FILMS FROM PROTEINS - AS A PACKAGING MATERIAL

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Abstract

The thermal and mechanical properties of corn zein (CZ) films plasticized with (polyethylene glycol) PEG of two different molar masses were studied using differential scanning calorimeter (DSC), tensile strength measurements, moisture absorption isotherms and water vapor transmission rate (WVTR) measurements. The molar mass of the plasticizer PEG, was found to significantly affect the film properties at high relative humidities. Plasticizer contents up to 30% significantly improve the tensile strength of the protein films and PEG with higher molar mass is more effective than the low molar mass PEG. (*This research was carried out at the Department of Chemistry, University of Auckland, Auckland, New Zealand.)

Introduction

Increased interest has been drawn towards biodegradable plastics as a possible strategy to alleviate environmental pollution caused by plastic waste. Plastics are largely used in nominally disposable applications such as packaging. A considerable quantity of plastic is disposed of irresponsibly around the world. Plastics, however can be the origin of a serious pollution problem even after they have been responsibly disposed.

A large quantity of plastic waste is either dumped directly into the sea or eventually finds its way there. For example in 1982 an estimate was made of the amount of plastic rubbish dumped by the world's shipping and concluded that 639,000 plastic containers were thrown into the sea every year

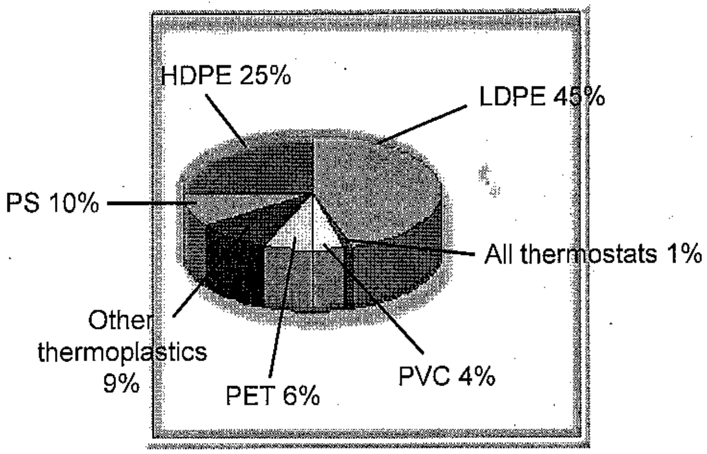
It is instructive to consider the sources of plastic waste. Table -1 shows waste generation classified by end use.

Table -1: *Plastic waste generation classified by end use.*

(from ' Encyclopedia of Polymer Science and Engineering' vol. 5, John Wiley 1986,p,105)

End use	**Approximate life** *years*	*% discards*
Packaging	1	100
Transport	5	20
Furniture and house ware	10	10
Electrical appliances	10	10
Building and construction	50	2

The data given above clearly demonstrates that packaging is the principal offender. These materials are used once and then thrown away as waste.



In Sri Lanka with incipient industrial and commercial activity, plastics have replaced many traditional materials. A major segment that has been taken over by plastics is the packaging market. In the packaging market low density polyethylene (LDPE) is used in the highest proportion.

This market segment, being the largest market, will continue to grow if traditional materials are replaced with plastics and if new packaging products are developed from plastics. Producers prefer plastics in packaging for the following reasons:

low cost

light weight

durability

can be adopted to their diverse packaging and product presentation.

However, this "wonder" product poses a greater threat to the environment in developing countries like Sri Lanka than in developed countries due to the following reasons:

1. Absence of proper methods of collection and waste disposal.
2. Absence of properly organized recycling industries
3. Lack of public awareness of the dangers of plastic pollution; and public attitude

The two common methods available to deal with municipal waste are land filling and incineration. The land filling is carried out because of limited space. Space is dwindling while the amount of waste is growing. Estimates have shown that the amount of waste will increase by 50% by the year 2000.

