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Sodium Alginate and Poly(ethylene glycol) Blends: Thermal and Morphological Behaviors

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Sodium alginate (SA) was blended with varying amounts of poly(ethylene glycol) (PEG) viz., 10, 20, 30, 40 and 50 wt % by using water as a solvent. The obtained SA/PEG blends have been characterized for thermal behavior by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) and surface morphology by scanning electron microscopic (SEM) methods. DSC analysis indicates the increase in glass transition temperature (T_g) of the blends with an increase in PEG content in the blend, which is due to chain entanglement. TGA results reveal the enhancement of thermal stability of SA/PEG blends in terms of the onset of degradation and percentage of weight loss. SEM photomicrographs shows the two phase morphology. This result indicates the immiscible nature of the SA/PEG blends.

Keywords: Sodium alginate, poly(ethylene glycol), blends, differential scanning calorimetry, thermogravimetric analysis, morphology

1 Introduction

Long life and attractive properties have made plastics as a material of choice for many applications. Due to tremendous growth in applications, plastics are one of the fastest growing segments of the waste stream because, a vast majority of plastic products are made from petroleum based synthetic polymers that do not degrade in a landfill site or in a compost-like environment. Polyolefins like polyethylene (PE) and polypropylene (PP) are especially very resistant to hydrolysis and are totally non-biodegradable. 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 eco-system and can replace the conventional non-degradable synthetic plastic products. In addition, it is desirable that these biodegradable polymers originated primarily from agriculture or other renewable resources for a sustainable environment.

Sodium alginate (SA), is an abundant linear polysaccharide obtained from marine brown algae, a biodegradable biopolymer and the simplest fundamental unit of sodium alginate is related to cellulose and the structural configuration is better represented by (1,4)- β -D-mannuronate and (1,3)- α -L-guluronate residues (1), 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. Sodium alginate, polyelectrolyte having rigid molecular chain and good film forming ability, has been extensively exploited and studied in detail on biomedical applications as drug carrier (2–4), because of its biodegradability and biocompatibility. Sodium alginate is hydrophilic and rigid polymer used as a membrane material for dehydration studies (5).

Polymeric blends containing starch have been developed for different applications and are the subject of several patents (6–8). The first important commercial application of starch plastics has been the blending of polyethylene with starch as filler. It was assumed that starch would accelerate the degradation of PE, but polyethylene is virtually non-biodegradable (9,10). 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

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respond to certain norms of biodegradability. Then, blending of starch with biodegradable synthetic polymers like poly (caprolactone) (PCL) (11–14), poly(hydroxybutyrate-co-hydroxyvalerate) (PHBV) (15–20), poly (hydroxybutyrate) (PHB), poly(lactic acid) (PLA) (21, 22) and poly (vinyl alcohol) (PVA) (23–28) have become the objective.

Recently, many researchers have studied the blends of SA for various applications (29–35), with the ongoing research efforts aimed at miscibility studies and other characterizations of water soluble polymer blends (35,36). In this article, the authors prepared a series of SA/PEG blends. The prepared blends have been characterized for thermal and morphological behaviors. The study of blends properties is of importance to explore further application of the resulting blend films for biomedical and pharmaceutical devices. Poly(ethylene glycol)s (PEGs) are water soluble and hydrophilic polymer, although, technically these products should be called polyethylene oxides, the term PEG is normally used to indicate the significant influence of the hydroxyl end groups on the chemical and physical properties of these molecules. PEGs with mean molecular weight above 3000 are solids and the melting range goes up to 60°C. The most important property of all PEGs is their solubility in water, which makes them ideally suitable for use in countless different applications in cosmetic and pharmaceutical industries. The change of structure and properties of SA/PEG blends were measured by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). We predict that this work may contribute basic information to the further application of this kind of blends.

2 Experimental

2.1 Materials

The raw materials used in this study, SA (M_w 4.96 KDA, Research grade) and PEG (M_v 6000), were supplied by M/s. Thomas Baker Chemicals Ltd., Mumbai, India and M/s. E. Merck (India) Ltd., Mumbai, India, respectively. These polymers were kept in a dry environment to prevent moisture absorption prior to use.

2.2 Preparation of SA/PEG Blends

A series of SA/PEG blends were prepared into films by a solution casting process by varying the PEG content from 10 to 50%. Aqueous solutions of individual polymers (1% w/V) were mixed to obtain desired composition and stirred for 30 min at $25 \pm 2^\circ\text{C}$. The pure and mixture solutions were cast on petri dishes by water evaporation. The films were dried under vacuum at $60 \pm 2^\circ\text{C}$. After drying, the films were removed from the petri dishes with varying formu-

lation and used for further study. SA rich SA/PEG films were prepared because PEG has poor film forming ability.

