

Sodium Alginate and Its Blends with Starch: Thermal and Morphological Properties

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ABSTRACT: A series of sodium alginate (SA) and starch blends, namely 100/0, 90/10, 80/20, 70/30, and 60/40, were processed into films by solution casting process and the obtained SA/starch blends have been characterized by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). DSC analysis shows single glass transition temperature (T_g) up to 30 wt % starch content in the blend, indicating the compatibility and interaction between SA and starch molecules. The

TGA reveals the reduction in thermal stability of SA/starch with increase in starch content. FTIR analysis demonstrated the existence of specific intermolecular interactions between carbonyl groups of SA and hydroxyl groups of starch. The morphological analysis by SEM shows the homogeneous distribution of starch in the SA matrix. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 4075–4081, 2008

Key words: sodium alginate; polymer blends; infrared spectroscopy; thermal properties; surface morphology

INTRODUCTION

Long life and attractive properties have made plastics as a material of choice for many applications. Because of the tremendous growth in applications, plastics are one of the fastest growing segments of the waste stream. Vast majority of plastic products are made from petroleum-based synthetic polymers that do not degrade in a land fill site or in a composite like environment. Especially polyolefins such as polyethylene (PE) and polypropylene (PP) are very resistant to hydrolysis and are totally nonbiodegradable. As a consequence, the disposal of these products poses a serious environmental threat. An environmentally conscious alternative is to design/synthesis polymers that are biodegradable. Biodegradable plastics provide opportunities for reducing municipal solid waste through biological recycling to the ecosystem and can replace the conventional nonbiodegradable synthetic plastic products. In addition, it is desirable that these biodegradable polymers come primarily from agriculture or other renewable resources for a sustainable environment.

Starch is one of the most abundant and naturally occurring polymers next to cellulose. The most important sources of starch are wheat, potato, rice,

tapioca, and corn. Starch is the major polysaccharide reserve of plants. Starch occurs in nature as water insoluble granules, and it is a polymer of D-glucose. The average granule size of starch varies from source to source; rice starch granules are roughly 3 μ in diameter, corn starch has an average granular size of 10 μ , whereas potato starch granules are about 35 μ in diameter. The starch granules consist of highly branched amylopectin and linear amylose molecules, with some minor components such as lipids and proteins. Amylose is a crystalline linear molecule with molecular weight ranging from 10^5 to 10^6 g/mol, which constitute nearly 20% of starch and is soluble in hot water. Amylopectin is a highly branched molecule with molecular weight ranging from 10^6 to 10^8 g/mol, and it is insoluble in hot water. However, both amylose and amylopectin can be hydrolyzed at acetal link by the enzyme. Starch has been considered as a low-cost alternative to synthetic plastics in production of disposable plastics.¹ Starch is totally biodegradable in a wide variety of environmental conditions and that permits the development of totally biodegradable starch products. Starch by itself was plasticized and shaped into consumer items.^{2–5} But plasticized starch alone swells and deforms on exposure to moisture. To compensate the inconvenience of plastics made by pure starch, starch was blended with petroleum polymers.^{6–8}

Polymeric blends containing starch have been developed for different applications, and they are

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the subject of several patents.^{9–11} The first important commercial application of starch has been the blending of polyethylene (PE). It was assumed that starch would accelerate the degradation of PE, but PE is virtually nonbiodegradable.¹² Currently, plastic films used in agriculture mulch are made with low-density polyethylene (LDPE) containing transition metal compounds soluble in the thermoplastic matrix and about 6–15% starch. However, the degradation duration is still high and can reach a few years, for some of these products that do not respond to certain norms of biodegradability. Then blending of starch with biodegradable synthetic polymers like poly (caprolactone) (PCL),^{13–15} poly(-hydroxybutyrate) (PHB), poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV),^{16–21} poly(lactic acid) (PLA),^{22,23} and poly (vinyl alcohol) (PVA)^{24–27} have become the objective of many studies.