Incineration is a good method of waste disposal but environmentalists have opposed to it due to the formation of toxic gases such as dioxin and toxic ashes in addition to carbon dioxide.

Unfortunately in Sri Lanka very little attention has been paid to waste disposal. There is no proper and scientific method either to collect waste or to dispose of it. Furthermore the existing methods are limited to urban areas. Garbage piles proliferating with polythene bags on road sides is a common sight. Nearly all merchandise is displayed in polythene bags in the supermarket, and grocery bags are very popular among the general public. These polythene wrappers and grocery bags inevitably find their way to the garbage piles in a very short time. Because of their light weight these materials are blown hither and thither by the wind. Rain water carries them down the drains and in many instances clos the storm water drains causing roads to go under water on rainy days. In addition, sea beaches and aesthetically valuable places are polluted with polythene.

In order to battle the pollution caused by plastic waste, epecially packaging waste - the highest contributor to the waste stream, much attention has been drawn world wide towards biodegradable packaging materials. Natural materials such as proteins and lipids are capable of forming films which can be developed as packaging materials[2-4]. Edible films can be used to meet many challenges involved with the marketing of food. These films can be used as barriers to gases and water vapour.

The function of a packaging material is two-fold. Firstly, it restricts the loss of moisture to the environment and lessens absorption of oxygen that promotes decomposition. Secondly, it stabilizes the water activity gradients and preserves textural properties of foods.

Studies of protein based films from wheat, corn and soy protein have been reported by Gennadios and Weller[5,6]. Due to the presence of a high proportion of hydrophobic amino acids[7], zein shows high resistance to water compared to other proteins such as casein and gelatin[8, 9]. Films formed by proteins are brittle in nature due to strong intermolecular and intramolecular forces present in protein molecules.

Plasticizers reduce these intermolecular forces and increase the mobility of protein chains, resulting in flexibility and extensibility[4,10,11] with reduced cracking and chipping of the film during handling. The plasticizer must be compatible with the polymer and is added at concentrations ranging from 10 to 60% of dry weight depending on the rigidity of the polymer matrix[2].

Since most plasticizers are polar in nature, they generally increase gas, water vapor and solute permeability[11, 12] of films and may decrease elasticity and cohesion[13].

The most commonly used plasticizers for zein are glycerol, polyethylene glycols (PEG) and higher fatty acids and their derivatives. Some plasticizers cause internal plasticization and the plasticizing effect depends on the ability for hydrogen bond formation[14]. In addition to the effect of plasticizer, physical and barrier properties are influenced by the water concentration in the films[15, 16].

Glycerol and PEG have been intensively studied recently as plasticizers for zein[17, 18]. These molecules are able to penetrate into the protein network, forming hydrogen bonds with the protein chains and thus increasing the separation between them. This effect facilitates the movement of protein chains in response to stress.

The effect of addition of PEG 400 (with molar mass 400 $gmol^{-1}$) up to 25-30 weight % are to increase both tensile strength and elongation at break: at higher PEG levels the tensile strength decreases[17]. In addition the permeability of the film to oxygen starts to increase[17] rapidly at about 25% PEG.

In developing a successful packaging material from proteins, the knowledge of the interaction between the plasticizer and the protein molecules is essential. As a step in this process the author has carried out the following research with an objective to study the effect of molar mass of the plasticizer, particularly PEG on the physical properties of corn zein films.

Experiment

Film forming solutions were prepared by dissolving CZ in 95% ethanol at 75 ± 5^0 C. After adding the plasticizer the solution was homogenized for about 30 minutes. Films were cast on a plate of polymethyl methacrylate using a thin layer chromatography applicator. Films dried at ambient temperature were stored in a desicator until tested.

The films so obtained were tested for their thermal, film barrier and physical properties. All the tests were carried out according to ASTM standards.

