

## Research Article

# Preparation and Characterization of HPMC/PVP Blend Films Plasticized with Sorbitol

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The aim of this present work is to investigate the effect of plasticizers like Sorbitol on microstructural and mechanical properties of hydroxypropyl methylcellulose (HPMC) and Polyvinylpyrrolidone (PVP) blend films. The pure blend and plasticized blend films were prepared by solution casting method and investigated using wide angle X-ray scattering (WAXS) method. WAXS analysis confirms that the plasticizers can enter into macromolecular blend structure and destroy the crystallinity of the films. FTIR spectra show that there are a shift and decrease in the intensity of the peaks confirming the interaction of plasticizer with the blend. Mechanical properties like tensile strength and Young's Modulus decrease up to 0.6% of Sorbitol content in the films. Percentage of elongation at break increases suggesting that the plasticized films are more flexible than pure blend films. These films are suitable to be used as environmental friendly and biodegradable packaging films.

## 1. Introduction

Polymer blending is one of the most useful ways to have new materials with required properties and there have been great scientific and commercial progress in the area of polymer blends. This was driven by the realization that new molecules are not always required to meet the need for new materials and blending can usually be implemented more rapidly and economically than the development of new materials [1, 2]. Blends of synthetic and natural polymers represent a new class of materials and have attracted much attention especially in bioapplications. The success of synthetic polymers as biomaterial relies mainly on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained at low production costs. Biological polymers represent good biocompatibility, but their mechanical properties are often poor; the necessity of preserving biological properties complicates their processability and their production costs are very high [3, 4].

Packaging plays an important role in marketing food and food related articles (processed food, bakery products,

beverages, food grains, vegetables, and fruits). Food quality and safety are major concerns in the food industry. Packaging can be considered as an emerging trend that could have an impact on shelf-life extension and food safety. In general a packaging material has to fulfil certain requirements. Packaging makes distribution easier and protect the article from environmental conditions like sun light, dust, oxygen, moisture, microbes, mechanical stress, and so on. A packaging has to satisfy all these requirements effectively and economically. Nowadays we saw a lot of change in the process, distribution, storing, and retailing, which reflected the continuing increase in consumer demand for improved safety, quality and extended shelf-life for packaged materials. Packaged materials now available are nondegradable. These materials after their disposal cause environmental concern in terms of solid waste management, health problems to both human beings and animals. Hence research activity is focussing on to produce degradable packaging materials. Some of the researchers have already worked on degradable packaging materials using chitosan [5, 6], PVA [7, 8], starch, cellulose, and their blends [9, 10]. Here we are using

TABLE 1: Microstructural parameters of HPMC/PVP blend films plasticized with Sorbitol {Sample = HPMC + PVP [S]}.

Sample	$2\theta$ (deg)	$d$ (Å)	$\langle N \rangle$	$D = \langle N \rangle \cdot d$ (Å)	g (%)	$\alpha^d$	$\beta$	$\delta$	Crystallinity (%)
S + 0	12.74	6.93	25.20	174.63	0.1	$3.90E - 05$	$6.64E - 06$	0.3	54.50
	20.43	4.34	3.08	13.36	0.1	$1.70E - 05$	$4.46E - 05$	0.06	
S + 0.2 g Sorbitol	13.60	6.49	1.60	10.38	0.1	$5.07E - 06$	$4.76E - 06$	0.04	13.07
	20.67	4.29	2.75	11.79	0.2	$3.69E - 07$	$4.92E - 07$	0.06	
S + 0.4 g Sorbitol	12.83	6.89	1.4	9.64	0.1	$1.08E - 06$	$1.93E - 07$	0.08	11.54
	20.27	4.37	3.50	15.29	0.2	$1.86E - 05$	$1.71E - 05$	0.05	
S + 0.6 g Sorbitol	12.55	7.04	2.85	20.06	0.2	$7.04E - 07$	$7.08E - 06$	0.06	10.76
	20.73	4.28	3.15	13.48	0.1	$1.64E - 05$	$8.34E - 05$	0.05	
S + 0.8 g Sorbitol	14.77	5.99	2.25	15.79	0.2	$2.17E - 05$	$9.53E - 05$	0.05	23.88
	20.41	4.34	3.15	13.67	0.1	$4.87E - 07$	$5.85E - 04$	0.13	

hydroxypropyl methylcellulose (HPMC), a biopolymer, and poly vinylpyrrolidone (PVP), a synthetic polymer for blend preparation. Blend films of these two polymers have not been investigated so far, It's potential use as a packaging material. From our study we found that blend films have a very good mechanical property which makes these films well suited for packing purpose.

