy, topography or roughness, and the presence of specific chemical groups on the surface. Thus, morphology of a biomaterial surface is an important aspect to be understood for gaining insights into the correlation between the blood compatibility and materials surface. This has been achieved by recording scanning electron microscope (SEM) images of the prepared semi-IPNs of varying compositions. The SEM images may be discussed in the following paragraphs.

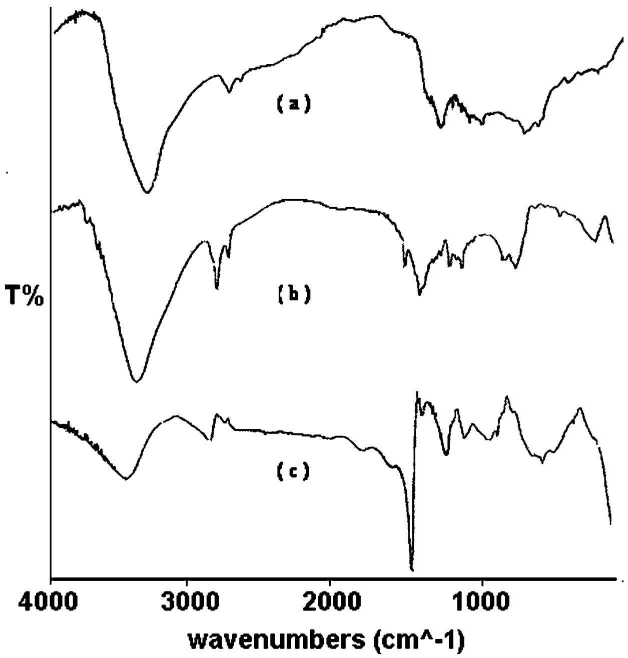


**Fig. 1** IR spectra of (a) pure PVA, (b) pure PAM and (c) PVA-acrylamide semi-IPN.

When the concentration of PVA is varied in the range of 1.0–4.0 g in the feed composition of the semi-IPN, the observed SEM images are shown in Figs. 2(a–c) respectively for 1.0, 2.0 and 4.0 g of PVA content. It is clear from the image (a) that at the lowest PVA content the network surface appears loose and separated hydrophilic domains of PVA and PAM of varying size between 20 to 50 $\mu$m are clearly seen on the surface. When the concentration of PVA becomes 2.0 g, the network surface appears quite compact and porous. However, at the highest PVA content, i.e. 4.0 g, the network appears little heterogeneous due to enhanced volume fraction of polymer (PVA).

The influence of polyacrylamide content on the morphology of the semi-IPN has been investigated by varying acrylamide concentration in the feed mixture of the semi-IPN in the range of 2.0–6.0 g. The obtained micrographs are shown in Figs. 3(a–d) respectively. Upon close