Thermal properties were studied using differential scanning calorimeter (DSC) at different temperature ranges. In determining physical properties the conditions, under which films were made , were kept constant in order to minimize errors. For tensile measurements rectangular test pieces (25.4 x 100mm) were cut and the variation of thickness was maintained within 10% through out the samples. All tensile samples were conditioned at respective relative humidities for 24 hrs. prior to testing.

Prior to beginning moisture absorption measurements, samples were brought to zero moisture content by freeze drying at -550C for 24 hrs. Different relative humidity environments were obtained by using sorbostats[8].

Results and Discussion

The technique used for film making produced transparent, homogeneous films with a good control of thickness.

Films with both PEG 400 and PEG 1000 had comparable flexibility at 30% by weight of zein. At lower proportions films elasticized with PEG 1000 were brittle compared to films with PEG 400. The plasticizing effect of both PEG 400 and PEG 1000 increased with plasticizer concentration, but, at higher concentrations, films plasticized with PEG 400 became soft and sticky[17].

The thermal behaviour of CZ with PEG 400 and PEG 1000 show similar characteristics. The glass transition temperature, T_g is highly dependent on the amount of moisture in the films and decreases with the loss of moisture.

PEG plasticizers contain two types of hydrophilic groups: terminal hydroxide groups (-OH) and ether groups (-O-). Since OH groups are more polar than -O- groups more moisture is absorbed through -OH groups than -O- groups. Film plasticized with PEG 400 contain more terminal -OH group density than in the case of PEG 1000 as the plasticizer. The plasticization of amorphous or partially crystalline polymers such as gluten[19] and gelatine[20,21], by water is well established. Since zein is an amorphous polymer similar behaviour could be expected.

Films made with PEG 1000 showed higher tensile strength than with the same proportion of PEG 400 (fig:1). A higher tensile strength was observed in the spreading direction of films plasticized with PEG 1000 than in the direction perpendicular to it (Fig:1). Elongation to break showed a similar behaviour too (Fig:2). The tensile strength difference, for example in the two directions decreases significantly as the plasticizer content is increased beyond 30% by weight of zein (Fig:3). The apparent anisotropy can be attributed to partial orientation of the zein molecules during spreading of the casting solution, since spreading was unidirectional.

Moisture sorption by CZ films plasticized with PEG 400 and PEG 1000 showed an exponential increase with increasing water activity (Fig:4). At low RH values (<50%) the moisture sorption of films plasticized by both PEG 400 and PEG 1000 showed similar behaviour. At higher RH (50 and 75%) films with PEG 400 showed higher moisture absorption compared to films with PEG 1000.

In films with PEG, -O- groups and -OH groups can act as hydrophilic sites in addition to the hydrophilic sites present in the protein itself. Since PEG 400 provides more hydrophilic sites than PEG 1000, the moisture uptake of CZ films with PEG 400 is larger at higher RH.

Films with PEG 1000 showed a significantly low water vapor transmission rate (WVTR) compared to films with PEG 400 at 50% RH and 75% RH (Fig:5). PEG 400 provides more hydrophilic group density than PEG 1000 resulting higher rate of water vapor transmission.

Furthermore the absorbed water tends to swell the protein network and the WVTR is increased by the plasticization of the film by absorbed water.

Conclusion

Poly(ethylene glycol)s are effective plasticizers for corn zein. Higher molar mass PEG significantly increases the physical properties (tensile strength) and barrier properties of CZ films which are essential characteristics of packaging films. Moisture absorption of protein films is largely dependent on the hydrophilic group density of the protein network.

This study concerns only one aspect in the development of a packaging material. In developing proteins to be an effective packaging material, continuous research must be directed towards minimizing hydrophilic sites in the protein network.

It is also important to analyze the products obtained upon biodegradation. These products should be benign and environmental friendly. Young scientists are encouraged to divert their research capabilities towards developing biodegradable polymers specially as packaging materials in order to build up a plastic pollution free world.

