

Thermal and Morphological Properties of SA/HPMC Blends

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ABSTRACT: Sodium alginate (SA) was blended with varying amounts of hydroxypropyl methylcellulose (HPMC) viz., 10, 20, and 30 wt % by solution casting process. Thus, the obtained blends were characterized by using different analytical techniques such as differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). FTIR studies reveal the hydrogen bond formation between hydroxyl groups of SA and HPMC polymer chains. DSC analysis shows single glass transition temperature (T_g) for SA/

HPMC blends indicating compatibility and physical interaction between SA and HPMC polymer chains. TGA analysis indicates variation of thermal stability of SA with change in compositions of HPMC. SEM studies reveal uniform distribution of second phase in the blends. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2235–2240, 2009

Key words: sodium alginate; hydroxypropyl methylcellulose; blends; Fourier transform infrared spectroscopy; thermal behavior; surface morphology

INTRODUCTION

The blend materials from either synthetic or natural polymers alone are not always able to meet all the complex demands of the biomaterials. The success of synthetic polymers as biomaterials relies on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained, and at low production cost. Biological polymers present good biocompatibility, but their mechanical properties are often poor. The necessity of preserving biological properties complicates their processability, and their production or recovery costs are very high.¹ Therefore, biologically useful polymeric materials based on the blends of synthetic and natural polymers, such as poly(*N*-vinyl-2-pyrrolidone)-kappa carrageenan (PVP/KC), poly(*N*-vinyl-2-pyrrolidone)- ι -carrageenan (PVP/IC),² poly(ethylene oxide)-hydroxypropyl methylcellulose (PEO/HPMC),³ and poly(vinyl alcohol)-chitosan (PVA/C),⁴ have been studied.

Generally, the formation of specific intermolecular interactions through hydrogen bonding between two

or more polymers is responsible for the observed mixing behaviors and properties of the blends prepared from aqueous solutions.⁵ The analysis of the blends properties is of importance to explore further applications of blends for biomedical and pharmaceutical devices. Studies by Kondo and Sawatari³ have established that the primary hydroxyl group on cellulose and methylcellulose's can form a hydrogen bonding through hydroxyl groups of sodium alginate (SA).

Synthetic polymers have gained credibility in several technological applications because of properties such as low cost and density, thermoplasticity, hydrophobicity, and strength. However, the high amount of plastic waste created every year associated with the decreasing availability of landfills, and has encouraged the development of biodegradable materials that could substitute for synthetic polymers, at least in some of their applications. SA is one of the most promising materials to achieve this goal. It is an abundant linear polysaccharide obtained from marine brown algae, a biodegradable biopolymer. The simplest fundamental unit of SA is related to cellulose, and the structural configuration is better represented by (1,4)- β -D-mannuronate and (1,3)- α -L-guluronate residues.⁶ SA has carboxylic groups in every repeating unit that has α and β configurations. These characteristics are expected to improve compatibility. It is a polyelectrolyte having

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rigid molecular chain, and good film forming ability, has been extensively exploited, and studied in detail on biomedical applications such as drug delivery and proteins,⁷⁻¹⁵ because of its biodegradability and biocompatibility. SA is also used as a membrane material for dehydration studies.¹⁵ SA find many applications in agricultural^{16,17} also after crosslinking with glutaraldehyde.