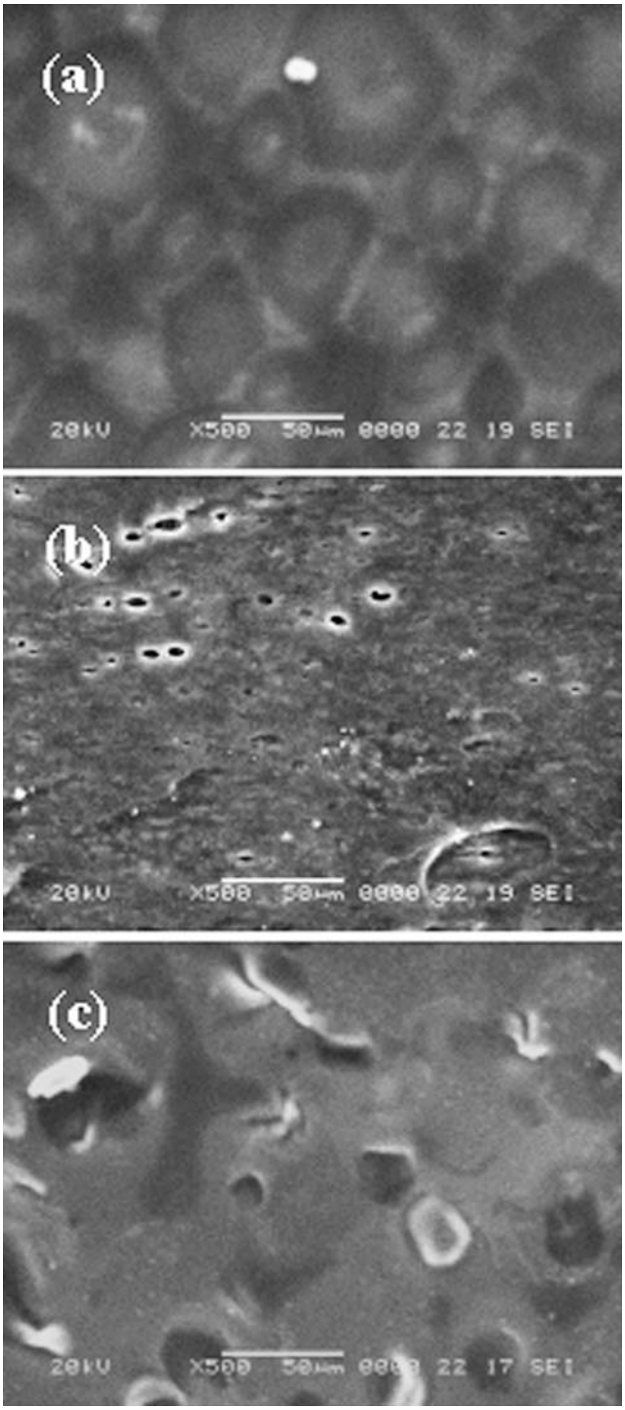


**Fig. 2** SEM images (secondary electron image with 500 Mag. and 20 kV) showing the influence of PVA on morphology of the semi-IPN surfaces PVA = 1.0 g (a), 2.0 g (b), 4.0 g (c) for definite concentration of [AM] = 2.0 g and [MBA] = 0.020 g.

examination of SEM images, it is clear that with increasing content of AM in the semi-IPN, the surface acquires increasing heterogeneity, which is well evident from the separated domains visible in the micrograph. It is also clear from the SEM image (c) that at much higher acrylamide content, the constituent polymeric chains form irregular shaped clusters, which may be attributed to the extensive formation of hydrogen bonds between the amide and hydroxyl functional of polyacrylamide and polyvinyl alcohol macromolecules.

Another important constituent of the semi-IPN is the crosslinker (N,N′-methylene bis acrylamide), whose effect on the surface morphology of the network has been studied by varying its concentration in the range 0.010 g–0.100 mg in the feed composition of the semi-IPN. The images of the respective micrographs of the semi-IPN are depicted in Fig. 4 which clearly indicates that at lowest employed concentration of crosslinker, the IPNs surface 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 build-up 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 nearly homogeneous morphology.

### 4.3 XRD analysis

Most of the important properties of polymer systems are directly related to the structural feature called crystallinity and, therefore, its measurement is frequently sought. The morphology of most polymers is semi crystalline, i.e., they form mixtures of small crystals and amorphous material. The crystallization depends on the degree of miscibility and mobility of crystallizable and non-crystallizable components in the blend specimens. Crystallinity is a measure of regularity in arrangement of structural element. The crystalline material shows a high degree of order formed by folding and stacking of the polymer chains. The amorphous structure shows no long-range order and the chains are tangled. In the semi-IPN of crystalline and amorphous polymers, chain tangles and disordered region surround the crystalline areas. XRD has been utilized to detect crystallinity in polymer blends [25]. The present investigation enables to understand the crystallinity changes in prepared semi-IPNs.

The effect of chemical composition of the hydrogel on crystallinity is depicted in Table 1. It is clear from Fig. 5 that XRD pattern for PVA shows sharp and intense peak at 17.5° of $2\theta$ and its evaluated crystallinity is highest which suggests the presence of ordered crystalline phase. On the other hand XRD pattern of PAM is quite broad which suggest for relatively small sized crystals of the polymer, which appear justified also as the hydrogen bounding interaction between amide groups of PAM chains may result in the formation of smaller crystallites. Moreover, the broad XRD pattern also indicates relatively lower crystalline nature of the PAM. From Fig. 5, it is noticed that on varying the amount of PVA in hydrogel composition, crystallinity varies, for 2.0 g of PVA the XRD pattern of which is sharper than for the specimen with 1.0 g of PVA content in IPN.