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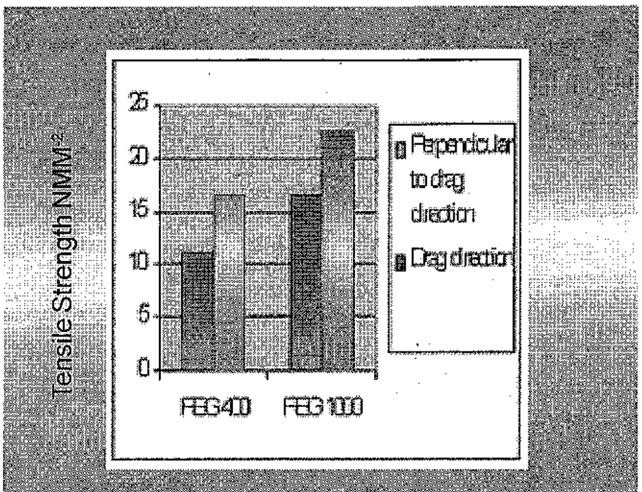

Fig.1. Variation of tensile strength with molecular weight of PEG

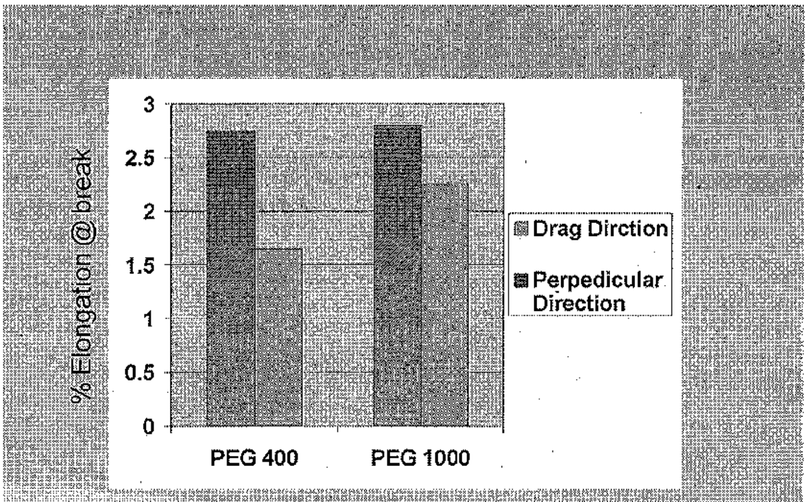

Fig.2. % Elongation @ break with PEG 400 and PEG 1000

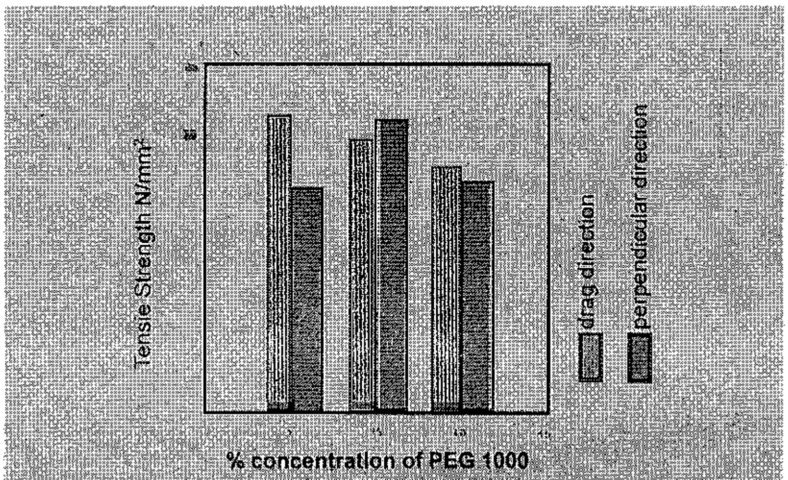