2.3 Measurements

These films were analyzed by differential scanning calorimetry (DSC 2010 module, TA instruments, New Castle, DE) to determine the thermal transition in the temperature range from ambient to 400 °C in nitrogen atmosphere at the heating rate of 10°C/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, Inc., TGA 2950 module (USA) thermal analyzer at a heating rate of 20°C/min in nitrogen atmosphere. The TGA profiles were recorded over a temperature range from ambient to 700°C. The weight of the samples used for each analysis was 6–8 mg. For morphological analysis, approximately 6 mm \times 6 mm section was cut from cast films and mounted on a specimen holder. A gold coating of approximately 200 Å thick was deposited on the surface of the specimen and then the micrographs of these material surface was recorded using Jeol JSM 5300 SEM, Japan.

3 Results and Discussion

3.1 Thermal Analysis

Sodium alginate and PEG blended specimens were prepared by a solution casting method containing 10, 20, 30, 40, and 50 wt % PEG. The thermal properties of these samples were investigated by DSC technique to analyze the effect of PEG content on T_g and T_m . Many techniques have been used to determine the miscibility of polymer blends. The most widely used criterion relies on the measurement of T_g and T_m by DSC.

3.2 Glass-transition Temperature

The T_g is used to describe chain segmental motion. Sodium alginate 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 of 80.6°C (Fig. 1). Since SA contains two hydroxyl segments and one carboxylate segment, which forms very strong inter- and intra-molecular hydrogen bonding and shows broad T_g as can be seen from Figure 1. The incorporation of 10, 20, 30, 40 and 50 wt % PEG content into SA matrix increase in T_g from 80.6°C to 84.4, 87, 89.6, 90.4 and 93.4°C (Table 1), respectively was noticed. The enhancement of T_g indicates the restricted segmental mobility. This may be due to the interaction between the carboxyl groups of SA and ethereal oxygen of PEG and/or due to the chain entanglement of PEG with SA.

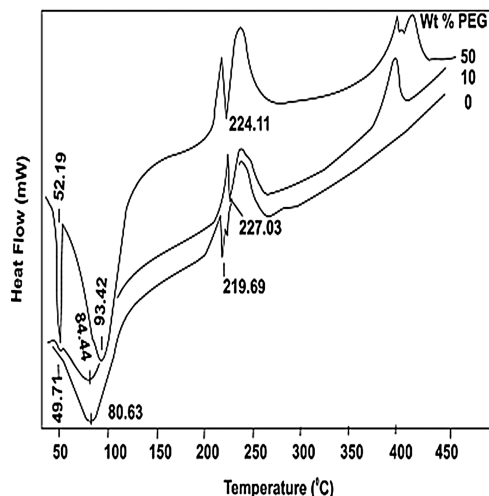


Fig. 1. DSC thermograms of SA/PEG blends.

3.3 Melting Temperature (T_m)

The geometrical structures (configuration of the chain) of the polymers are the most important factors which determines whether a polymer can crystallize or not. Sodium alginate molecules contains, at least three different types of polymer segments; poly(β -D-mannopyranosyluronate) segment, poly(α -L-gulopyranosyluronate) segment and segment 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; this is because of the irregularity in shape and size of the SA molecules. The intensity of the SA melting peak is not affected further with incorporation of 10, 20, 30, 40 and 50 wt % PEG into the SA polymer. However, a slight increase in temperature (227.0, 224.2, 225.3, 224.4 and 224.1°C) with increase in PEG content was noticed (Table 1). The melting peak corresponding to PEG appears at 49.7°C (SA/PEG, 90/10) and does not shift significantly (49.8, 50.5, 52.2 and 52.2°C). Overall, the DSC analysis indicates a significant shift in the T_g , but the melting peaks of both SA and PEG did not shifted significantly. This may ascribed to the physical entanglement of SA polymer chains

Table 1. Data obtained from DSC thermograms of SA/PEG blends

SA/PEG Blends Composition (wt./wt. %)	Transition temperature in °C		
	T_m of PEG	T_g of SA	T_m of SA
100/0	—	80.6	219.7
90/10	49.7	84.4	227.0
80/20	49.8	87.0	224.2
70/30	50.5	89.6	225.3
60/40	52.2	90.4	224.4
50/50	52.2	93.4	224.1