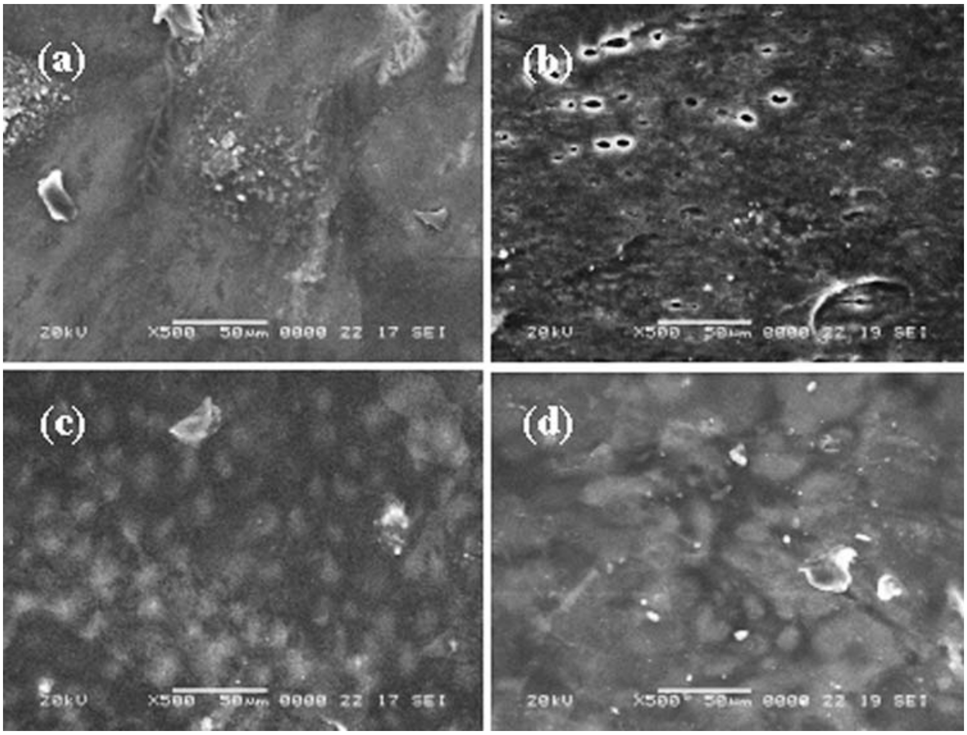


**Fig. 3** SEM images depicting the effect of PAM variation on the morphology of IPN surfaces AM = 1.0 g (a), 2.0 g (b), 4.0 g (c), 6.0 g (d) for definite concentration of [PVA] = 2.0 g and [MBA] = 0.020 g.

The influence of acrylamide (less-crystalline) on the behavior of the hydrogel is investigated by using different amounts of acrylamide (AM) in the hydrogel preparation. When AM is used in the concentration range of 1.0 g–4.0 g, the decreased crystallinity is observed (Fig. 6). This suggests that presence of PVA in hydrogel gives the relatively ordered crystalline phase.