With the ongoing research efforts aimed at preparation and evaluation of biodegradable polymer blends,^{28,29} in this article authors reported the properties of blend of two polysaccharide polymers, sodium alginate (SA) and starch. SA is one of the most promising materials to achieve this goal. SA is an abundant linear polysaccharide obtained from marine brown algae, a biodegradable biopolymer and 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.³⁰ SA was chosen because of its structural features, with carboxylic groups in every repeating unit that has α and β configurations. These characteristics were expected to improve compatibility. SA, polyelectrolyte, having rigid molecular chain, and good film forming ability, has been extensively exploited and studied in detail on biomedical applications as drug carrier,^{31–33} because of its biodegradability and biocompatibility. SA is, hydrophilic and rigid polymer, used as a membrane material for dehydration studies.³⁴ The change of structure and properties of SA/starch blend was analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

The SA ($M_w = 4.96$ kDa, research grade) and starch (soluble, potato extra pure), were obtained from M/s Thomas Baker Chemicals Ltd. (Mumbai, India) and M/s S.D. Fine Chemicals Ltd., (Mumbai, India) respectively.

Preparation of the blends

A series of SA/starch blends, namely 100/0, 90/10, 80/20, 70/30, and 60/40, were processed into films by solution casting process. Aqueous solutions of individual polymers (1% w/v) were mixed to obtain desired composition and stirred for 30 min at $25^\circ\text{C} \pm 3^\circ\text{C}$. The pure and mixture solutions were cast on glass mold to obtain films by water evaporation. The SA/starch blends were dried under vacuum at $60^\circ\text{C} \pm 3^\circ\text{C}$ for 24 h.

Characterization techniques

The SA/starch blends were analyzed by DSC (DSC 2010, TA instruments) to determine the thermal transition in the temperature range from ambient to 400°C in nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. DSC cell was calibrated with 99.9% pure metallic indium. The TGA thermograms were obtained using TA instruments Inc., TGA 2950 thermal analyzer at a heating rate of $20^\circ\text{C}/\text{min}$ in nitrogen atmosphere. The TGA profiles were recorded over a temperature range from ambient to 700°C . About 6–8 mg of the sample was used for each analysis. FTIR spectra of the blends were measured on a Nicolet 520 FTIR spectrophotometer. All the spectra were recorded in the wave number range of 4000 cm^{-1} – 400 cm^{-1} at a resolution of 4 cm^{-1} with a maximum of 100 scans. The spectral calibration of the instrument was made using polystyrene (PS) film at regular intervals of time. The surface morphology of the samples was carried out using Jeol JSM 5300 SEM after gold coating the specimens.

RESULTS AND DISCUSSION

Differential scanning calorimetric analysis

The thermal properties of SA/starch blends were investigated by DSC technique to analyze the effect of starch content on glass transition temperature (T_g) and melting temperature (T_m) of SA. SA is a polysaccharide polymer, containing two hydroxyl segments and one carboxylate segment in every repeating unit that has α and β configurations. SA polymer has a T_g at 81°C (Fig. 1). As SA contains hydroxyl and carboxylate groups, which forms very strong inter- and intramolecular hydrogen bonding and shows wide transition as can be seen from the thermogram. This broad transition cannot be considered or compared with dehydroxylation or evaporation of moisture from the polymer and further, all the polyhydroxyl polymers especially polyvinyl alcohol (PVA)^{28,29} are having similar transition in the region under investigation. The incorporation of 10, 20, and 30 wt % starch granules into SA matrix,