## 2. Materials and Methods

HPMC, PVP, and Sorbitol powdered samples were purchased from Loba chemie, Mumbai, India. Pure blend and plasticized blend films were prepared by using solvent casting method [11–13]. 5 g HPMC was dissolved in 100 mL of distilled water with continuous stirring. After complete dissolution, the solution was filtered using filter paper to remove undissolved particles. 2% PVP solution was prepared. Now 50 mL of 5% HPMC solution and 50 mL of 2% PVP solutions were mixed together and stirred continuously using magnetic stirrer for 20 min to ensure uniform mixing of the solutions in the blend matrix. During stirring 0.2% of Sorbitol predissolved in distilled water was added to the blend solution and stirred for 10 more minutes. The stirred solution was allowed for a while and then it is poured onto the clean levelled glass plate and allowed to dry for a week. After complete drying, the films were peeled out of the glass plate and stored in desiccators to avoid moisture. The prepared films appear to be transparent, smooth, and flexible. This indicates that the two polymers may possibly be fully miscible with Sorbitol creating a new single polymer matrix [14]. Following the same procedure, other samples of different concentrations and different wt(%) of plasticizers were prepared.

### 2.1. Experimental

**2.1.1. X-Ray Diffraction.** X-ray diffraction patterns of the samples were recorded using Rigaku MiniFlex II diffractometer with Ni filtered Cu  $k\alpha$  radiation of wavelength 0.15406 nm, with graphite monochromator. Samples were scanned in the  $2\theta$  range  $6^\circ$ – $40^\circ$  with a scan speed of  $5^\circ/\text{min}$  and in step of  $0.02^\circ$  working voltage and current were 30 kV and 15 mA. The X-ray diffraction pattern recordings for various

concentrations of Sorbitol in HPMC/PVP polymer blends are as shown in Figure 1.

**2.1.2. FTIR Spectra.** Fourier transform infrared spectrum of these films was recorded using Perkin Elmer spectrometer (Spectrum 65). The spectrum was recorded in the frequency range of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$  at room temperature. FTIR spectra recordings for the HPMC/PVP/Sorbitol films are given in Figure 2.

**2.1.3. Mechanical Properties.** Mechanical properties like tensile strength, Young's Modulus, and elongation at break were measured using universal testing machine (UTM) according to ASTM standard.

## 3. Results and Discussion

**3.1. X-Ray Diffraction Study.** The pure HPMC/PVP blends and plasticized films of different concentrations were investigated using WAXS method. From the diffraction pattern obtained it is found that a film consists of both crystalline and amorphous regions. In blend film it is observed that there is one sharp peak at around  $2\theta = 12^\circ$  and one broad peak at around  $2\theta = 20^\circ$ . In plasticized films sharp peak widens and the width of the broad peak also increases with concentration of the plasticizer along with area under the peaks. The position of the peaks also shifts slightly. This indicates that there is change in molecular plane density in blends. Blending of HPMC with PVP decreases the crystallinity of HPMC. Further plasticizing with Sorbitol destroys crystallinity, with further increasing amorphous region. The computed microstructural parameters using Whole Powder Pattern Fitting Technique (WPPFT) are given in Table 1. From Table 1 it is observed that lattice strain in all the samples lies between 0.1 and 0.2%. The statistical percentage of deviation of parameters arises because computation is around 0.04–0.3. With these parameters as input we have further refined the parameters against whole pattern ( $2\theta = 6^\circ$  to  $40^\circ$ ). The detailed procedure of the Whole Powder Pattern Fitting Technique to compute these microstructural parameters was given in our earlier paper [15]. An in-house program was developed for this

