

Microstructural Parameters of HPMC/PVP Polymer Blends Using Wide Angle X-Ray Technique

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Abstract: Hydroxypropylmethylcellulose (HPMC) and Polyvinylpyrrolidone (PVP) polymer virgin and blend films were prepared and investigated using wide angle X-ray scattering method. Microstructural parameters like lattice strain (g %), the crystallite size for individual the Bragg's reflection (hkl) have been computed using line profile analysis and hence by whole pattern fitting method. The X-ray diffraction study reveals that the blending of PVP decreases the crystallinity of HPMC up to 5:4 concentration and then increases. Measured tensile strength decreases, Young's Modulus decreases, and % elongation increases as the concentration of PVP increases. The surface morphology investigated using scanning electron microscope, shows that the two polymers were miscible in all concentration range.

Keywords: Polymer blends, Crystallite size, Tensile strength, WAXS.

INTRODUCTION

In recent years, there is an increased interest in the research activity in the man made polymers to bring out new materials which are suitable for packaging and for drug delivery [1]. Packaging is an important component of marketing. It is vital that packaging materials are of high quality and have sustainable value. Majority of the packaging materials now available in the market are non degradable. This causes environmental concern [2]. As an alternative to these non degradable packaging materials stress is on to produce degradable materials. These materials undergo degradation by radiation like, Ultra-violet, microwave, gamma, alpha, electron beam, etc, bio, thermal and so on. American society for testing of materials (ASTM) and international standards organisation (ISO) have defined degradable polymer as those which undergo a significant change in chemical structure under specific environmental conditions. In India consumer packaging is about half of one percent of the global packaging volume [3] Keeping all these developments in mind we have prepared a polymer blend film which is degradable and suited for packaging industry. For this purpose we have chosen Hydroxypropylmethylcellulose (HPMC), a bio-polymer-derivative of cellulose, and polyvinylpyrrolidone (PVP), both are available in powder form, non-ionic, water soluble and forms films. The HPMC is, used in suspension syrup, increasing solubility of drugs, in drug release system

[4, 5] in cosmetics, general healthcare products, as thickening agent, and widely accepted as food additive in Europe [6-8], it is widely used cellulose as film forming agent for conventional tablet film coatings [9, 10]. PVP is used in medicine, pharmacy, cosmetics, industrial productions detergents, pigments, coating electronics and bio engineering materials [11], supports solubility of drugs in water, binds to polar molecules exceptionally well, as adhesive in paints, postage stamps and envelopes, glue sticks, in contact lens solution, has good complexing ability and bio compete ability [12-14]. PVP can also be used as blood plasma. Here an attempt is being made to establish the blend of these two polymers to get another material useful for packaging with good mechanical properties and degrade ability which is the need of the hour. These polymer blends have been characterised using X-ray diffraction technique and line profile analysis method [16, 17].

MATERIALS AND METHODS

Preparation of Polymer Blends

HPMC and PVP powdered samples were purchased from Loba, chem, Mumbai. Pure and blend films were prepared by using solvent cast method [10, 18]. PVP (2%-5%wt) dissolved in 100ml of distilled water with continuous stirring. After complete dissolution the solution was filtered using filter paper to remove undissolved particles. HPMC (5%wt) dissolved in distilled water; following the same procedure 5% HPMC solution was prepared. Now 50ml 5% HPMC solution and 50ml of 2% PVP solutions were mixed together and stirred continuously using magnetic stirrer

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for 20 min to ensure uniform mixing of the solutions in the blend matrix. The stirred solution was allowed for a while and then it is poured on to the clean glass plate and allowed to dry for a week. Care was taken to avoid dust particles by covering the glass plates. Complete dry the film were peeled out of the glass plate and are stored in a desiccators to avoid moisture. The prepared films appears to be milky transparent which is an indication that two polymers may possibly fully miscible creating a new polymer matrix constituted by one phase [19]. Figure (1a) shows the scheme of films preparation, and Figure (1b) shows the films grown for varied percentage of PVP in HPMC.