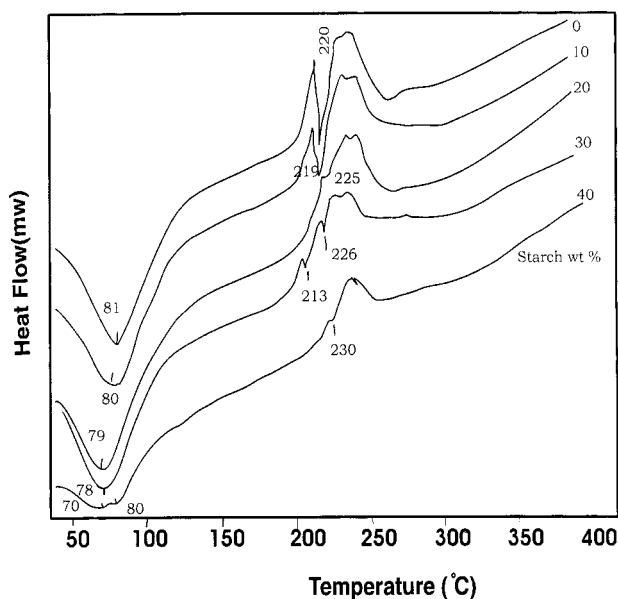


Figure 1 DSC thermograms of SA/starch blends.

reduces the T_g peak maxima from 81°C to 80°C, 79°C, and 78°C respectively, in sequence. In all the compositions, the SA/starch blends show only single T_g corresponding to SA, this may be considered as the miscibility of starch with SA and also the reduction in T_g is not drastic, because of the similarity between SA and starch molecules like both are hydrophilic, hydroxyl, heterocyclic, and biopolymer. However, the reduction in T_g from 81°C to 78°C may be because of the reduction in the concentration of carboxylate segment of SA with increase in starch content, which contains only hydroxyl segments. The concentration of carboxylate segment has significant impact on T_g . Figure 2 shows the reduction in T_g with increase in starch content and splitting of T_g at 40 wt % of starch content; one is at 70°C and another one is at 80°C, indicating multiple phases. This phase separation may be due to increase in free volume and discontinuity of the SA matrix. Because at higher loading, too many starch granules are confined in between the SA chains.

The SA is an amorphous polymer with irregular structure and does not crystallize. The most important factor that determines, whether a polymer can crystallize or not, is its geometrical structure (configuration of the chain). SA molecules contain, at least three different types of polymer segments: poly(β -D-mannopyranosyluronate) segments, poly(α -L-gulopyranosyluronate) segments, and segments with alternating sugar units. The shape of these segments is quite different and based on diaxial and diequatorial links, it shows a very weak and small melting peak at 220°C (Fig. 1), indicating its amorphous

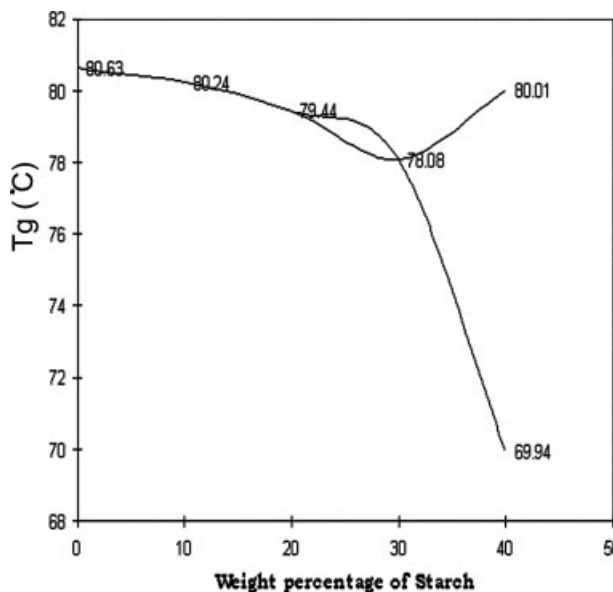


Figure 2 Effect of starch content on T_g of sodium alginate.

nature. This is because of the irregularity in shape and size of the SA molecules. The incorporation of starch (10, 20, 30, and 40 wt %) into SA matrix shifts its melting temperature to 219, 225 (213, 226), and 230°C, respectively. These variations indicate increase in free volume of the SA/starch matrix.