HPMC is cellulose ether in which hydroxypropyl groups have been substituted on one or more of the three hydroxyl groups present in each anhydroglucose ring of cellulose. By controlling the amount and type of substitution, it is possible to produce a range of widely varying properties. By varying the hydroxypropyl content, a series of polymers is produced, which ranges from alkali soluble to organic soluble. The water soluble commercial derivatives contain approximately two substituted groups per anhydroglucose ring, while the organic soluble polymers approach almost total substitution, that is, three groups per anhydroglucose unit. Also, HPMC polymers possess increased organo solubility and thermo-plasticity over the methylcellulose counterparts. HPMC with a hydroxypropyl substitution of 7 to 12% has the unique property of water solubility combined with solubility in hot and cold organic solvents. When properly formulated, this product is thermoplastic and can be fabricated by a number of techniques including extrusion, injection and compression molding, hot casting, and hot dipping. HPMC is a hydrophilic, water-soluble, and aerobically biodegradable polymer extensively used as a matrix for drug delivery,^{18,19} in building materials, for dye and paint, in adhesives, cosmetics, coating processes, and in agricultural and textile areas.²⁰ Because of its excellent biocompatibility and very low toxicity, the potential use of HPMC in biomedical applications has attracted a great deal of attention from both the industrial and scientific points of view.²¹⁻²⁴ HPMC is being widely used as coating agent, film former, stabilizing agent, suspending agent, table binder, and viscosity increasing agent. It is also used in oral and topical pharmaceutical formulations. In oral products, HPMC is used as tablet binder and as an extended release tablet matrix.²⁵ Recently, many researchers have studied the blends of SA.²⁶⁻²⁹

Hence, the miscibility studies of SA/HPMC blends might be important to enhance some of the above said properties. The change of structure and properties of SA/HPMC blends were measured by differential scanning calorimetry (DSC), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM). We predict that this work may contribute basic information to the further application of this kind of blends.

EXPERIMENTAL

Materials

The raw materials used in this study, SA (Mw – 4.96 KDA, Research grade) and HPMC (apparent viscosity -15 cPa; residue on ignition-1% and loss on drying-1%) were supplied by M/s Thomas Baker Chemicals, Mumbai, India and M/s Loba Chemie Pvt, Mumbai, India, respectively.

Preparation of the blends

A series of SA/HPMC blends were processed into films by solution casting process by varying the HPMC content from 10 to 30 wt %. Aqueous solutions of individual polymers (1% w/v) were mixed to obtain desired composition and stirred for 30 min at $25 \pm 3^\circ\text{C}$. The blend films with different compositions were cast on cleaned petri dishes, and the films were released on water evaporation. The films were dried under vacuum at $60 \pm 3^\circ\text{C}$ for 3 h.

Measurements

The blends were analyzed by (DSC 2010, TA instruments, New castle, DE) to determine the thermal transition in the temperature range of $25\text{--}350^\circ\text{C}$ in nitrogen atmosphere at heating rate of $10^\circ\text{C}/\text{min}$. DSC cell was calibrated with metallic indium with 99.9% purity. The error in each measurement was estimated to be $\pm 0.5^\circ\text{C}$. The TGA thermograms were obtained using TA instruments, 2950 thermal analyzer (USA) at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The TGA profiles were recorded over a temperature range of ambient to 700°C . The weight of the samples used for each analysis was 6–8 mg. FTIR spectra of the films were recorded on a Nicolet 520 FTIR spectrophotometer. All the spectra were recorded using KBr pellet method at a resolution of 4 cm^{-1} in the wave number range of $4000\text{--}400\text{ cm}^{-1}$.

For morphological analysis, $\sim 6\text{ mm} \times 6\text{ mm}$ dimension was cut from the blends and was mounted on a specimen holder. A gold coating of $\sim 200\text{ \AA}$ thick was deposited on the surface of the specimen by vacuum evaporator method, and then the micrographs were recorded in Jeol JSM 5300 SEM, Japan.

RESULTS AND DISCUSSION

Thermal analysis by DSC

The thermal properties of SA/HPMC blends were investigated by DSC technique to study the effect of HPMC content on T_g and crystalline melting point (T_m) of SA. The T_g is used to describe the chain

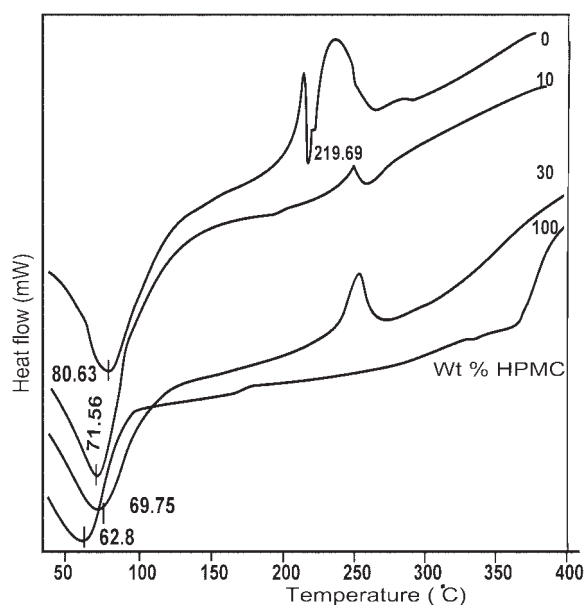


Figure 1 DSC thermograms of SA/HPMC blends.

