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Alginate/Polyvinylalcohol Blends for Agricultural Applications: Structure-Properties Correlation, Mechanical Properties and Greenhouse Effect Evaluation

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Summary: Biodegradable blend films containing sodium alginate, polyvinyl alcohol and glycerol, for agricultural applications, were prepared by casting of aqueous solutions. Since the mechanical properties of alginate are not suitable for agricultural applications, the addition of polyvinyl alcohol and glycerol was necessary in order to improve some mechanical parameters like the strain at break. The interaction between different components was studied by thermogravimetric analysis and DSC, while mechanical parameters and the transmittance in the IR region were investigated in order to identify the compositions with suitable properties for application in agriculture.

Keywords: biodegradable polymers; blends; films; mechanical properties; polysaccharides

Introduction

In the last decade there has been a great increase in the demand of natural biodegradable polymers to minimize the problems related to the disposal of used plastics. The interest for this field of applied research not only comes from an extended ecological and environmental concern, but also from the need to reduce the dependence on petroleum. Unfortunately, in the majority of cases, the properties of natural polymers do not fit the needs for specific applications and the blending with synthetic polymers is a route largely used to gain the desired properties.[1,2] As a matter of fact, candidates for those applications are the natural polymers such as agar, starches, alginates, pectins or cellulose derivatives, along with synthetic biodegradable polymers, such as polycaprolactones (PCL), polylactide (PLA) or polyvinylalcohol (PVA). In a recent paper[3] the

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biodegradation behavior of films based on agar, hydroxyethylcellulose and polyvinylalcohol was studied.

One of the problems that in the last years has been approached with polymeric films is the solarization of soils. The solarization is a technique that uses the solar energy to kill insects, harmful bacteria and fungi, and weed seeds.[4] This technique consists in covering the soil with a plastic film, transparent to the visible and ultraviolet light and opaque to the infrared radiation. A film with these characteristics works in the same way as a greenhouse, trapping the sun's heat. The polymeric film lets the sun's rays (visible light) in, to warm the soil. During the night, when the soil tries to radiate the heat (infrared light) back out into space, the energy is trapped by the polymeric film. It takes four to six weeks of sunny weather to pasteurize the soil. Solarization is often as effective as herbicides, fumigants, and other hazardous and expensive pest control methods.

The aim of our study is to use sodium alginate as a base for the preparation of films for the solarization. Our choice is related to the fact that alginates are a renewable and biodegradable resource present in marine brown algae. Moreover, it is known that water resistance of alginates strongly increases upon their treatment with bivalent ions, such as Ca^{++}. Alginates [5] are a family of natural polysaccharides comprising linear chains of 1,4-linked α-D-mannuronic acid (M) and β-L guluronic acid (G) of widely varying composition (Fig. 1).

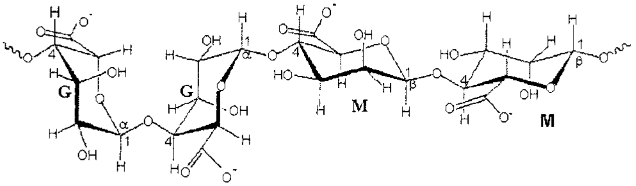

Figure 1. The alginate chain

The different composition depends on the organism and tissue from which it is isolated. It has also been proved that alginate is a true block copolymer containing M blocks and G blocks, although some sequences GGM and MMG are also present.[6]

Films of pure alginate do not have mechanical properties in a suitable range to be considered as films for the solarization. The addition of polyvinylalcohol and glycerol was necessary to reduce the fragility of films of pure alginate. In this study films with different compositions were prepared in order to understand the chemical interaction between the different components and to find compositions with the desired properties.

Experimental

Sodium alginate (A), high viscosity from macrocystis pyrifera was purchased from Sigma. Polyvinylalcohol (P) (M_w 70,000 – 100,000 g/mol) with degree of hydrolysis 96-98 % was purchased from Sigma. Glycerol (G) was a commercial product (Fluka).