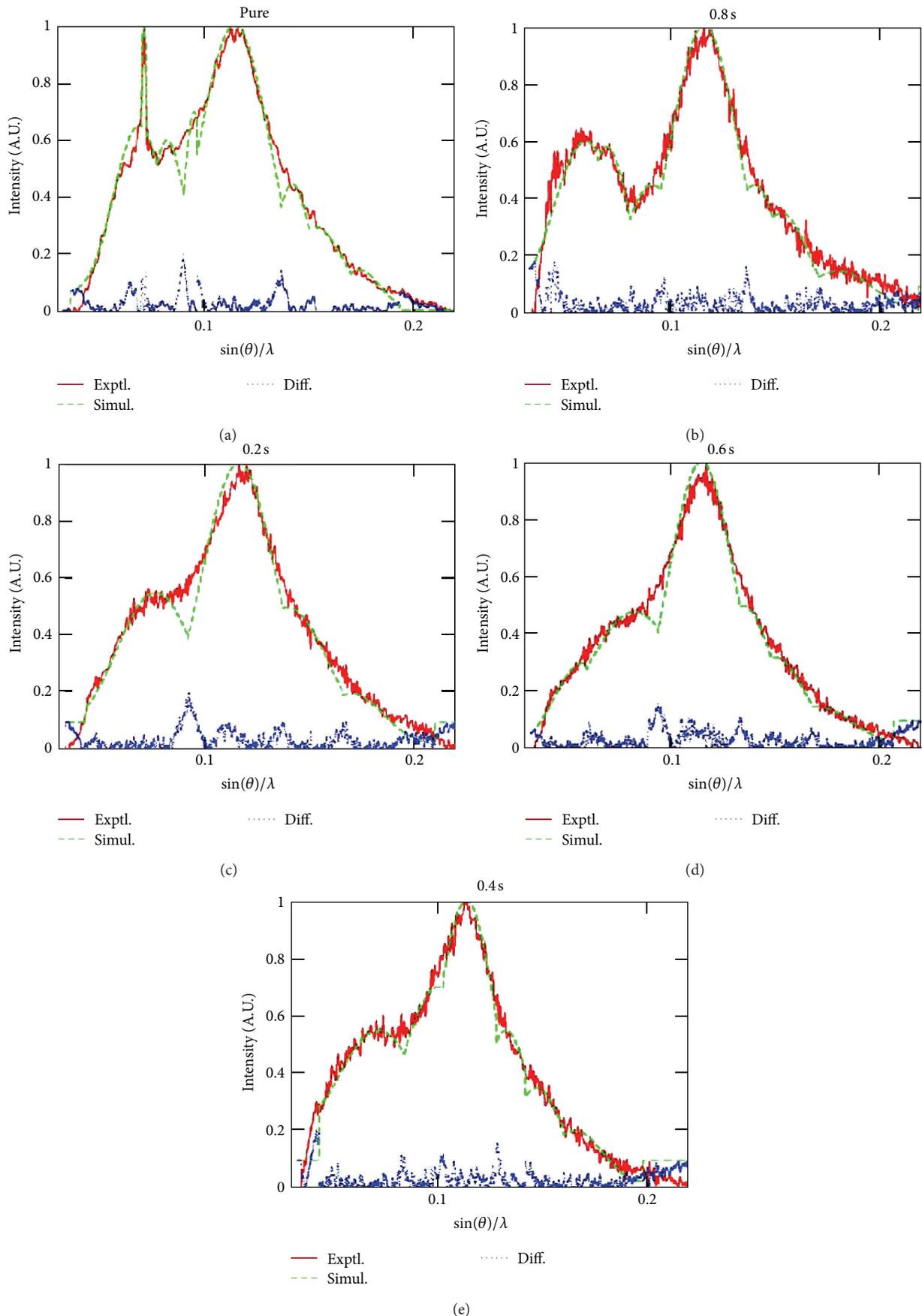


FIGURE 1: Whole pattern fitting for plasticized HPMC/PVP blend film Figures. Note: Pure = HPMC + PVP + 0, 0.2 s = HPMC + PVP + 0.2 g Sorbitol, 0.4 s = HPMC + PVP + 0.4 g Sorbitol, 0.6 s = HPMC + PVP + 0.6 g Sorbitol, 0.8 s = HPMC + PVP + 0.8 g Sorbitol.