segmental motion. SA is a polysaccharide polymer containing two hydroxyl groups and one carboxylate group in every repeating unit that has α and β configurations. SA polymer has a glass transition at 80.6°C and HPMC at 62.8°C (Fig. 1). Because SA contains two hydroxyl groups and one carboxylate group, which forms very strong inter- and intramolecular hydrogen bonding, it shows wide glass transition peak as can be seen from the Figure 1. The incorporation of 10 and 30 wt % HPMC into SA matrix reduces the T_g from 80.6°C to 71.6 and 69.8°C, respectively. In both the compositions, the SA/HPMC shows only single T_g corresponding to SA in the temperature range under investigation indicating the miscibility of SA with HPMC. The observed single T_g of the blends may be due to the similarity in chemical structure between SA and HPMC molecules like both are hydrophilic, hydroxyl, heterocyclic and biopolymer. However, the reduction in T_g may be due to the reduction in the concentration of carboxylate groups of SA with increase in HPMC content; which contains hydroxyl groups. The concentration of carboxylate group has significant impact on T_g .

The most important factor that determines whether a polymer can crystallize or not, is its geometrical structure or the configuration of the chain. SA molecules contain, at least three different types of polymer segments; poly(β -D-mannopyranosyluronate), poly(α -L-gulopyranosyluronate), and segments with alternating sugar units. The shape of these segments are quite different and based on diaxial and diequatorial links, it has a very weak and small melting peak at 219.7°C (Fig. 1), indicating its amorphous nature. However, the SA/HPMC blends do not show any melting peak in the temperature

region under investigation. This may be due to the stiff molecular chain of NaAlg, which has a significant effect on the overall chain mobility in the mixture and retards the rate of crystal growth.

Thermal analysis by TGA

TGA is one of the widely used techniques to evaluate thermal stability, composition and thermal degradation kinetics of the polymeric materials, blends, and composites. The TGA thermograms of SA and SA/HPMC blends containing 10 and 30 wt % of HPMC (Fig. 2) shows that SA undergoes two stage thermal degradation. The thermal degradation occurs in the temperature range of 106–219°C and 219–261°C for first and second steps, respectively. The weight loss in the first stage is attributed to the loss of volatile products formed during the dehydration process, and the weight loss in second stage is attributed to the formation of a carbonaceous residue and finally the Na_2CO_3 . The SA with 10 wt % HPMC blend also showed two steps thermal degradation processes, which occurred in the temperature range 218–292°C and 292–377°C for first and second steps, respectively. However, with increase in HPMC content, the onset degradation temperature is increased from 106°C (SA) to 218°C (10 wt % HPMC). The significant increase in onset of degradation temperature may be due to the increase in cohesive strength and physical interaction of the SA/HPMC blends. In case of 30 wt % HPMC, only single step degradation was found in the temperature range of 233–389°C. The marked difference in the thermal properties of these blends illustrates the significant change in the configuration of anomeric linkage from α -D to β -D. The SA confers flexibility