All films were prepared by casting from aqueous solutions. One component films were prepared by dissolving, under stirring, 2 g of polymer in 200 ml of water. For the alginate the temperature was 70-75°C, while for polyvinylalcohol the temperature was 80-85°C. For the blends with two or three components, the alginate was first dissolved, under stirring, at 70-75°C. When the dissolution was completed, the temperature was risen by 10°C and the polyvinylalcohol was added. For films with three components, the glycerol was added when the dissolution of polymers was completed. All solutions were filtered and kept for few minutes under vacuum. After this treatment the solutions were poured, avoiding bubbles formation, into a polyester mold kept in plane to ensure the homogeneous thickness of the films. All films were allowed to form during exposure to the atmosphere for three days. The films thickness was in the range of 45 –50 μm. Prior to testing, the films were equilibrated at 48% relative humidity by storing them in a desiccator over a saturated solution of calcium nitrate at room temperature. The compositions and the codes of films are reported in Table 1.

Table 1. Compositions

MATERIAL	CODE	ALGINATE (%)	PVOH (%)	GLYCEROL (%)
Alginate	A	100	0	0
PVOH	P	0	100	0
Glycerol	G	0	0	100
Alginate + Glycerol	AG	50	0	50
PVOH + Glycerol	PG	0	50	50
Alginate + PVOH	AP	50	50	0
Alginate + PVOH + Glycerol	APG1	33	33	33
Alginate + PVOH + Glycerol	APG2	50	17	33
Alginate + PVOH + Glycerol	APG3	50	33	17

Thermogravimetric analyses were carried out by using a Mettler Thermogravimetric Analyzer (TGA) Model TG 50. The measurements were performed under nitrogen from 40 to 400°C at a heating rate of 10°C/min.

Differential Scanning Calorimetry (DSC) was carried out on the samples over a temperature range 0 – 400°C using a Mettler TA 3000 DSC purged with nitrogen and chilled with liquid nitrogen, with a heating rate of 10°C/min.

Young's moduli and stress-strain curves were performed at room temperature using an Instron tensile testing machine at a crosshead speed of 2 mm/min for the determination of moduli and 10 mm/min for the stress-strain curves.

Transmission FTIR spectra were obtained in the mid-infrared range (4000 – 400 cm^{-1}), using a Perkin-Elmer spectrometer, Mod. Paragon 500.

Results and Discussion

Interaction between the components

In Fig. 2 the mass loss of pure alginate (A), pure polyvinyl alcohol (P), and their blend at 50% (AP) is reported. In the figure two regions are visible.

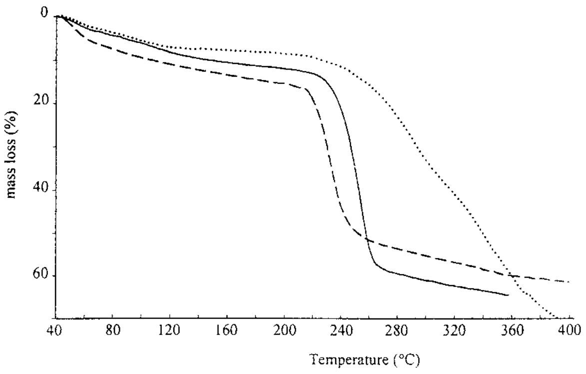

Figure 2. TGA curves of films A (- - - - -), P (⋯⋯), and AP (——)

The first, from 40 to 180°C, in which the loss is moderate, and the second, at temperatures greater than 200°C, in which the loss is considerable. The first loss can be ascribed to the elimination of water, while in the second region decomposition processes take place. From the profiles of the first region we notice that sample A contains more water than the other samples. This is predictable since the alginates are largely used industrially for their ability to retain water. In the second region, the decomposition of samples A and P are well separated. Sample A decomposes in a temperature range well below the temperatures at which sample P decomposes. Sample AP decomposes in one step, in a temperature range intermediate between the decomposition temperature of A and P. This means that between polymeric chains of A and B there are interactions. Without interactions, the decomposition would occur in two steps: the first in which the alginate decomposes, and the second in which the polyvinylalcohol decomposes. This hypothesis is also confirmed by the DSC. In Fig. 3 the heating runs of samples A, P, and AP are reported.