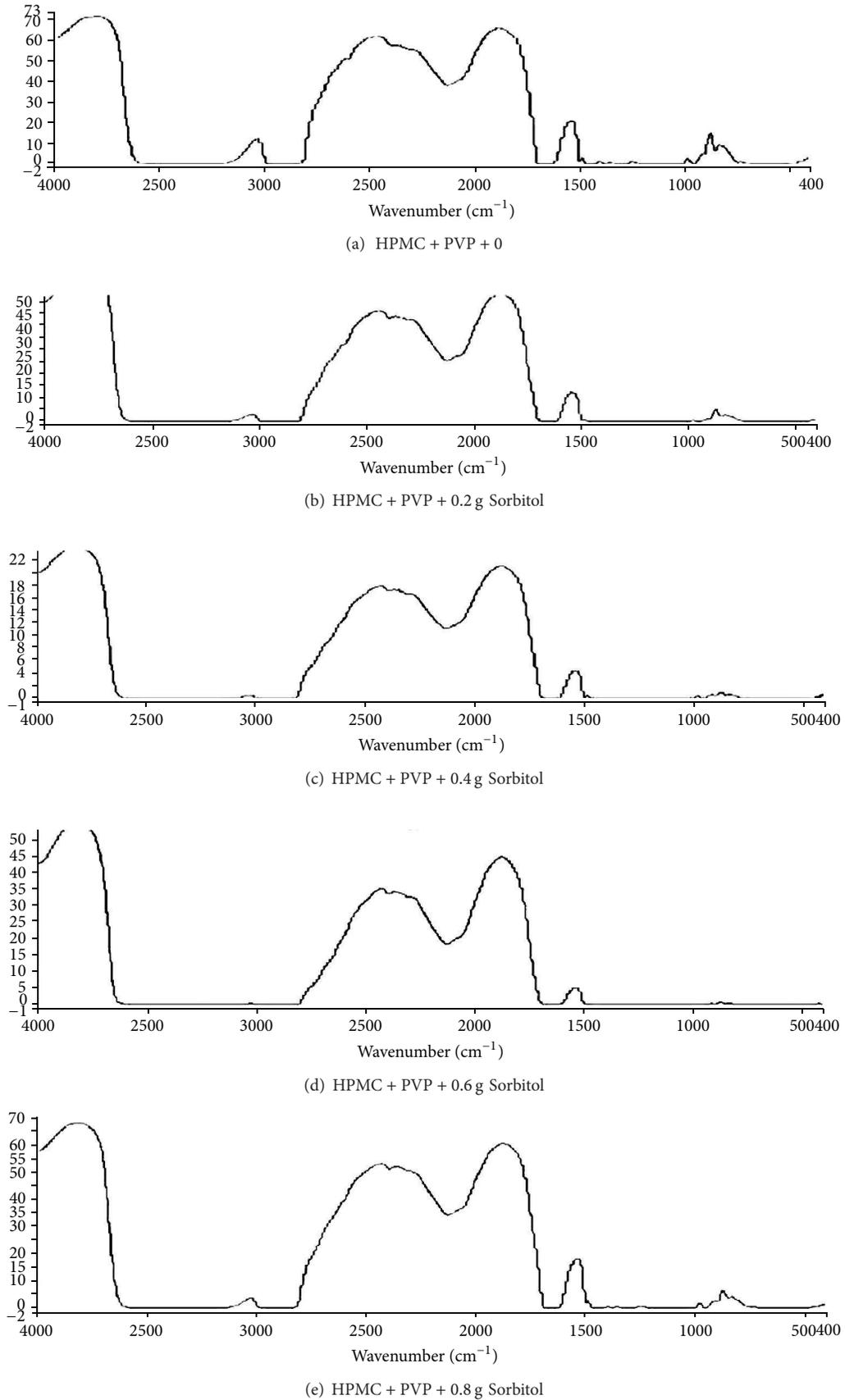


FIGURE 2: FTIR spectra of HPMC/PVP/Sorbitol films.

TABLE 2: Spectroscopically measured wavenumbers of HPMC/PVP polymer blend films plasticized with Sorbitol.