EXPERIMENTAL PROCEDURE

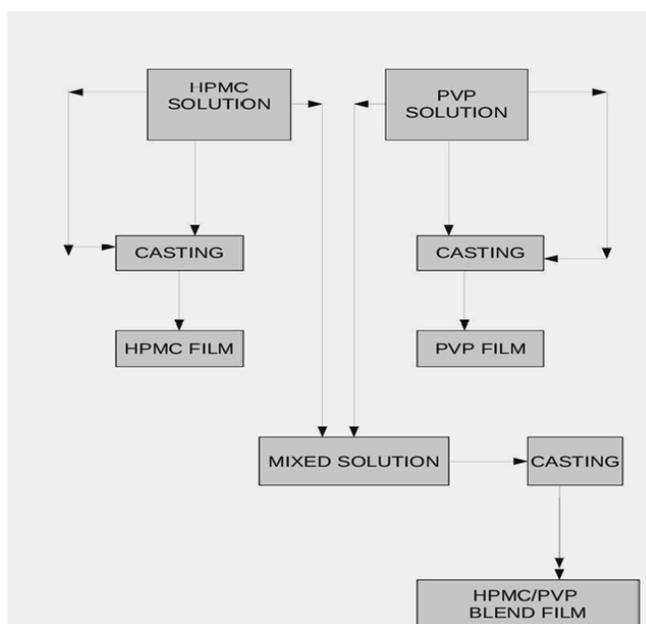
X-Ray Diffraction Patterns

X-ray diffraction pattern of the samples were recorded using Rigaku miniflex-II diffractometer

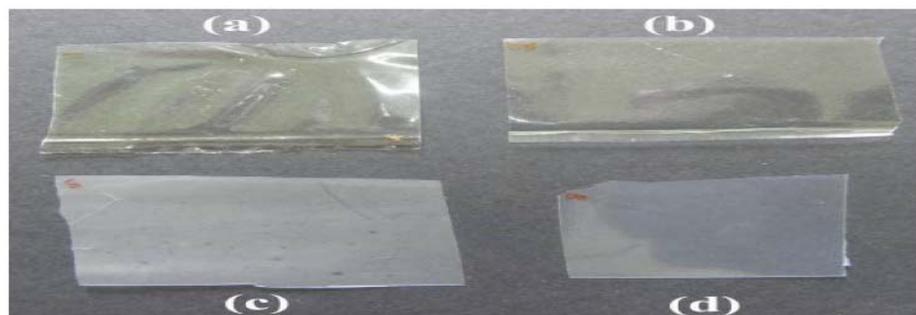
employing Ni filtered $\text{CuK}\alpha$ radiation of wavelength 1.5406\AA , with graphite monochromator. Samples were scanned in the 2θ range 6° - 40° with a scan speed of $5^\circ/\text{min}$ and in step of 0.02° . Specification used for recording were 30KV and 15mA.

Mechanical Properties

Mechanical properties were measured using Universal testing machine. Lloyd's instrument U.K. LRX Plug Model 5 KN. loads Tensile strength of the films was calculated by dividing the maximum load for break the film by cross sectional area. Young's Modulus is the ratio of stress to strain at the linear portion of the curve, or slope of the linear portion of the curve of the stress strain. Elongation at break was calculated by the ratio of the film elongation at rupture to initial gauge length and multiplied by 100.



(a)



(b)

Figure 1: (a). Flow chart showing the method of preparation of blend films. (b). Prepared pure HPMC (a), (b) and HPMC /PVP Blend (c), (d) Films.

FTIR Measurements

FTIR spectra of the samples were recorded using Perkin Elmer (Model 65) spectrometer in air medium at room temperature in the range of 4000 cm^{-1} to 400 cm^{-1} .

Scanning Electron Microscopy

The prepared films were examined under scanning electron microscope to understand the miscibility of the polymers in the blend matrix.

Theory of X-Ray Line Profile Analysis

Fourier coefficients of Intensity profile of an X-ray Bragg reflection is given by,

$$I(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi n d(s - s_0)\} \quad (1)$$

Here s is the modulus of the scattering vector, n is the harmonic number, d is the (hkl) spacing and $I(s)$ is the scattered X-ray intensity along s . These Fourier coefficients can be factorized into crystallite size $A_s(n)$ and lattice disorder $A_d(n)$ coefficients. We have also included in our computation, the calculation of stacking faults $AF(n)$ present in these polymer blends.

$$A(n) = A_s(n) \cdot A_d(n) \cdot AF(n) \quad (2)$$

Various analytical forms for the distribution of crystallite sizes have been investigated by Hall and