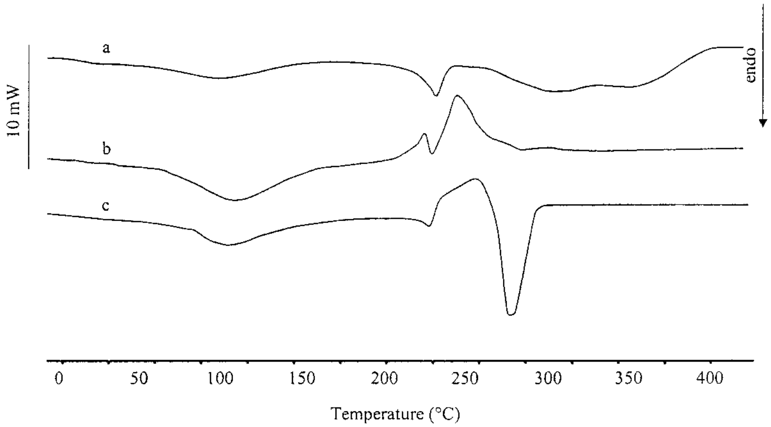

Figure 3. DSC curves of films P (a), A (b), and AP (c)

All three samples show an endothermic signal in the range 80 – 150°C related to the elimination of water. The wide range in which the release of water occurs can be related to different interactions between molecules of water and the interactive groups in the polymeric chains. In fact, in a well established model the existence of three spectroscopically distinguishable species denoted S_0, S_1, and S_2, where the subscripts indicate the number of hydrogen atoms of the molecules of water involved in hydrogen bonding, is assumed[7]. Sample P shows an endothermic peak at 226°C, related to the melting of crystals of polyvinylalcohol, and a double endotherm at 291 and 335°C related to the decomposition of P. Alginate does not present any endothermic peak ascribable to the melting of crystals. It presents two exothermic peaks connected with the decomposition. From the DSC data we understand that the decomposition mechanisms of A and P are completely different. The blend at 50% presents a reduced endotherm at 223°C due to the melting of crystals of P followed by an exotherm at 248°C and an endotherm at 265°C ascribable to the decomposition of the blend. The data of DSC confirm the hypothesis introduced before about the existence of interactions between A and P. This interaction has to be relevant since the decomposition of the blend can be considered completed at about 280°C, that is a temperature well below the temperature at which the degradation of pure polyvinyl alcohol is over.

Further work is in progress in order to better understand in more details the interaction between alginate and polyvinyl alcohol.

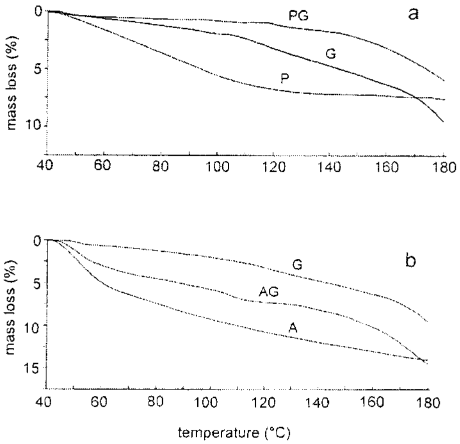

Figure 4. TGA curves of P, G, and PG (a), and A,G, and AG (b)

In Fig. 4a the thermogravimetric curves of polyvinyl alcohol, glycerol, and their blend at 50% are reported in the interval of temperature 40 – 180°C.

The curve related to the glycerol exhibits a slight mass loss in the first region, due to the elimination of absorbed water. At temperatures greater than 120°C the curve becomes steeper because of the evaporation of glycerol. Sample P eliminates water till about 120°C. The curve relative to sample PG is interesting. In fact, in all the interval of temperatures, the mass loss is always lower than the correspondent losses observed in samples P and G. This can be due to a strong interaction between the OH groups present in both polyvinylalcohol and glycerol. Due to this interaction, the active sites for water uptake in sample P strongly decrease.

In Fig. 4b the thermogravimetric curves of alginate, glycerol, and their blend at 50% are reported. The curve of the blend perfectly interpolates between the curves of alginate and glycerol. This means that alginate and glycerol in the blend absorb water in the same amount as in the pure state, and therefore their interaction is less pronounced with respect to the interaction between P and G. The reduced interaction between A and G can also be due to the steric complexity of the alginate chain that reduces the formation of secondary bonds between chains of alginate and glycerol.

Mechanical and optical properties

In Fig. 5 the stress-strain curves of pure samples, binary and ternary blends are reported, and the mechanical parameters are summarized in Table 2.