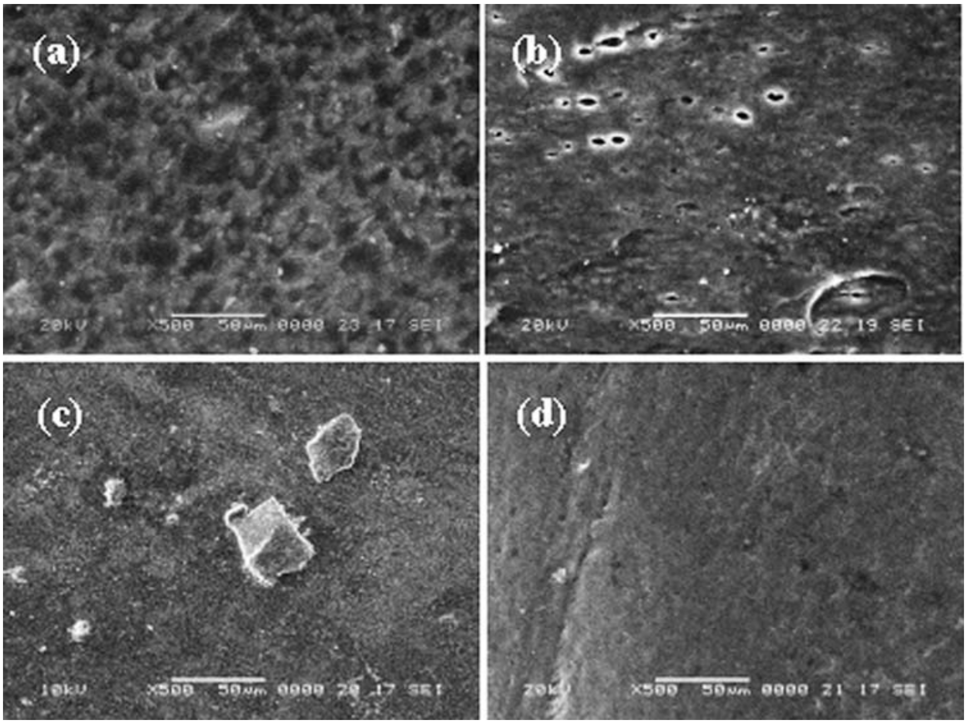
The influence of crosslinker (MBA) also affects the extent of crystallinity and size of the crystals of hydrogels. It is clear from Fig. 7 and Table 1 that on varying the MBA concentration in the range of 0.01 g–0.04 g the broadness of the XRD peaks gradually increases. The observed widening of XRD peaks clearly suggest for reduced crystallinity and crystal size of the semi-IPN. The reason for the observed finding 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 at crystallinity may be explain 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.

The evaluated interplaner distance “d” for native PVA and various semi-IPNs with varying compositions is shown in Table 1. It is clear from Figs. 5–7 and Table 1 that the value of $2\theta$ at peak intensity for native PVA is observed at 17.5°, which is less then the value those observed for semi-IPNs. It is also clear that the values of $2\theta$ at peak intensity and interplaner distance “d” are found to be almost similar for all the semi-IPNs and they are different from the “d” value of native PVA. Thus change in the interplanner spacing in the semi IPNs as compared to that of native PVA explains the changes in the peak position due to change in morphology.

**Table 1** Crystallinity and Interplaner distance “d” of the semi-IPNs of different concentrations

| S. No. | PVA (g) | AM (g) | MBA (g) | Crystallinity | Peaks at $2\theta$ (°) | Interplaner distance “d” (Å) |
|---|---|---|---|---|---|---|
| 1. | 4 | — | — | 0.88 | 17.5 | 5.07 |
| 2. | 1 | 2 | 0.020 | 0.39 | 19.56 | 4.54 |
| 3. | 2 | 2 | 0.020 | 0.60 | 19.54 | 4.54 |
| 4. | 2 | 1 | 0.020 | 0.77 | 19.54 | 4.54 |
| 5. | 2 | 2 | 0.020 | 0.60 | 19.54 | 4.54 |
| 6. | 2 | 4 | 0.020 | 0.48 | 19.6 | 4.53 |
| 7. | 2 | 2 | 0.010 | 0.74 | 19.46 | 4.56 |
| 8. | 2 | 2 | 0.020 | 0.60 | 19.54 | 4.54 |
| 9. | 2 | 2 | 0.040 | 0.53 | 19.46 | 4.56 |

**Fig. 4** Scanning electron micrographs showing the effect of crosslinking agent on the morphology of semi-IPNs, MBA = 0.010 g (a), 0.020 g (b), 0.040 g (c), 0.100 g (d) for definite concentration of [PVA] = 2.0 g and [AM] = 2.0 g.