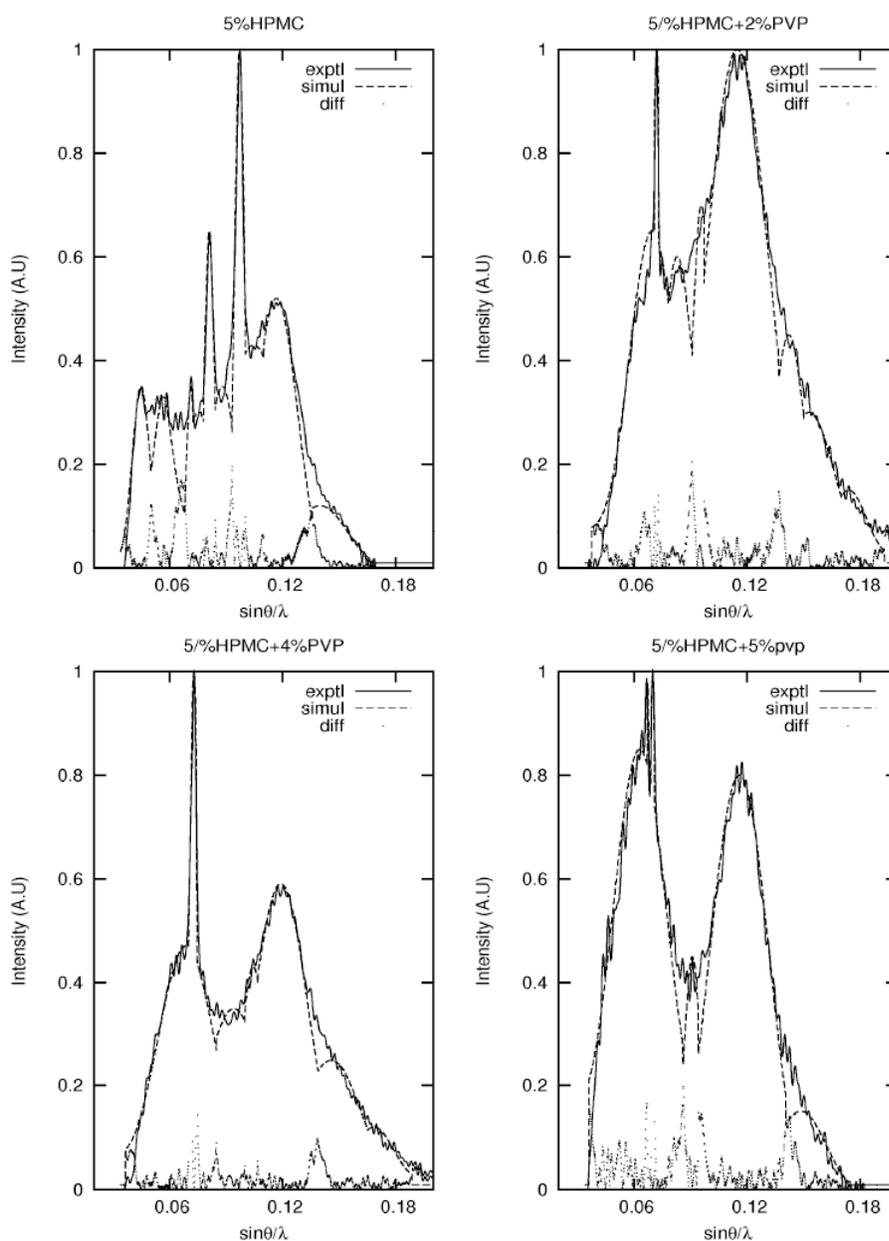


Figure 2: Whole powder pattern for prepared films.

Somashekar. Procedure for computing the microcrystalline parameters is given in our earlier paper [20, 21]. In fact, this method has been appreciated in the recently concluded Round Robin test by IUCr, UK. Initial values of $\langle N \rangle$ and g were obtained using the method of Nandi *et al.* (1978). Using these values in the equations given in our earlier paper, the corresponding values for the distribution function are obtained. Goodness of the fit is determined by computing

$$\Delta^2 = [I_{\text{cal}} - (I_{\text{exp}} + BG)]^2 / \text{number of points.} \quad (3)$$

The computation is extended to the whole X-ray powder pattern of samples. The goodness of the fit is shown in Figure 2. The microcrystalline parameters are given in Table 1.