5% HPMC + 2% PVP (S) wave no. (cm <sup>-1</sup> )	S + 0.2 g Sorbitol wave no. (cm <sup>-1</sup> )	S + 0.4 g Sorbitol wave no. (cm <sup>-1</sup> )	S + 0.6 g Sorbitol wave no. (cm <sup>-1</sup> )	S + 0.8 g Sorbitol wave no. (cm <sup>-1</sup> )	Correlation
3361.50	3358	3326	3335	3305.5	O-H stretch
2911	2908.50	2921.50	2911.50	2910.0	C-H stretch
2127.23	2126.61	2126.96	2130.15	2127.27	C=N stretch
1657.50	1656	1654	1651.50	1651	-C=C stretch
1495.30	1495.6	1495.52	1495.85	1494.50	-C-C stretch
1443.50	1440.0	1444.50	—	—	-C-H bend
1374.50	1324	1375.50	1363	—	-C-H rock
1299.0	—	1299.50	—	1230	-C-H wag(methyl)
1108.50	1114.0	1107.50	1117.50	—	-C-N stretch

computation. The goodness of the fit between simulated and experimental XRD profiles for the samples along with the difference is also given in Figure 1. A casual glance at Table 1 reveals that, except for crystallinity, the other parameters such as lattice strain and stacking fault probability do not vary much during refinement. Further the low deformation fault probability value indicates that 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. Miscibility in the polymer is the important factor which decides the nature and property of the material [16]. The accuracy of the method used here has been discussed in our earlier papers [17–20].

**3.2. FTIR Analysis.** Spectroscopically measured wave numbers of HPMC/PVP polymer blend films plasticized with Sorbitol are given in Table 2. In the prepared miscible blends, it is expected that intermolecular hydrogen bonding between the hydroxyl groups of HPMC and the carbonyl groups of PVP might be created. For a thorough understanding of these interactions, FTIR spectra of all prepared blends were recorded. In this, two regions are of great importance, that is, the carbonyl group situated between 1600 and 1750 cm<sup>-1</sup> and the respective of the hydroxyl groups at 3350–3700 cm<sup>-1</sup> (Figure 2). In the PVP spectrum the characteristic peaks are observed at 1660 cm<sup>-1</sup> and at 1290 cm<sup>-1</sup> attributed to the stretching of amide >C=O and >N-C groups, respectively. On the other hand the characteristic peaks of HPMC are at 3050–3750 cm<sup>-1</sup> and are attributed to the -O-H stretching and the triple peak in the so-called finger print spectrum area of C-O- is at 960–1230 cm<sup>-1</sup>. A broad band at 3360 cm<sup>-1</sup> denotes the superposition of stretching for two types of hydroxyl groups in HPMC. Free at 3585 cm<sup>-1</sup> and self-association hydroxyl groups through intermolecular and intermolecular hydrogen bonding at 3362 cm<sup>-1</sup> which is not easily observed due to the peak broadness. The intensity and the position of these characteristic peaks of both polymers permit us to interpret rather easily the influence of interactions between these polymer groups. From the FTIR spectra of the prepared blends it can be seen that, as the amount of HPMC increases, the hydroxyl band moves to lower wave

numbers. In PVP/HPMC blend containing 50/50 w/w, the peak can be found at 3418 cm<sup>-1</sup> while, as the amount of PVP increases, it seems that the peak moves again at higher wave number (Figure 2). Thus in PVP/HPMC blend containing more than 50/50 w/w, the peak is detected at 3362 cm<sup>-1</sup> which is similar to that of initial HPMC. This indicates that hydrogen bonding between the carbonyl groups of PVP and the hydroxyl groups of HPMC is stronger when HPMC is used in excess rather than PVP. A similar trend is exhibited for the C-O groups recorded at the finger print area.

