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REGULATED DEGRADABILITY OF COMPOSITE BIOBASED FILMS

Degradable biobased (derived from agriculture) composites are emerging materials that offer benefits to the environment thus minimizing waste that would be otherwise deposited in landfills. Single-use primary packaging materials have been identified as suitable items to be replaced by biodegradable materials from renewable resources. Materials composed of starch, soy protein and polyvinylalcohol, modified by hydrophobic fatty acids, are evaluated in terms of water resistance as promising substitutes for packaging materials.

Розглянуто відновлювані продукти сільського господарства, що можуть бути використані як вихідні матеріали для створення біодеградированого пакувального матеріалу, здатного замінити одноразові пластмасові вироби і скоротити кількість відходів на полігонах. Розроблено матеріали з крохмалю, білка, сої і полівенілового спирту. Вивчено їх деградацію у штучних умовах залежно від їх модифікації гідрофобними жирними кислотами.

Introduction

A wide range of materials are used for packaging applications including plastics. Most plastics, at present, are petroleum-based and do not degrade over many decades under normal environmental conditions. They are applied in primary packaging, i.e. in contact with the goods which are taken home by consumers. When discarded, food packaging can become the most obvious source of litter generated by the public. These materials later pose problems in recycling or reuse. Significant amount of packaging waste is generated, comprising about one-third of all municipal solid waste in developed countries. This has caused increasing environmental concerns since little success has been achieved in reducing plastic packaging wastes in landfill.

Analysis of researches and publications

Recently, there have been efforts to manufacture single-use articles from biodegradable materials. The objectives in the development of degradable packaging are two-fold: to utilize renewable sources of raw materials (crops instead of crude oil) and to facilitate waste management approaches (so as to reduce landfill).

Many researchers have provided overviews of various partially and completely biodegradable biobased products.

Biobased materials such as starch and soy protein are receiving attention as ingredients due to their low cost, easy availability and their advantage of being biodegraded into compost [1; 2; 3].

However, soy protein containing materials have been shown to suffer from high moisture sensitivity and low strength.

These properties have limited their use, they are also difficult to process into sheets without any plasticizer [3].

Starch has been used to produce biodegradable films and starch-based foams to partially or entirely replace plastic polymers and the expanded polystyrene packaging currently in use. However, wide application of starch film is limited by its water solubility and brittleness, also little information is available on composites and the effect of each major constituent on the physical and mechanical properties of materials [1; 2; 4].

In order to overcome these shortcomings we used polyvinylalcohol (PVA) as the basis for the films and hydrophobic fatty acids as plasticizers to increase the water resistance of the composite films and to increase their tensile strength.

Polyvinylalcohol is considered to be one of the very few vinyl polymers soluble in water and susceptible to biodegradation in aqueous media by specific microorganisms [5; 6; 7; 8; 9].

Polyvinylalcohol has been used in blending with other polymeric materials (starch, chitin, chitosan) for the better mechanical properties because of its flexibility and good film-forming capability [3; 4; 7].

The nature of PVA as a truly biodegradable synthetic polymer was repeatedly and intensively assessed. Since 1936, it has been observed that PVA is susceptible to ultimate biodegradation when submitted to the action of Fusarium lini and Pseudomonas vesicularis strain and Bacillus genus and ligninolytic enzymes generated by fungal species such as Phanerochaete chrysosporium [3; 4; 5; 6; 7; 8; 9].

Objectives

This paper discusses biodegradable materials made of PVA and biobased products.
Comparison is made with the common packaging paper.
The objective of this study was to make composite films from PVA, soy protein, starch, fatty acids (as hydrophobic additives), and hydroxyapatite (calcium phosphate) as inorganic filler and to evaluate their physical properties, namely, water resistance (water absorbtion at room temperature and artificially enhanced degradability at elevated temperatures). Fatty acids have been tentatively added as hydrophobic plasticizers to overcome material brittleness, obtain freestanding films and increase water, resistance.