RESULTS AND DISCUSSION

Microstructural Parameters

It is evident from the diffraction patterns that polymer blend films consist of both crystalline and amorphous regions. For pure HPMC films, we observe 2- 3 Bragg peaks and the sharpness increases with concentration of HPMC. For pure PVP films, we observe one Bragg reflection which is reasonably sharp. In addition there is one broad Bragg peak which is observed for all concentrations of PVP. These observations confirm the presence of both crystalline and amorphous region in the films. Blend of HPMC and PVP results in only one broad peak. Broadness of the peak increases with increase in concentration of PVP in HPMC. Miscibility in the polymer is an important factor which decides the nature and property of the material. It is due to the specific interaction between

the polymeric components, which gives rise to -ve free energy of mixing in spite of high molecular weight. The most common interactions are hydrogen bonding, ionic, dipole-dipole interaction, pi-electrons, and charge transfer complexes [22]. In the polyvinylpyrrolidone, pyrrolidone ring contains a proton acceptor carbonyl group, while HPMC has hydroxyl group as side group. Hence a hydrogen bonding may takes place between these two chemical groups in the blends. For the same interaction, these two polymers miscible in water. Interactions by hydrogen bonding observed between the hydroxyl-hydroxyl groups and the hydroxyl-carbonyl groups can occur as intra chain and inter chain multiple hydrogen bonding in crystalline HPMC region. Further, cross interaction of a PVP carbonyl group with a hydroxyl group whose oxygen atom is involved as a proton acceptor of another HPMC hydroxyl group in the crystalline interface. Cross interaction between a PVP carbonyl group and a hydroxyl group of HPMC in the amorphous region, or simple hydrogen bonding between two hydroxyl groups in amorphous HPMC region. Using the method briefly mentioned above, we have computed micro structural parameters and are given in Table 1.

It is observed that lattice strain in all the samples varies around 0.1%-0.6%. The statistical percentage of deviation of micro structural parameters is less than 5%. With these parameters as input we have further refined these parameters against whole pattern ($2\theta=6^\circ$ to 40°). The goodness of the fit between simulated and experimental whole powder pattern for various polymer blend samples are shown in Figure 2. It is worth noting that none of the other parameters such as lattice strain, stacking fault probability varied much during refinement, against the whole pattern data of the samples. The deformation fault probability values given

Table 1: Microstructural Parameters of HPMC and HPMC/PVP Blend Films

Sample	Con. In gm/cc	g(%)	Ds in Å	$\alpha^d \times 10^{-5}$	$\beta \times 10^{-5}$	Young's Modulus MPa	Transparency	Statistical Performance Index
HPMC	2	0.1	63.5	0.7	8.7	650.06	2.8	2.056
	3	0.1	87.6	6.5	3.3	587.46	4.9	2.379
	4	0.1	115.6	1.6	1.9	771.71	3.2	2.361
	5	0.1	59.7	2.9	1.4	990.23	3.2	4.402
HPMC+PVP	5+2	0.1	53.5	5.7	4.6	1480.31	2.1	6.542
	5+3	0.2	28.5	15.7	9.2	1640.68	2.4	12.53
	5+4	0.2	37.5	2.6	10.6	891.00	1.5	9.725
	5+5	0.6	67.9	2.1	5.8	948.73	1.7	4.889
PVP+HPMC	5+4	0.4	34.3	3.9	7.7	865.43	2.1	6.06