Thermogravimetric analysis

The thermogravimetric analysis (TGA) thermograms of SA/starch blends, containing different amount

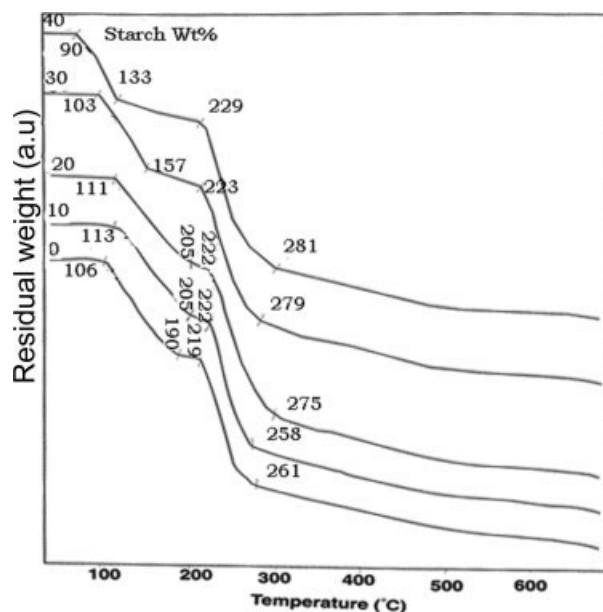


Figure 3 TGA thermograms of SA/starch blends.

TABLE I
Thermal Transition Data Obtained from TGA
Thermograms of SA/Starch Blends

SA/starch blend composition (wt/wt %)	I-stage (°C)	II-stage (°C)
100/0	106–190	219–261
90/10	111–205	222–258
80/20	110–205	222–275
70/30	103–157	223–279
60/40	90–133	229–281

(%) of starch were presented in Figure 3. These thermograms showed that SA undergoes two-stage thermal degradation processes. The first-stage thermal degradation occurred in the temperature range of 106–190°C and the second-stage in the range of 219–261°C. The weight loss in first stage is attributed to the loss of volatile products like dehydration, and the weight loss in second stage is attributed to the decrosslinking of polymer networks, formation of a carbonaceous residue and finally yields Na_2CO_3 as char. SA/starch blends also showed thermal degradation in two stages. This may be due to both SA and starch is hydrophilic and heterocyclic polymers containing —OH groups and shows similar degradation profile. However, with increase in starch content, the temperature at which the sample starts to lose its weight is reduced from 106°C (SA) to 90°C (40 wt % starch). The reduction in temperature of onset weight loss of blends may be due to the reduction in cohesive strength and physical intactness of the SA/starch blends. Starch occurs in the form of granules which consists of highly branched amylopectin and linear amylose molecules. Highly branched nature of amylopectin does not form compact packing with other polymers like SA. Therefore, as starch content increases, the weight loss temperature gets reduced and further difference between the first and second stage is increased (Table I). The weight loss temperature in the second stage is increased from 219 (SA) to 229°C (40 wt % starch) with increase in starch composition. This may be attributed to the presence of methylene groups in starch molecules. Because the major structural difference between SA and starch is carboxylate groups in SA and methylene groups in starch. The carboxyl groups of SA undergo degradation in first stage, and the methylene groups of starch can undergo degradation only in second stage. The percentage weight loss at different temperatures obtained from TGA thermograms are given in Table II. This shows that up to 200°C the percentage of weight loss increases with increase in starch content and at 250°C, the percentage of weight loss decreased with increase in starch content. The two

TABLE II
Data Obtained from TGA Curves of SA/Starch Blends

SA/starch blend composition (wt/wt %)	Percentage weight loss at (°C)						
	100	150	200	250	300	350	400
100/0	0	2.1	19.0	65.5	75.4	78.9	81.7
90/10	0	7.4	27.5	57.7	73.9	77.5	81.0
80/20	0	12.5	27.1	49.7	75.7	80.9	84.0
70/30	0	18.9	27.3	54.5	75.5	79.0	82.5
60/40	0	23.1	25.9	51.0	73.8	79.4	83.2

stage degradation of SA/starch composite was well reflected in the derivative TGA thermograms as shown in Figure 4, which shows two peaks. The quantum of weight loss/area under the first peak is less as compared with the area under the second peak, which indicates that the major weight loss occurs in the second stage. With reference to the DSC analysis, the first stage weight loss occurs between the T_g and T_m of the blend and the second stage occurs above the T_m as expected.