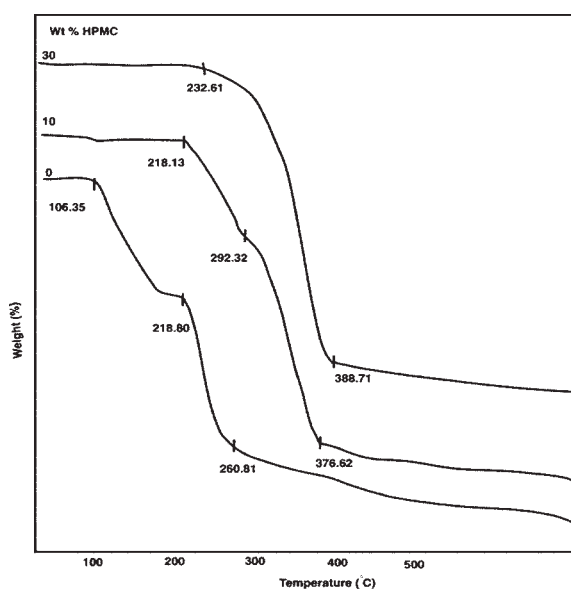


Figure 2 TGA thermograms of SA/HPMC blends.

TABLE I
Data Obtained from the TGA Thermograms of SA/HPMC Blends

SA/HPMC blend composition (wt/wt, %)	Percentage of weight loss at different temperatures (°C)					
	150	200	250	300	350	400
100/0	2.11	19.01	65.49	75.35	78.87	81.69
90/10	0	0	09.29	29.99	60.71	86.42
80/20	0	0	02.36	11.81	51.18	85.83
70/30	0	0	02.09	08.04	37.06	87.76

on the polymer chain and permits it to melt and degrade, whereas the HPMC gives linear and strongly hydrogen bonded rigid molecules, which shows high thermal stability. Similar results are obtained in terms of percentage weight loss with respect to temperature as shown in Table I. From the table, it was noticed that the percentage of weight loss decreased with increase in HPMC content. The two stage thermal degradation of SA/HPMC blends were well reflected in the derivative thermograms (Fig. 3) also. The quantum of weight loss/area under the first peak is less when compared with the area under the second peak, which indicates that the weight loss in the second stage is more for SA. The incorporation of HPMC into the SA matrix shows two steps degradation processes. However, the incorporation of HPMC shows a new derivative peak significantly at a higher temperature apart from the derivative peak corresponding to the SA. The introduction of HPMC has enhanced the thermal stability of SA matrix.

Fourier transform infrared spectroscopic analysis

FTIR analysis of the blends was carried out to probe the interactions between SA and HPMC. FTIR spectra for SA, HPMC and their blends are shown in Figure 4. The FTIR spectra of blends show spectral

features similar to those for the homopolymers, but a slight change in the positions of the bands. The characteristic absorption peaks for pure SA were noticed at 3386, 2906, 2181, 1604, 1411, 1091, and 622 cm^{-1} whereas the SA/HPMC (70/30) blend shows the characteristic absorption band at 3391, 2903, 2119, 1622, 1455, 1416, 1374, 1314, 1071, 947, and 622 cm^{-1} . The FTIR spectra of SA, HPMC and its blends are shown in Figure 4 and the characteristic band positions are tabulated in Table II. The molecular chains of SA contain $-\text{OH}$ and $-\text{COO}-$ groups, these groups can interact with $-\text{OH}$ groups of HPMC. The strong absorption owing to $\text{O}-\text{H}$ stretching vibration of SA was noticed at 3386 cm^{-1} and, the asymmetric and symmetric stretching vibrations of $-\text{COO}$ groups appeared at 1604 and 1411 cm^{-1} , respectively. The spectrum of SA/HPMC blends were characterized by the presence of absorption peaks with intensity roughly proportional to the blending ratio. The hydrogen bonding has strongest influence on the SA characteristic bands. The asymmetric (1604 cm^{-1}) and symmetric (1411 cm^{-1}) stretching vibrations of $-\text{COO}$ groups in SA shifted to a higher wave numbers, 1622 and 1455 cm^{-1} with increase in HPMC content in the blends. The absorption band centered at 3388 cm^{-1} concerned with stretching of $-\text{OH}$ of SA was broadened and shifted