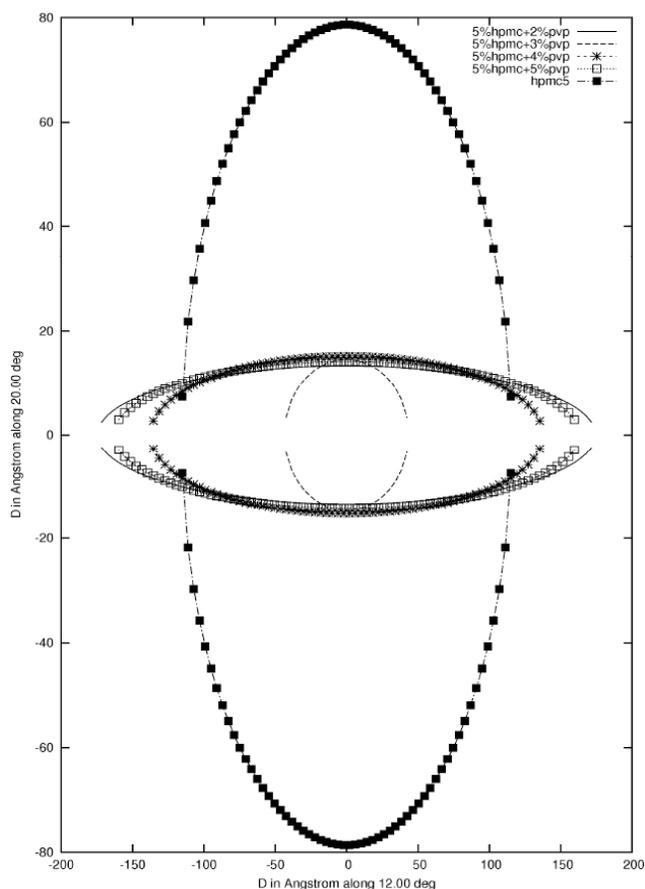


Figure 3: Variation of crystallite shape of, (a) pure HPMC.

in the Table 1 indicates that the values are low, because there are too many layers between two successive deformation fault layers. This is due to the fact that there are pockets of crystalline like order in a matrix of amorphous regions.

Since there are too many physical parameters have been experimentally determined, we had difficulty in

interpreting the quality of the blend films in terms of these parameters. In order to get over this difficulty, we have used multivariate analysis technique which is as follows. Each parameter that we have determined has been given a weight age. Then the sum of the weight age times the value of the physical parameters has been computed by normalising it with total sum of the weight age. This parameter has been identified as Statistical performance index, and we find from our computation that 5% HPMC and HPMC+PVP (5:3) gives maximum Performance index compared to all other samples, hence quite reliable for practical applications in the packaging industry.

A graphical plot of the crystallite shape ellipsoid was obtained by projecting the results in to a plane Figure 3. The strength of the polymer sample is proportional to crystallite area, which is essentially equal to area of ellipse. It is evident from the graph that crystallite area is more in 5%HPMC and 5%HPMC+2%PVP blend films.

Mechanical Properties

Mechanical properties measured from UTM instrument were given in Table 2. Variation of Mechanical properties with the concentration of PVP are given in Figure (4a) and (4b). It is observed that changing the concentration of PVP in HPMC matrix modifies the mechanical properties of the blend films. It is evident from the table that as the concentration of PVP increases, Tensile strength, strain at break decrease up to (5:4) Blend and then increases. Young's modulus, increases up to (5:3) and then decreases. For (5:4) all measured values are minimum. The wide variation in Tensile strength from 42.21MPa to 10.09 MPa, Strain at break from 3.70 % to 0.88%,

Table 2: Mechanical Properties of HPMC and HPMC/PVP Blend Films

Sample	Load at Break(N)	Tensile Strength(MPa)	Young's Modulus(MPa)	Strain at Break (%)
2%HPMC	34.46	53.17	650.06	5.16
3%HPMC	38.09	47.61	587.46	6.22
4%HPMC	61.48	41.95	771.74	5.65
5%HPMC	46.55	51.55	990.23	13.20
5%HPMC+2%PVP	63.31	42.21	1480.31	3.70
5%HPMC+3%PVP	64.56	32.28	1640.68	2.36
5%HPMC+4%PVP	32.03	10.09	891.00	0.88
5%HPMC+5%PVP	36.03	10.72	948.73	0.93
4%HPMC+5%PVP	34.74	33.74	865.43	4.04