Materials

Soy protein isolate was obtained from MDM Group, USA. Analytical grades of fatty acids were acquired from Fluka, Germany: stearic acid (Fluka, 85679); sodium lauryl sulfate (Fluka, 71725); lauric acid (Fluka, 61609). PVA with the degree of polymerization of 1700 and the saponification value greater than 98% was purchased from Merc, Germany.
Hydroxyapatite (calcium phosphate) was synthesized according to [10].

Preparation methods

20 different samples were evaluated in forming biobased films.
They contained different content of ingredients as options for forming materials of biobased products.
For all preparations PVA was heated in distilled water, until dissolved. Starch, soy protein and fatty acids were added to the PVA solution.
The resultant mixtures were again heated and blended thoroughly.
Finally the blends were cast into teflon-coated pans (ca.50 ml per ca.200 cm^2) and allowed to dry at room temperature.
A summary of the formulations prepared is provided in table.
Common brown postal packaging paper served as a control sample.
Dry films and packaging paper were cut in disks with diameters 4 mm for water absorption and enhanced degradation experiments.
Some samples (containing amounts of PVA lower than 10 %) were found to be too brittle to manipulate and were exluded from further experimentation and table.
The samples were then submitted to the water absorption (swelling) and enhanced biodegradation experiments in aqueous medium.

Measurments of swelling

Swelling experiments were used to investigate the time-dependent water absorption behaviour of the films prepared using the various preparation methods. Dry samples (disks) were weighed and then immersed in distilled water at ambient temperature.
Then disks were removed from water at predetermined times, blotted dry, and weighed.

Samples composition

Sample	Content	Sample	Content
0	Control (common packaging paper)	13	PVA 30 %, soy 5 %, starch 2,5 %
1	PVA 10 %	14	PVA 30 %, soy 5 %, starch 2,5 %, hydroxyapatite 2,5 %
2	PVA 20 %	15	PVA 30 %, soy 10 %, sodium lauryl sulfate 2,5 %
3	PVA 30 %	16	PVA 30 %, soy 10 %, stearic acid 2,5 %
4	PVA 40 %	17	PVA 30 %, soy 10 %, lauric acid 2,5 %
9	PVA 40 %, soy 10 %	18	PVA 30 %, soy 5 %, lauric acid 5 %
10	PVA 40 %, 10 % starch	19	PVA 30 %, soy 10 %, lauric acid 5 %
11	PVA 40 %, soy 10 %, starch 10 %	20	PVA 30 %, soy 10 %, lauric acid 10 %
12	PVA 30 %, soy 2,5 %, starch 2,5 %		

Measurements of degradability

Dry samples were immersed in small vials (20 ml) containing water, closed and immediately autoclaved for 20 min at 131 ^{0}C, cooled and degradability was immediately evaluated according to the scale from zero to 5 (see inscription to fig. 1).

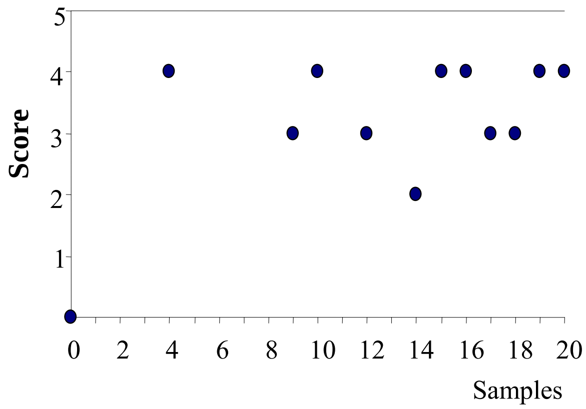

Fig. 1. Degradability of various formulations at 131ºC for 20 min

Statistical evaluation

Single factor analysis of variance (ANOVA) was used to assess statistical significance of results for water absorption.
Statistical analysis of the values between groups was performed using the students test with the confidence levels of 0,01 and 0,05.

Effect of conditioning time

The results of conditioning on swelling (water absorption) are shown in fig. 2.

It did not show a significant increase on further increasing the conditioning time from 1 to 2 hrs except for sample #13.