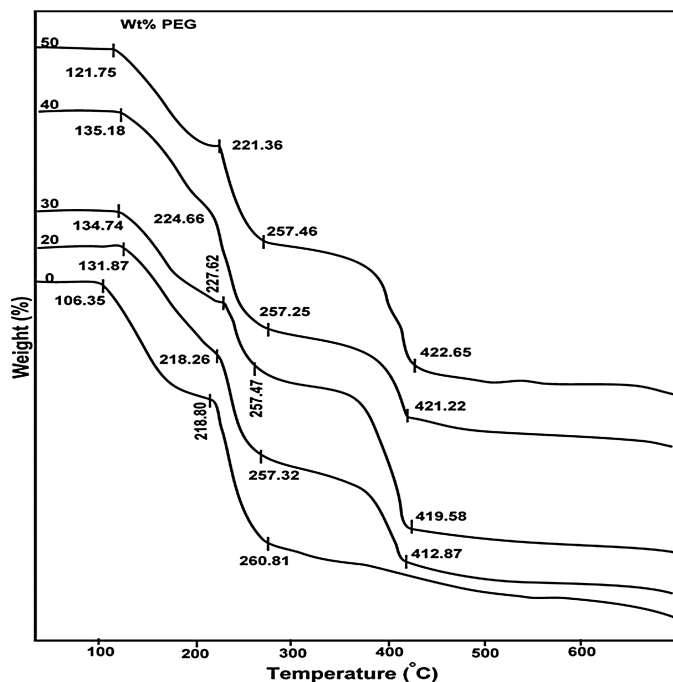


Fig. 2. TGA thermograms of SA/PEG blends.

which restricts the segmental motion of SA, but the chemical interaction between the SA and PEG polymer chains are comparatively weak, when compared to the inter and intra molecular interaction between the SA chains through $-\text{COO}^-$ and $-\text{OH}$ groups.

3.4 Thermogravimetric Analysis

The TGA thermograms of SA/PEG blends containing 20, 30, 40 and 50 wt % of PEG are shown in Figure 2. These thermograms shows that SA undergoes two step thermal degradation processes, the first step thermal degradation process occurred in the temperature range 106–190°C and the second step, in the range 219–261°C. The weight loss in first stage is attributed to the loss of volatile products like dehydration accompanied by the formation of volatile products and the second step is attributed to the depolymerization of polymer and formation of a carbonaceous residue and finally yields Na_2CO_3 as char. SA/PEG blends show a

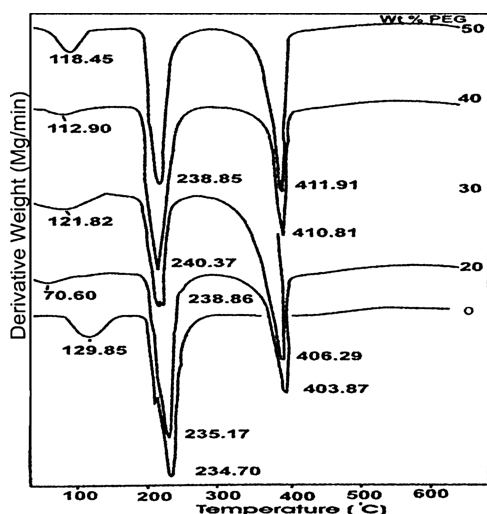
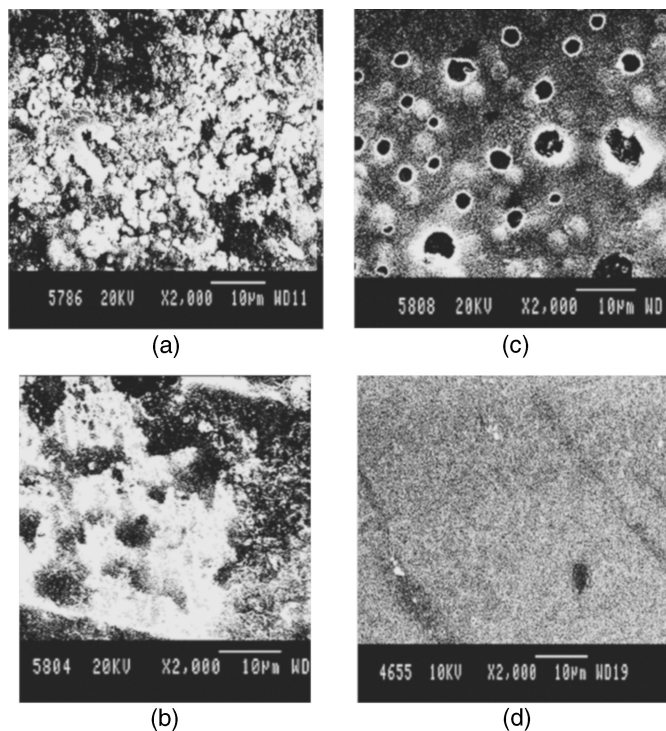
Table 2. Thermal transition data obtained from TGA thermograms of SA/PEG blends