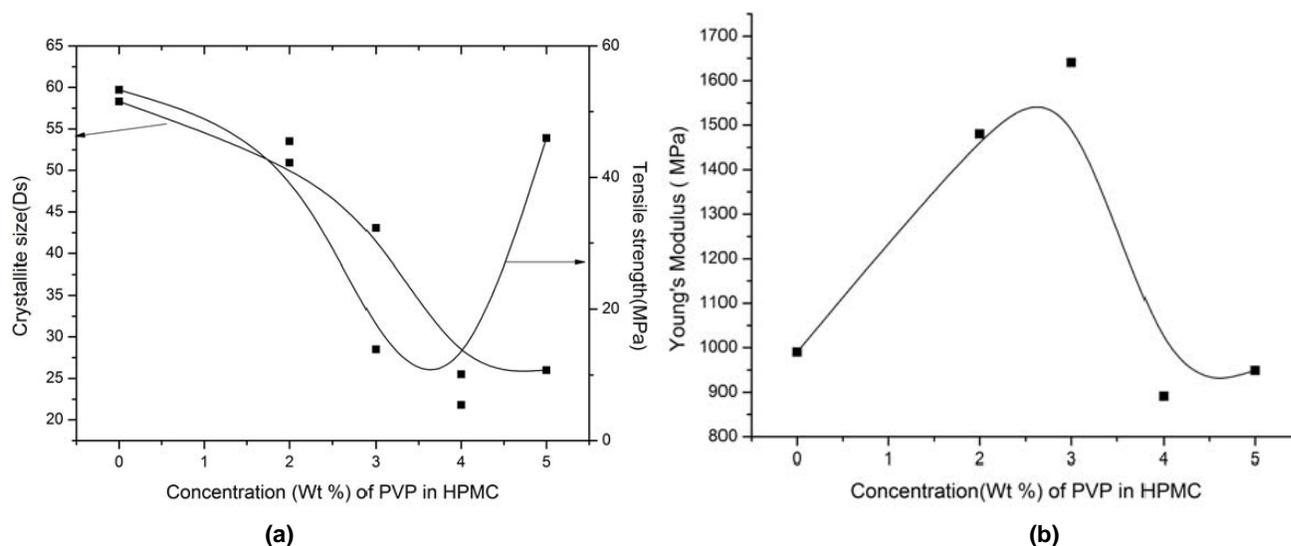


Figure 4: (a) Variation of mechanical properties of HPMC with concentration PVP. (b). Variation of Young's Modulus of HPMC with concentration of PVP.

Young's Modulus from 1480.31 to 891 MPa can be explained as follows.

Mechanical properties such as Tensile strength, Young's Modulus, % elongation strain at break, depends upon the intermolecular forces, chain stiffness and molecular symmetry of individual polymers used in the blend preparation [23]. According to Willemse *et al.*, Tensile modulus of the polymer blends is strongly depends on composition and morphology of blends [24]. Intermolecular interactions improve the mechanical properties of the blends. Kim and other researchers [25, 26] also support these results. The process of blending, solvent drying time, concentration, molecular weight of the sample used, influence the over all mechanical properties. The longer film formation time favours the molecules to re-organise, and there by crystallinity of the HPMC decreases with increasing order of PVP. This reduction in the crystallinity causes the reduction in the tensile strength and other parameters. These changes also well correlated to our XRD study.

FTIR Analysis

Fourier Infrared spectra of the prepared films were given in Figure 5. In the prepared blends it is expected that inter-molecular Hydrogen bonding between hydroxyl groups of HPMC and carbonyl group of PVP might have been created. Both HPMC and HPMC/PVP polymer blend films shows hydroxyl band at 3200 cm^{-1} - 3600 cm^{-1} and typical C-H alkyl stretching band (2800 cm^{-1} - 3000 cm^{-1}). peak at 1456 cm^{-1} corresponds to C-H bend shifted lower frequency first and then increases

almost equal to pure HPMC and further shift towards lower frequency. The peak at 1641.94 cm^{-1} in pure HPMC film increases to higher frequency side and broadening takes place in the blend samples. This broadening may be due to stretching of -C=C- between carbonyl group of PVP and HPMC polymers in the blend matrix. The peak at 1455.98 cm^{-1} corresponding to C-C in pure HPMC shifts to lower frequency and then increases in blend films and the peak at 948.85 cm^{-1} shifts towards higher frequency. HPMC and HPMC/PVP blend films can be differentiated by C-N