The moisture content increased for the first 2 hrs and then leveled in all samples as shown in fig. 2.

Effect of fatty acids on water absorption

Data showing the effect of fatty acids on the moisture absorption of various samples are presented in fig. 2 (curves 15–20). In all samples, containing various fatty acids, water content was increased for the 1 hour and leveled thereafter.
Samples containing fatty acids differed significantly from the samples devoid of fatty acids and control, $F = 1,4$, $p < 0,05$, and both groups combined differed from control $F = 1,38$, $p < 0,05$.
In 1, 2 and 3 hrs the same groups of samples differed significantly between each other and control, however failed to produce significant results in 4h, though still differed from control, $p < 0,01$.
Fig. 1 shows the effect of heat treatment in water for 20 min at 131^0C for samples in terms of their sustainability (see inscription to fig. 1). Samples containing 2,5−5% lauric acid tend to show lower degradability compared to the samples containing PVA and one additional constituent only.

The sample containing calcium phosphate showed the greatest resistance in terms of heat/water induced degradability.
Control swelled but remained intact.
Therefore, it appears that the different degradation behaviour of PVA biobased films in aqueous media could be influenced by the presense of lauric acid. The presence of lauric acid resulted in increased resilience to water absorption and degradation.
The lauric acid, being a mono-functional molecule with a long hydrophobic hydrocarbon chain, can undergo various events, resulting in the following outcomes: the hydrophobic chain of lauric acid just by its presence can reduce the moisture content of the biobased films, it can react at various functional sites such as amino and imine groups of the soy protein and act as an internal plasticizer; unreacted lauric acid can blend uniformly at the amorphous phase with the soy protein, starch molecules, resulting in external plasticization.

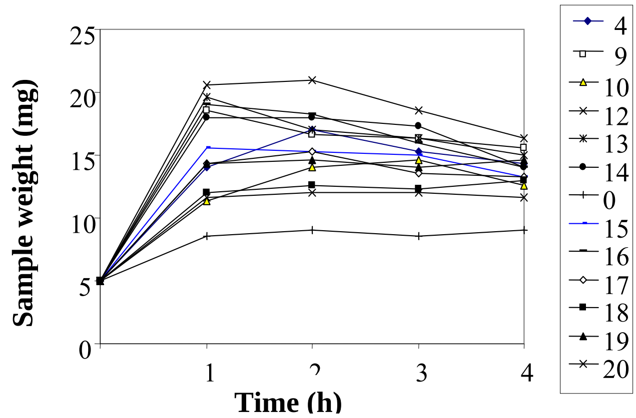

Fig. 2. Effect of conditioning time on water absorption by composite films

Estimation according to point scale: absence of any signs of destruction corresponds to 0 point, essentially unchanged sample, appearance of small flakes refers to 1 point, destroyed sample and large flakes correspond to 2 points, 3 points mean full destruction of the sample and the residues in the form of small flakes, and 4 points represent complete destruction (i.e. dissolution of the sample and clear solution).

Conclusion

Composite films were made from blends of PVA/soy protein/starch/fatty acids. The composite films had decreasing water absorption and increasing water resistance (lowered degradability at elevated temperatures in aqueous media) with increasing fatty acids to starch, soy protein and PVA ratios.

At 5 % lauric acid content, resistance increased significantly.

However, further increase in lauric acid content from 5 to 10 % led to an enhanced degradability.

The results herein reported clearly show the key role played by the content of fatty acid containing samples in hindered water absorption and degradability in aqueous media. Lauric acid and soy protein PVA blends form a compatible system to give films with improved moisture resistance properties.

However, further study is required to improve the formulations of the compounds formed during this modification.

Following are the broad conclusions drawn from this study:

1) the formulations used were found to be robust to produce freestanding films;

2) lauric acid can be used to reduce water absorption in biobased PVA containing films;

3) addition of 5% lauric acid significantly increased resistance to heat-induced degradation in aqueous media;

4) the formulations used may be considered as basis for further development of biodegradable packaging materials.

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