SA/PEG Blends Composition (wt/wt %)	I-stage (°C)	II-stage (°C)	III-stage (°C)
100/0	106–190	219–261	—
80/20	132–219	219–257	257–413
70/30	135–228	228–258	258–420
60/40	136–225	225–258	258–421
50/50	122–222	222–258	258–423

Table 3. Data obtained from thermogravimetric analysis of SA/PEG blends

SA/PEG Blends Composition (wt/wt %)	Percentage of weight loss at ($^{\circ}\text{C}$)					
	150	200	250	300	350	400
100/0	2.1	19.0	65.0	75.4	78.9	81.7
80/20	6.2	20.7	48.3	61.0	64.1	75.9
70/30	4.3	20.3	36.4	46.9	50.4	70.6
60/40	2.1	19.6	51.8	63.2	66.4	75.0
50/50	5.2	23.6	44.4	54.2	56.9	68.8

three step thermal degradation process. This is because of the complicated chemical structure and morphology of the SA/PEG blends. SA is a plant-based polysaccharide with at least three different types of polymer segments; with alternating sugar units. The shape of these segments is quite different and weak physically compared to the PEG, which is a synthetic, linear, crystalline and relatively hydrophobic polymer. The onset degradation temperature is increased from 106 to 136 $^{\circ}\text{C}$ with an increase in PEG content (Table 2). The increase in onset temperature may be due to the reduction in SA content. Because the major structural difference between SA and PEG, carboxylate group is in SA and methylene group in PEG. The carboxyl groups of SA undergo degradation easily and release CO_2 and the methylene group of PEG can undergo degradation at a relatively higher temperature. Similar results were obtained in terms of percentage of weight loss at different temperatures as shown in Table 3. From the table it was noticed that below 200 $^{\circ}\text{C}$, the percentage of weight loss variation is much less and above 200 $^{\circ}\text{C}$, the weight loss is significant. The third step degradation of SA/PEG is well reflected in the weight loss of derivative TG curves as shown in Figure 3. The quantum of weight loss of the first peak is less as compared to the weight loss in second and third steps.

**Fig. 3.** DTG thermograms of SA/PEG blends.**Fig. 4.** SEM photomicrographs of, (a) SA100, (b) 80/20 (SA/PEG), (c) 70/30 (SA/PEG), and (d) PEG 100.

The derivative TGA curve peak area under the third peak corresponds to the PEG degradation and the peak maxima increases linearly from 403.9 to 411.9 $^{\circ}\text{C}$ with increase in PEG content. This clearly shows the enhanced thermal stability of SA/PEG films.

3.5 Scanning Electron Microscopic

The SEM photomicrographs of pure SA, PEG and its blends are shown in Figures 4(a-d). The SEM photomicrographs of pure SA (Fig. 4(a)) shows a homogeneous and rough surface with cavities. The incorporation of PEG into the SA matrix introduces inhomogeneity and roughness (Fig. 4(b)). At 30 wt % PEG content, the SA/PEG blend shows two phase morphology; one corresponding to the SA as continuous phase and the other one corresponding to the PEG in the form of dispersed phase (Fig. 4(c)). The SEM photomicrographs of blends clearly show the phase separation and partial incompatibility between SA and PEG molecules.

4 Conclusions

Sodium alginate was blended with varying amounts of PEG viz., 10, 20, 30, 40 and 50 wt % by a solution casting process. Blends with SA phase rich were prepared due to the good film formability nature of SA. DSC analysis indicates the increase in T_g of SA blends with an increase in PEG

content due to chain entanglement. TGA results reveal the enhancement of thermal stability of SA composites in terms of the onset of degradation and percentage of weight loss. SEM photomicrographs of the SA/PEG blends show the incompatibility and phase separation by formation of separate domains after incorporation of PEG in to the SA polymer matrix.

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