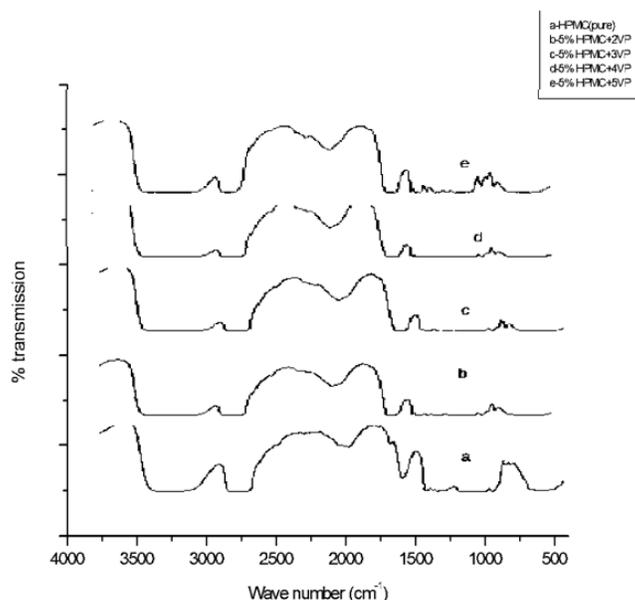


Figure 5: FTIR Spectra for HPMC and HPMC/PVP Blend films. (a) Pure HPMC (b) 5%HPMC +3%PVP (c) 5%HPMC+4%PVP (d) 5%HPM +5%PVP (e) 2%HPMC +5%PVP (f) 3%HPMC +2%PVP (g) 4%HPMC +3%PVP.

Table 3: Spectroscopic Data for Pure HPMC and HPMC/PVP Blend Films

HPMC (cm ⁻¹)	HPMC/PVP blends (cm ⁻¹)	Correlation (cm ⁻¹)
3367	3350 - 3371	O-H Stretch
2910	2911 - 2974	C - H Stretch
-----	2127 - 2134	C=C Stretch
1641.91	1657 - 1658	C=C Stretch
-----	1495	N-O Stretch
1455.98	1442 - 1444	C-C Stretch
-----	1297 - 1299	C-N Stretch
-----	1096 - 1111	C-N Stretch
948.50	946 - 974	O-H Stretch

Stretch (1096cm⁻¹ to1111cm⁻¹) and (1297 cm⁻¹to1299cm⁻¹) which are present only in blends. In addition no other peaks observed in the spectra. The above discussion confirms the interaction between HPMC and PVP polymers in the blend matrix. These aspects are tabulated in Table 3.

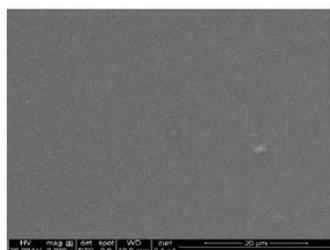
SEM Analysis

The pure HPMC and blends samples of different concentration were investigated by examining the sample cross section under field emission electron microscope. On observing the SEM photos Figure 6, it

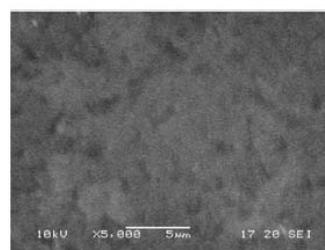
is confirmed that the miscibility is good for all concentration range.

CONCLUSION

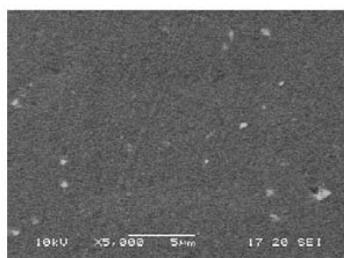
In this study we observe the blending of HPMC with PVP changes the crystallinity and mechanical properties of HPMC films. As the concentration of PVP increases crystallinity decreases up to 5:4 and then increases. Tensile strength, strain at break decreases, Young's modulus increases up to certain concentration. These observed changes impart flexibility to the films due to re-organisation of polymer net work. FTIR study



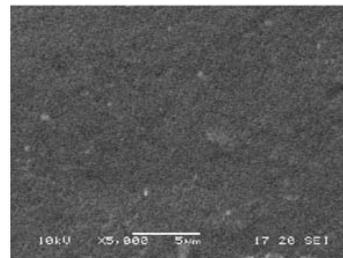
(a) Pure HPMC



(b) 2%HPMC + 5%PVP



(c) 5%HPMC + 4%PVP



(d) 5%HPMC + 5%PVP

Figure 6: SEM Photo's of (a) Pure HPMC, (b) 2%HPMC+5%PVP Blend film, (c) 5%HPMC+5%PVP Blend film, (d) 5%HPMC + 4%PVP Blend film.

also indicates there is an interaction between HPMC and PVP in the form of intra and inter molecular hydrogen bonding. SEM photo's clearly shows complete miscibility of the two polymers in the blend matrix. These blend films with flexible nature, and more degradable than pure HPMC are suitable for packaging, tablet coating drug delivery system etc.

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