Fourier transform infrared analysis

FTIR analysis of the blends was carried out to detect any shift that could be attributed to weak interactions between two polymers. Figure 5 shows the FTIR spectra of the pure SA and its blends with starch in the wave number range of 4000 cm^{-1} – 400 cm^{-1} . The FTIR spectra were recorded only for selective compositions. This is because it is difficult to cast the films for all the compositions. The character-

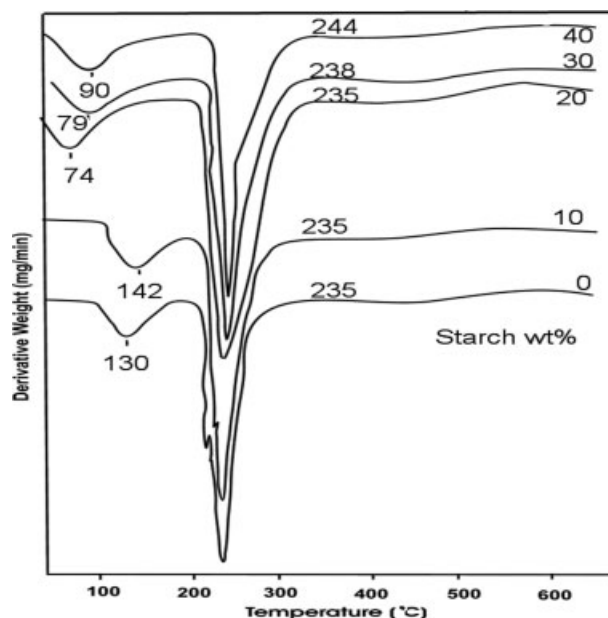


Figure 4 DTG thermograms of SA/starch blends.

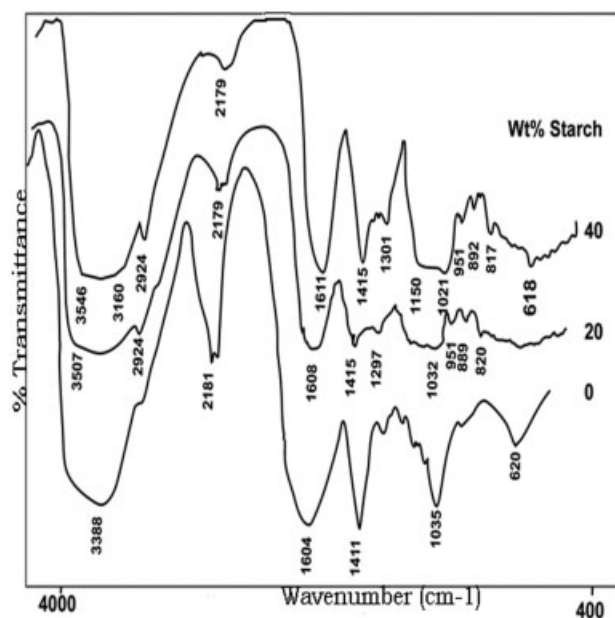


Figure 5 FTIR spectra of SA/starch blends.