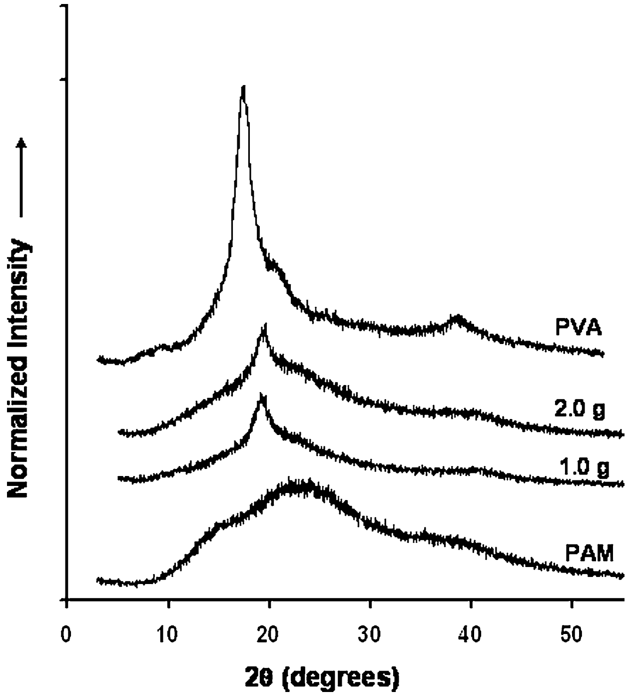


**Fig. 5** Influence of PVA on XRD patterns of semi-IPNs for definite concentration of [AM] = 2.0 g and [MBA] = 0.020 g.

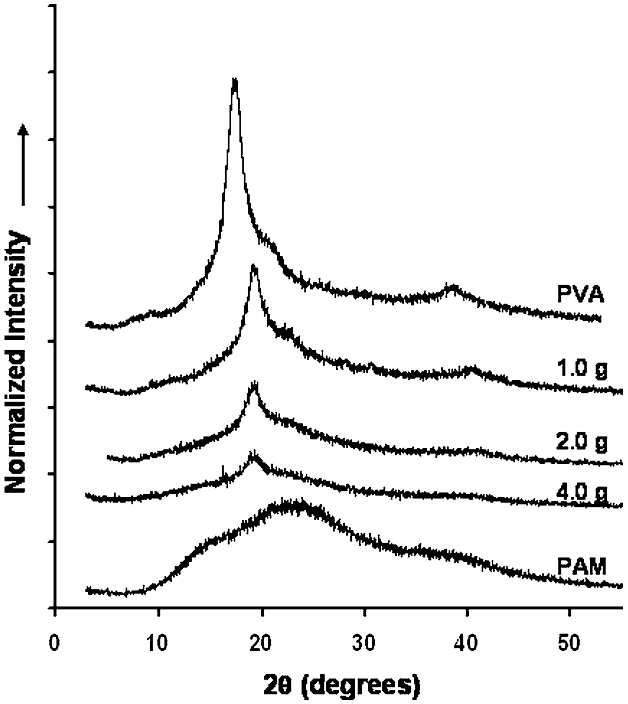


**Fig. 6** Effect of AM on XRD patterns of semi-IPNs for definite concentration of [PVA] = 2.0 g and MBA = 0.020 g.

### 4.4 Microhardness study

Microhardness of a material is greatly dependent on the chemical and morphological nature of the material and, therefore, by a proper selection of the components of the material, the hardness of the material may be desirably altered. The forthcoming paragraph discusses the impact of chemical composition of the semi-IPN on its microhardness at varying values of applied load (10 to 100 g).