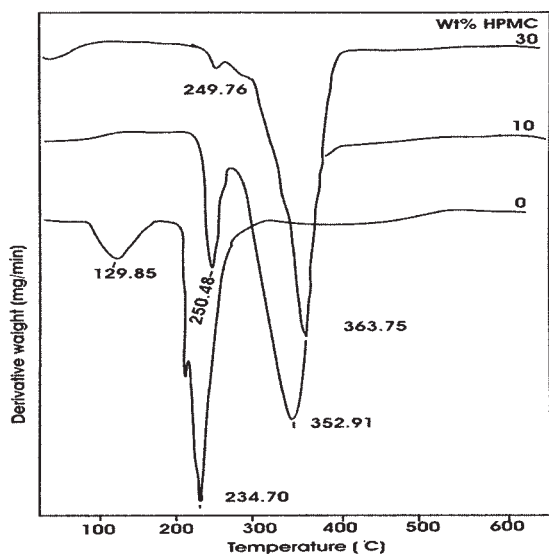


Figure 3 DTG thermograms of SA/HPMC blends.

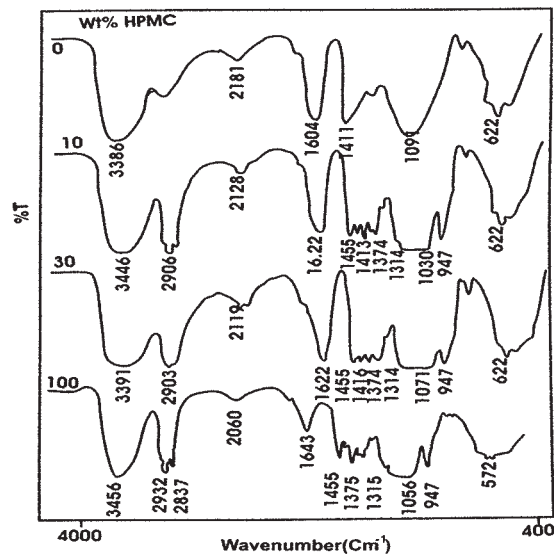


Figure 4 FTIR spectrum of SA/HPMC blends.

TABLE II
Band Assignments of FTIR Spectra of SA/HPMC Blends

Wave number of the peak (cm^{-1}) for A/HPMC blends				Band assignments
100/0	90/10	70/30	0/100	
3386	3446	3391	3456	O—H band stretching (intermolecular hydrogen bonded)
2906	2906	2903	2932 2837	C—H stretching
1604	1622	1622	1643	—O—C=O asymmetric stretching
1411	1455	1455	1455	—O—C=O symmetric stretching
	1413	1416		
	1374	1374	1375	C—CH ₃ bending
	1314	1314	1315	
1091	1030	1071	1056	C—O—C stretching
622	947	947	947	C—O—C bending
	622	622	572	C—H bending

with increase in HPMC content. Similarly the —OH stretching band in HPMC at 3456 cm^{-1} was also shifted to 3391 cm^{-1} due to hydrogen bonding. The shift of asymmetric (1604 cm^{-1}) stretching vibrations of —COO groups in SA toward higher wave number (1622) in SA/HPMC blends is again due to hydrogen bond formation with hydroxyl groups of HPMC. The blend films that have undergone the step transition show a change in the band position and shape when compared with the poor compo-

ments. All these changes may be due to the intermolecular hydrogen bonding between —COO— groups of SA and —OH groups of HPMC as reported for the blend films of silk fibroin/SA³⁰ and poly(acrylamide)/SA.³¹

Scanning electron microscopic analysis

The SEM photomicrographs of pure SA and its blends with HPMC are shown in Figure 5(a–e). The