istic absorption bands (Table III) in the IR spectra of the SA and SA/starch were noticed at 2924, 2181, 1604, 1411 and 1035 cm^{-1} . The molecular chain of SA contains $-\text{OH}$ and $-\text{COO}^-$ groups that can interact with $-\text{OH}$ groups of starch. The strong absorption owing to $\text{O}-\text{H}$ stretching vibration appears at 3388 cm^{-1} . It is typical of the polymeric association of hydroxyl groups. The peaks at 1604 cm^{-1} and 1411 cm^{-1} were assigned for the asymmetric $-\text{COO}^-$ stretching vibrations and symmetric $-\text{COO}^-$ stretching vibrations, respectively. The hydrogen bonding has strongest influence on the SA bands. In the spectra of SA/starch blends, with increase in starch content, the bands at 1604 cm^{-1} and 1411 cm^{-1} are shifted to a higher wave number. The shift to a higher wave number indicates reduction in bond strength and stretching frequency. It can be seen from the spectra that the absorption band centered at 3388 cm^{-1} concerned with $-\text{OH}$ stretching was broadened with intensification at

higher wave number region with increase in starch content. The broadening and increase in intensity at the lower frequency (higher wave number) region indicates weakening of $\text{O}-\text{H}$ bond strength. This kind of weakening accompanied by bond elongation is called red shift and represents the most common, easily detectable manifestation of the formation of H-bond.³⁵ All these changes suggest the intermolecular interaction through the formation of hydrogen bonds between $-\text{COO}^-$ groups in SA and $-\text{OH}$ groups in starch.

Scanning electron microscopic analysis

The SEM photomicrographs of pure SA, and its starch are shown in Figure 6(a-e). The SEM photomicrographs of pure SA shows a homogeneous and rough surface with cavities, and 90/10 (SA/starch) system also has almost similar surface. This supports the interaction between SA matrix and the starch. SA is in the form of continuous matrix and starch act as dispersed phase. The surface morphology is similar up to 30 wt % starch loading. However, at 40% starch, the blend show rougher surface with cavities and valleys revealing a phase separation. This phase separation at higher dosage of starch may be due to immiscible nature of blends above 40% starch content. Moreover, at higher loading, starch will agglomerate and are confined in between the SA chains.

CONCLUSIONS

SA/starch blend films can be easily obtained over the 10, 20, 30, and 40 wt % of starch composition range using water as a solvent. From DSC analysis it was noticed that the compatibility and physical interaction between SA and starch molecules in the form of single T_g up to 30% starch. TGA thermograms indicate a slight reduction in the onset of thermal degradation with increase in starch content. FTIR analysis revealed the existence of specific inter-

TABLE III
FTIR Spectral Band Assignments of SA/Starch Blends

Wave number range (cm^{-1}) of peaks for SA/starch blend composition (wt/wt %)			Band assignments
100/0	80/20	60/40	
3388	3507	3546	$\text{O}-\text{H}$ band stretching (intermolecular hydrogen bonded)
		3160	
2924	2924	2924	$\text{C}-\text{H}$ stretching
1604	1608	1611	$\text{O}-\text{C}=\text{O}$ asymmetric stretching
1411	1415	1415	$\text{O}-\text{C}=\text{O}$ symmetric stretching
-	1297	1301	$\text{O}-\text{H}$ bending of CH_2-OH
-	1150	1150	$\text{O}-\text{H}$ bending
1035	1032	1021	$\text{C}-\text{O}-\text{C}$ stretching
-	951	951	$\text{C}-\text{O}-\text{H}$ deformation