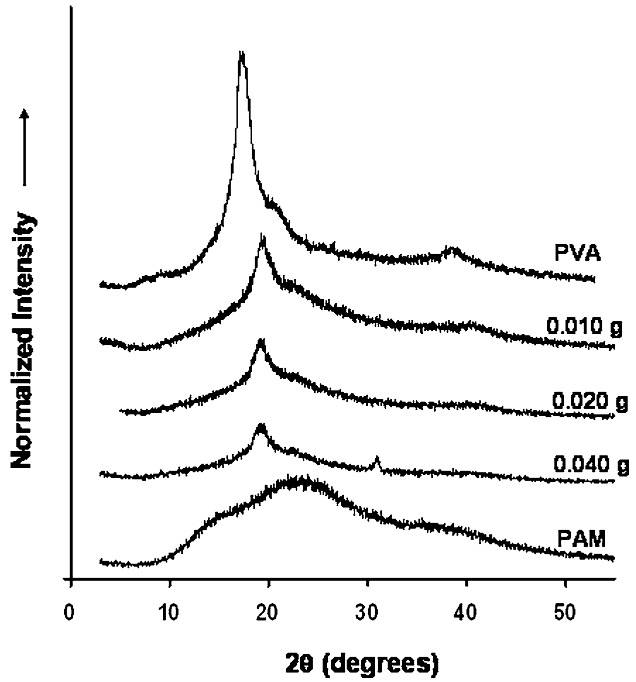


**Fig. 7** Influence of MBA on XRD patterns of semi-IPNs for definite concentration of [PVA] = 2.0 g and [AM] = 2.0 g.

### 4.4.1 *Effect of PVA*

The effect of PVA content of the semi-IPN on their microhardness has been investigated by varying the concentration of PVA from 1.0 to 4.0 g. The results are shown in Fig. 8, which reveal that the value of $H_V$ is maximum for pure AM and minimum for pure PVA. The microhardness of semi-IPNs decreases with increase in PVA content from 1.0 to 4.0 g. The results also the value of $H_V$ increases with increasing load (10–100 g) on the sample. The increase in $H_V$ with load is due to strain hardening in the specimens [26]. It is noticed that the rate of strain hardening is greater at lower loads and at lower PVA content and pure AM. The $H_V$ attains a limiting value beyond the load at 50 g as $H_V$ tends to be independent of the applied load.

### 4.4.2 *Effect of AM*

The effect of AM content of the semi-IPN on their microhardness has been studied by varying the concentration of AM from 1.0 to 6.0 g. The result is shown in Fig. 9, which indicates that the value of $H_V$ increases with increase in AM content. The value of $H_V$ of semi-IPN is greater than pure AM for 5.0 g and 6.0 g AM content, therefore, producing hardened semi-IPNs. The value of $H_V$ also increases with increasing load (10–100 g) and attains a limiting value beyond the load of 50 g.

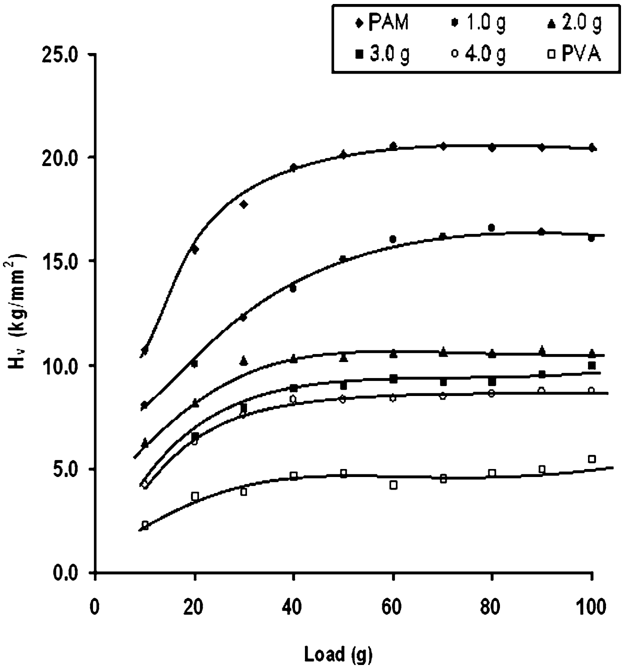


**Fig. 8** Influence of PVA on the hardness number ($H_V$) of the semi-IPNs for a definite concentration of [AM] = 2.0 g and [MBA] = 0.020 g.