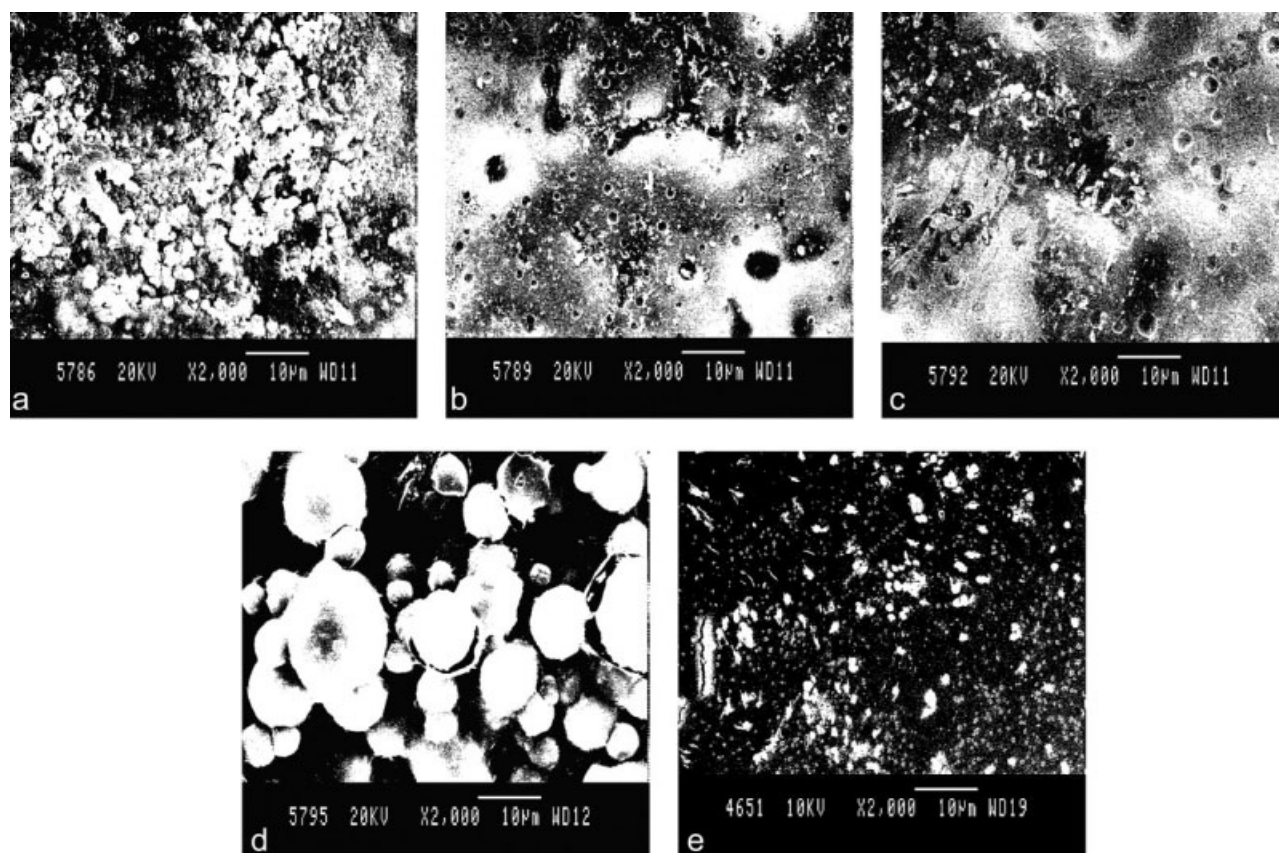


Figure 5 SEM photomicrographs for SA/HPMC blends, (a) 100/0, (b) 90/10, (c) 80/20, (d) 70/30 and (e) 0/100.

SEM images of pure SA shows a homogeneous and rough surface with cavities and pure HPMC shows a comparatively smooth surface with dispersed particles on the surface [Fig. 5(e)]. SEM images shows dispersion of HPMC domain in the SA matrix. With increase in HPMC content, the domain size of second phase increases [Fig. 5(b–d)]. This indicates variation in compatibility and phases at higher HPMC content.

CONCLUSIONS

The blend films of HPMC and SA have been obtained by solution casting method using water as solvent with 10, 20, and 30 wt % of HPMC. DSC analysis shows single T_g for SA/HPMC blends indicating the good physical interaction between SA and HPMC molecules. The TGA thermograms indicate the improvement in the thermal stability of the SA after incorporation of HPMC. FTIR analysis revealed the existence of specific intermolecular interactions between carboxyl groups of SA and hydroxyl groups of HPMC. The morphology of the blends indicates the increase in domain size with increase in HPMC content, which implies variation in compatibility.

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