From the figure and the data in the table we notice that films of pure alginate are too fragile to be considered for several applications. Alginate has to be blended with other components in order to have mechanical parameters in a desirable range. The choice of polyvinyl alcohol is motivated by the good mechanical performances of its films along with its good susceptibility to biodegradation. The addition of polyvinyl alcohol to the alginate improves the mechanical parameters. The film containing A and P at 50% could be a good compromise for our purpose, but from the table we notice that, while the Young's modulus reduces by 40% with respect to the pure alginate, the strain at break is still too low. The addition of glycerol, that acts as plasticizer, lowers the Young's modulus and increases the strain at break. In fact for the film AG, containing alginate and glycerol in a ratio 1:1, the Young's modulus is reduced by 10 times with respect to

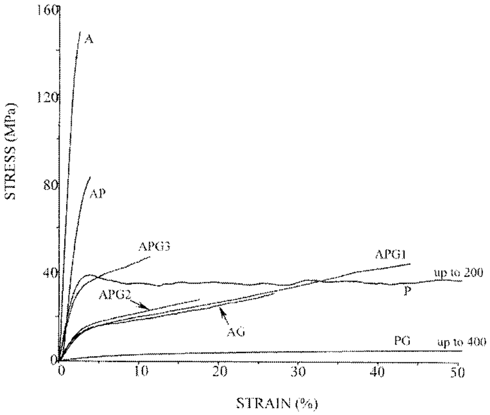

Figure 5. Stress-strain curves

the pure alginate. An even more pronounced reduction of the modulus is observed in the film PG, containing polyvinylalcohol and glycerol in a ratio 1:1. The modulus of the film PG is about 1/30

Table 2. Mechanical parameters

CODE	Young'sModulus (MPa)	Stress at Break (MPa)	Strain at Break (%)
A	5551 ± 307	147 ± 18	2.6 ± 3
P	1697 ± 46	47 ± 3	220 ± 30
AP	3275 ± 183	82 ± 2	4 ± 0.1
AG	500 ± 42	30 ± 2	27 ± 2
PG	58 ± 5	18 ± 2	380 ± 10
APG1	496 ± 38	43 ± 4	44 ± 0.5
APG2	581 ± 48	28 ± 4	18 ± 2
APG3	1615 ± 62	47 ± 3	11 ± 1

of that of pure P, and the strain at break is almost the double. The mechanical data of the ternary films fluctuate in a predictable way according to their composition.

Between them, APG1, containing A, P, and G in a ratio 1:1:1, has the lowest Young's modulus and the largest deformation at break that are reasonable for our purpose.

Optical analysis has been performed only on sample APG1. This film, as all the compositions, is completely transparent in the range of visible light. The transparency in the visible region is the first condition to create a mini greenhouse effect.

In Fig. 6 the infrared spectrum in transmittance of sample APG1 is reported.

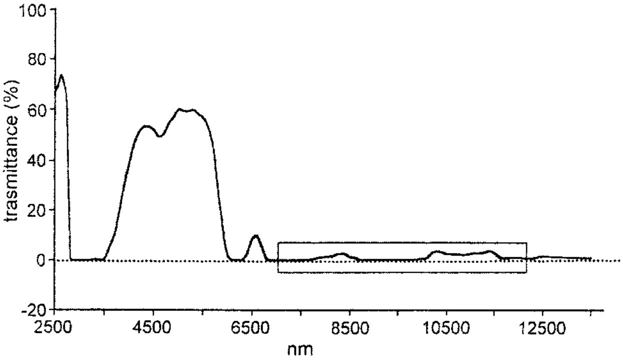

Figure 6. Infrared spectrum of APG1 film

We notice that, except the region in the range 3500 – 5800 nm, the infrared radiation is totally absorbed. In particular it is worth noting that hot objects, like the soil heated during the day, emit radiations in the range 7000 – 12000 nm where our film is completely opaque. The opacity in this region is the second condition to have the mini greenhouse effect. In a following paper the evaluation of the temperature at different depths of the soil will be investigated.

Conclusion

We have studied and reported the behavior of homopolymers and binary blends of sodium alginate and polyvinylalcohol with the aim of tailoring their mechanical properties with a view to their application as biodegradable thermal films for a sustainable agriculture. We found it necessary to add glycerol as a third component in order to reach a reasonable balance of deformability and rigidity. The thermal analysis data indicate a strong interaction between the blend components. The spectroscopic behavior of the films allows us to forecast their potential application for solarization in agriculture.

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