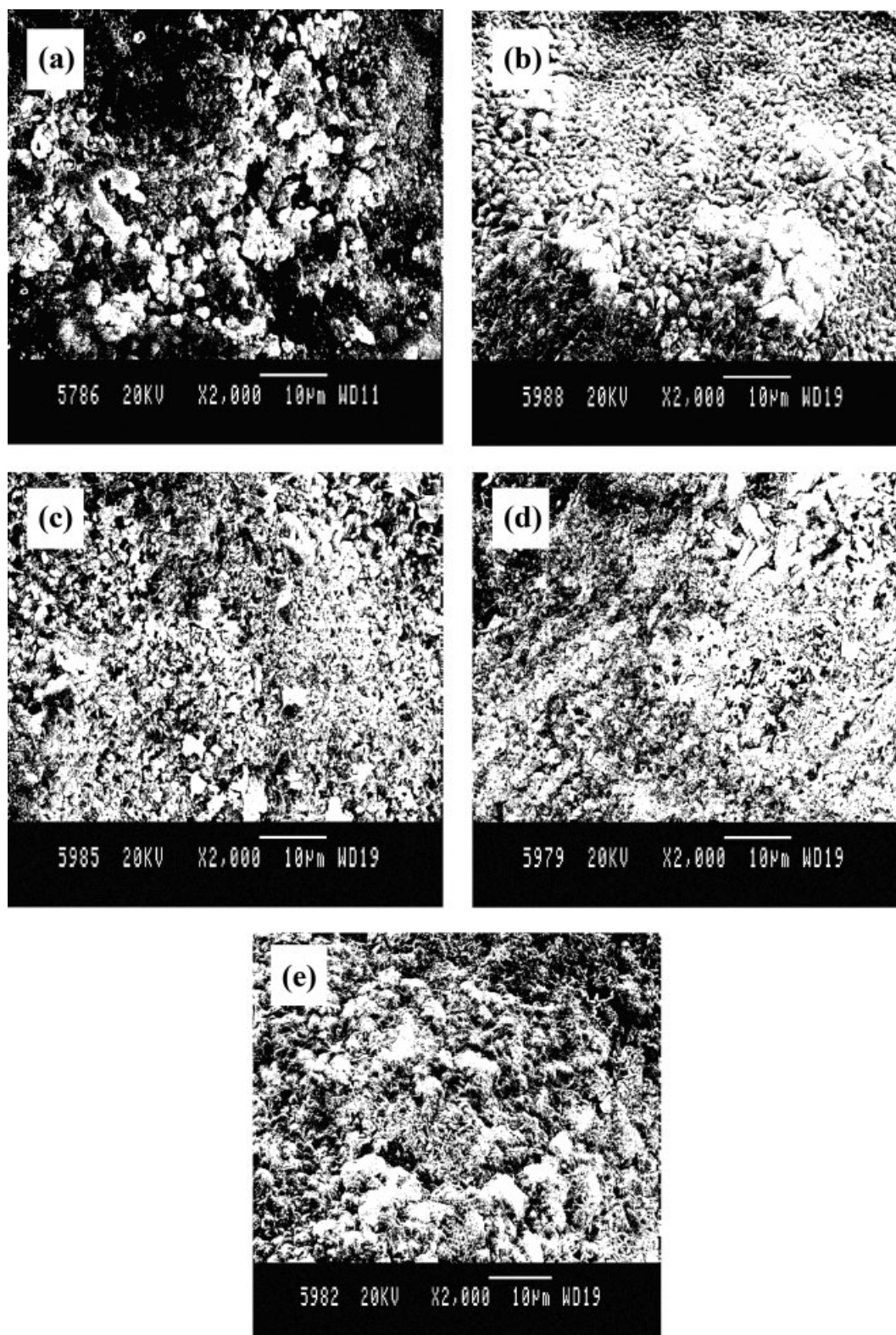


Figure 6 (a) SEM photograph of SA/starch (100/0); (b) SEM photograph of SA/starch (90/10); (c) SEM photograph of SA/starch (80/20); (d) SEM photograph of SA/starch (70/30); (e) SEM photograph of SA/starch (60/40).

molecular interactions between $-C=O$ groups of SA and $-OH$ groups of starch, from the shift and change in intensity of carbonyl and hydroxyl absorp-

tion bands. SEM studies revealed that the surface morphology of the blends was homogeneous and rough with cavities up to 30% starch content. How-

ever, at 40 wt % starch, the composite show rougher surface with cavities and valleys revealing a phase separation. This is well supported by the DSC analysis with multiple transitions.

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