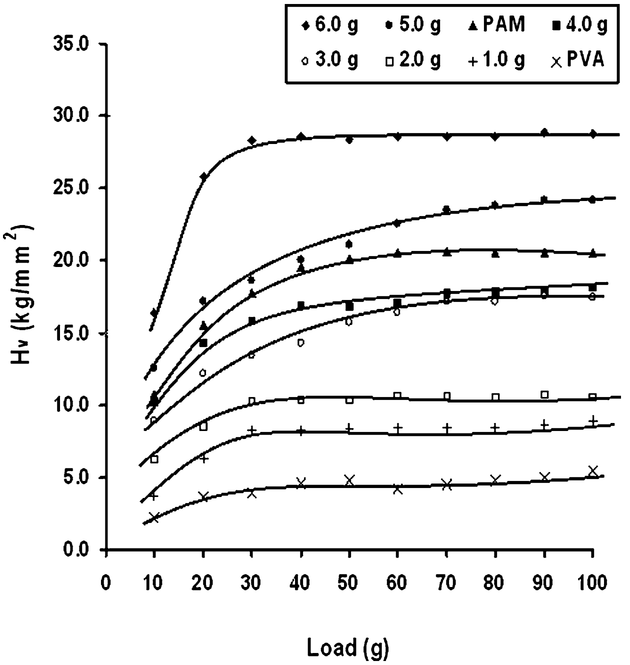


**Fig. 9** Effect of AM on the hardness number ($H_V$) of the semi-IPNs for a definite concentration of [PVA] = 2.0 g and [MBA] = 0.020 g.

### 4.4.3 *Effect of MBA*

The effect of crosslink density of the semi-IPN has been investigated on the $H_V$ of the semi-IPN by varying the concentration of MBA in the range 0.010 g–0.100 g as shown

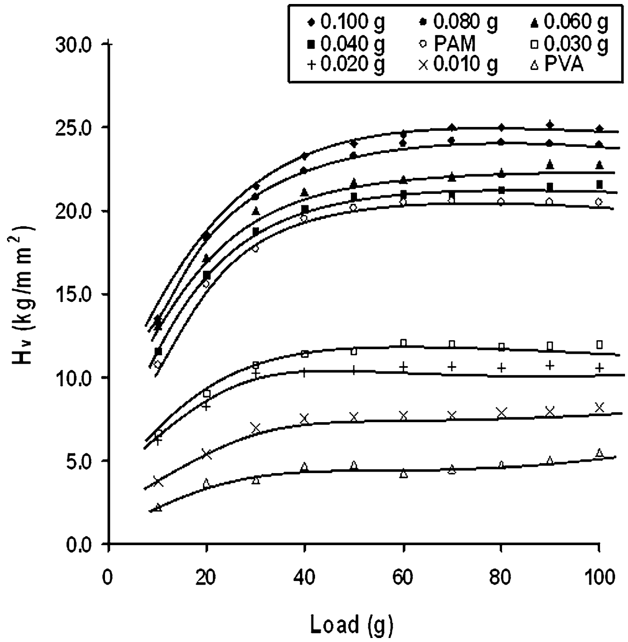


**Fig. 10** Effect of MBA on the hardness number ($H_V$) of the semi-IPNs for a definite concentration of [PVA] = 2.0 g and [AM] = 2.0 g.

in Fig. 10. The results clearly reveal that the microhardness of the semi-IPN increases with increasing concentration of MBA. The figure clearly shows that the value of $H_V$ of semi-IPN containing 0.040 g or more MBA content is greater than pure AM. The value of $H_V$ also increases with increasing load and attains a limiting value beyond the load of 50 g. The figure also shows that the rate of hardening is greater for lower load and higher content of MBA (0.040 g to 0.100 g). The increase in $H_V$ with increase in MBA is attributed to increase in crosslink density in the semi-IPN, which contributes to the hardness of the material [27].

## 5 Conclusions

The present study reveals that hardened semi-IPNs of PVA and PAM can be developed. The IR studies confirm the presence of crosslinked chains of PAM in the IPNs, which impart hardening to the semi-IPNs as detected from microhardness measurements. The morphological features of the semi-IPNs as revealed from the SEM micrographs illustrates the role of various contents of PVA, PAM and crosslinker in the semi-IPN. The morphology of lower content of PVA in semi-IPN yields more hardened material. Whereas the semi-IPN with higher content of PAM provides greater hardening. The crosslinker in the semi-IPN gives homogeneous morphology. The XRD exhibits development of more crystallinity in the IPNs with increase in the content of PVA. Whereas the degree of crystallinity decreases with increasing the content of PAM. This confirms that pure PVA, which is semi-crystalline and pure PAM, which is amorphous retain their inherited character in the semi-IPNs as well. Thus, the semi-IPN of PVA and PAM, which are compatible with varying morphological features and mechanical strength can be a suitable candidate as a biomaterial for desired biomedical applications.