Fig.3. % Variation of Tensile Strength with % concentration of PEG 1000

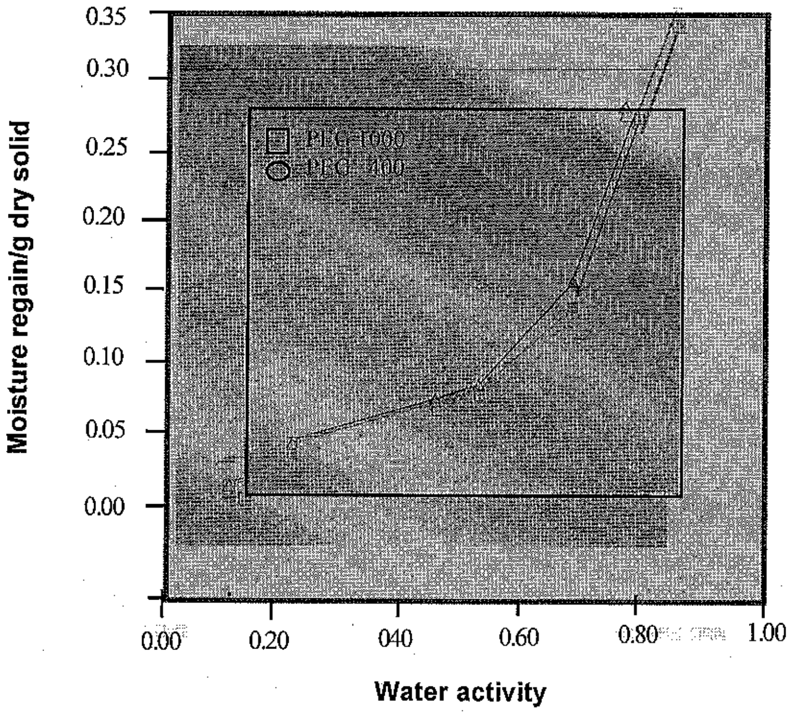

Fig:4. Moisture absorption isotherms for CZ

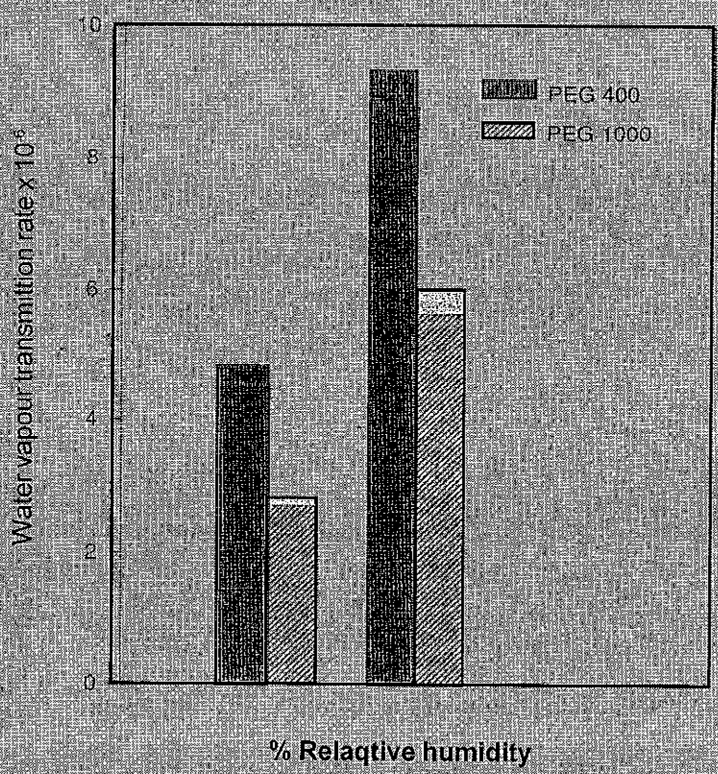

Fig:5. Variation of water vapour transmission rate with relative humidity for films with PEG 400 and PEG 1000