**3.3. Mechanical Properties.** Mechanical properties like tensile strength, Young's Modulus, and percentage of elongation at break of these films were measured using universal testing machine, according to ASTM standard. Tensile strength of the films was calculated by dividing the maximum load for breaking 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. The tensile strength and modulus of elasticity decrease first and then increase with increasing the concentration of Sorbitol in HPMC/PVP matrix. We mentioned in the XRD analysis that decrease in crystallinity leads to flexible backbone which results in the improvement in mechanical properties of the films. Table 3 shows that all mechanical properties are varying with concentration of Sorbitol. Variation of mechanical properties and crystallinity with the concentration of Sorbitol was given in Figure 3. Plasticizers are relatively low molecular weight materials which have a capacity to alter the physical properties of polymers to make them more useful as film forming agents. The function of plasticizer is to make the polymer more pliable, soft, thereby enhancing the flexibility and plasticity of the film. Physical and mechanical properties of the films change due to increased mobility of the polymeric chains. The electiveness of the plasticizer is intensely related to its chemical structure and the extent and rate of interaction with the polymeric material present in the formulation. The properties like the water uptake, erosion, solid state

TABLE 3: Mechanical properties of HPMC/PVP blend films plasticized with Sorbitol.

Sample	Tensile strength (MPa)	Young's Modulus (MPa)	Stiffness	% of elongation
HPMC + PVP + 0	22.90	986.80	54.80	3.12
HPMC + PVP + 0.2 g Sorbitol	18.9	734.62	48.9	8.23
HPMC + PVP + 0.4 g Sorbitol	9.83	332.35	36.92	9.45
HPMC + PVP + 0.6 g Sorbitol	6.60	193.78	21.53	6.83
HPMC + PVP + 0.8 g Sorbitol	7.56	424.78	47.19	4.28

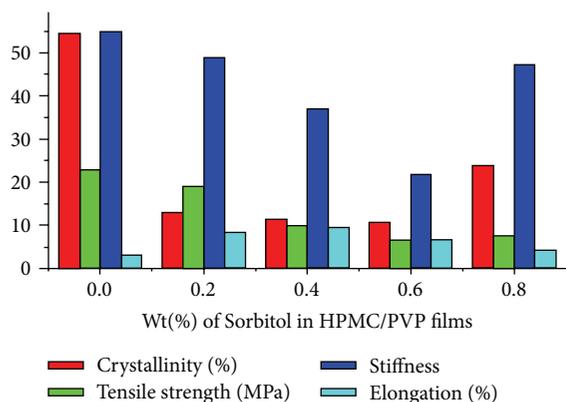


FIGURE 3: Variation of crystallinity and mechanical properties with the concentration of Sorbitol in HPMC/PVP blend films in column representation.

crystallinity, thermal behaviour, and water vapour permeability (WVP) are modified to great extent. The mechanism of action of plasticizer is defined as interposition between the individual strands of polymer due to which there is breakdown of polymer-polymer interactions. This breakdown of the polymer network increases the film elongation effect, thereby mechanical properties of the plasticized films like tensile strength, elastic modulus decrease whereas elongation increases. Sorbitol was used as plasticizer in our study since it has been described as good plasticizer [21–23], due to its ability to reduce the intermolecular hydrogen bonding and mechanical strength of the films. Sorbitol imparts flexibility to the edible/biodegradable blends films previously mixed [24, 25]. It also constitutes good nutritive substrate for promoting the degradation of the composite system. Sorbitol molecules are easily inserted between the HPMC strands resulting in decrease in mechanical property. This is due to increase in hydrogen bonds leading to reduction in intermolecular forces [26].

#### 4. Conclusion

Edible films based on HPMC/PVP blends, plasticized with Sorbitol, were prepared by solution cast technique, and effect of plasticizer has been investigated using XRD, FTIR, and UTM. From the XRD it is observed that the crystallite size decreases with the concentration of Sorbitol. Decrease in crystallite size leads to more amorphous nature of the film and increase in flexibility. The observed shifts in the absorption bands and decrease in the intensity confirm

the interaction of Sorbitol in blend matrix. A mechanical property decreases considerably due to the addition of plasticizer in the blend matrix. Sorbitol imparts flexibility by reducing the crystallinity of the film by which there is a decrease in tensile strength, stiffness, and modulus of elasticity up to 0.6% of Sorbitol and then increase in % elongation. These films with more flexibility are found in applications of flexible packaging, controlled drug delivery, tablet coating system, biomaterials, and so forth.

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