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## References

1. S. Y. KIM, H. S. SHIN, Y. M. LEE and C. N. JEONG, *J. Appl. Polym. Sci.* **73** (1999) 1675.
2. N. A. PEPPAS, P. BURER, W. LEABONDUNG and H. EZA ICHIKAWA, *J. Pharm. Biopharm.* **50** (2000) 27.
3. G. FILIPCSEI, J. FCHER and M. ZRINGI, *J. Mol. Struct.* **554** (2000) 109.
4. S. H. HYON, W. I. CHA, Y. IKADA, M. KITA, Y. OGURA and Y. HONDA, *Biomater. Sci. Polym. Ed.* **5** (1994) 397.
5. J. H. JUNAG, W. S. BONNER, Y. J. OGAWA, P. VACONTI and G. C. WEIR, *Transplantation* **61** (1976) 1557.
6. D. H. CHEN, J. C. LEU and T. C. HUANG, *J. Chem. Technol. Biotechnol.* **4** (1994) 351.
7. A. MUHLEBACH, B. MULLER, C. PHARIRA, M. HOFMANN, B. SEIFERLING and D. J. GUERRY, *Polym. Sci. Part A: Polym. Chem.* **35** (1997) 3603.
8. C. K. YEOM and K. H. LEE, *J. Membr. Sci.* **109** (1996) 257.
9. K. J. KIM, S. B. LEE and N. W. HAN, *Polym. J.* **25** (1993) 129.
10. H. MATSUYAMA, M. TERAMOTO and H. URANO, *J. Membr. Sci.* **126** (1997) 151.
11. A. K. BAJPAI and SMITHA BHANU, *J. Mater. Sci. Mater. Med.* **15** (2004) 43.
12. A. PEPPAS, NIKOLAOS and R. STAUFFER SHAUNA, *J. Control Rel.* **16** (1991) 305.
13. M. KOBAYASHI, J. TOGUCHIDA and M. OKA, *Biomaterials* **24** (2003) 639.
14. E. EL. SHAFEE and H. F. NAGUIB, *Polymer J.* **44**(5) (2003) 1647.
15. A. K. BAJPAI, J. BAJPAI and S. SHUKLA, *J. Mater. Sci. Mater. Med.* **14** (2003) 347.
16. W. PAUL and C. P. SHARMA, *J. Appl. Polym. Sci.* **57** (1995) 1447.
17. R. BAJPAI, V. MISHRA, P. AGRAWAL and S. C. DATT, *Bull. Mater. Sci.* **25**(1) (2002) 21.
18. R. BAJPAI, N. B. DHAGAT, R. KATARE, P. AGRAWAL and S. C. DATT, *Bull. Mater. Sci.* **26**(4) (2003) 401.
19. R. KATARE, R. BAJPAI and S. C. DATT, *Polymer Testing* **13** (1994) 107.
20. A. K. BAJPAI and M. SHRIVASTAVA, *J. Biomater. Sci. Polymer Ed.* **13**(3) (2002) 237.
21. S. K. AWASTHI and R. BAJPAI, *Ind. J. Pure Appl. Phys.* **39** (2001) 795.
22. W. O. STATTON, in "HandBook of X-ray Diffraction" edited by E. F. KAELBLE (McGraw Hill, New York, 1967) Chap. 21, p. 1.

23. M. RAMRAKHIANI, R. K. SONI, P. PARASHAR and S. C. DATT, *Indian J. Phys.* **70A**(5) (1996) 651.
24. M. RAMRAKHIANI, P. PARASHAR and S. C. DATT, *J. Appl. Polym. Sci.* **96** (2005) 1835.
25. R. BAJPAI and S. K. AWASTHI, in "Proceedings of the DAE Solid State Physics, India, December 27–31" edited by S. L. CHAPLOT, T. SAKUNTLA and S. M. YUSUF (Narosa Publishing, India, 2000) Vol. 43, p. 220.
26. R. KATARE, R. BAJPAI and S. C. DATT, *Polym. Testing* **10** (1991) 139.
27. A. K. MISHRA, P. AGRAWAL and R. BAJPAI, *J. Appl. Polymer Sci.* **92**(5) (2004) 3107.