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Biopolymer coating of corrugated paperboard

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ABSTRACT

Soy protein, as well as gelatin and a blend of them were selected as protein raw material to prepare coating solutions for corrugated carton. Poly ethylene glycol was used as a plasticizer, and the soy protein was used without treatment. The effect of pH of soy protein using NaOH on mechanical properties of corrugated carton was studied. It was found that the soy protein coating solution increases the thickness of carton more than gelatin coating solution. Blending of gelatin with soy protein in a ratio of 1:1 reduces the defects of soy protein and improves the physical properties of the coated carton. Microstructure, water uptake, water permeability and dye uptake of the coated carton were also studied.

KEYWORDS

Soy protein;
Gelatin;
Coating;
Corrugated carton;
Packaging.

INTRODUCTION

Corrugated board has a sandwich material structure. It comprises a central paper (called the corrugating medium, or, simply, the 'medium') which has been formed, using heat, moisture and pressure, in a corrugated, i.e. fluted, shape on a corrugator and one or two flat papers (called liners) have been glued to the tips of the corrugations.

The basic function of corrugated fibreboard packaging is the same as for any packaging – namely to protect products during distribution until the product is removed from the package. It may also protect the environment from the product – for example in the distribution of dangerous goods and liquids in glass or plastic containers. However, because of their poor functional barrier properties and, particularly, high moisture sensitivity, they are often associated with other materials, such as plastic materials and aluminium for their good barrier properties that could be advantageously combined with the stiffness of paper and board[1]. In an effort to produce more environmentally friendly materials, renewable and biodegradable biopolymers have been investigated as paper coating materials[2,3] Since 1980s the amount of research on protein-based materials has increased as a result of the present interest for renewable and biodegradable materials for non-food applications. The complexity of proteins and the diversity of their different fractions can be used to develop materials with original functional properties that differ markedly from those of standard synthetic plastic materials. Most of them have a good film-forming capacity and, due to their good gas barrier properties, such materials are highly suitable for packaging purposes[4,5]. Among many plant and animal proteins that can be considered as raw materials for producing films, corn zein is used[6]. Zein-based films are water insoluble, relatively shiny and greaseproof. Although, zein is relatively expensive to extract and purify, but their high barrier properties against water vapor and oxygen, or their retention and controlled-release ability of active compounds are an advantage to improve food shelf life.

Treza and Vergano[3] reported zein-coated papers were as effective as PE laminated paper used for quick-service restaurant sandwich packaging.

Recent reports[7] pointed out the use of soy protein isolate (SPI) to develop edible and biodegradable films. SPI is abundant, inexpensive, biodegradable, and nutritional raw material. It is a mixture of proteins with different molecular properties. Among them, the 7 and 11 S fractions that make up about 37% and 31% of the total extractable protein have the capability of polymerization. Sulfhydryl groups of 11 S protein were reported to be responsible for the formation of disulfide linkages that results in the formation of a three dimensional network[8,9].

Unfortunately, SPI has a light beany flavor. Its film rather brittle, and has relatively poor mechanical properties. Previous experimental results showed that the properties of soy protein can be modified by physical, chemical, or enzymatic treatments. One approach to improve physical properties of biopolymer films is to prepare composite films[7] It was found that the properties of soy protein films can be improved by blending with starch, sodium alginate, whey protein isolation[10-12] and layered silicates such as montmorillonite.

One kind of animal protein is the gelatin be that can obtained by partial degradation of collagen has gained more attention as edible films for its abundance and biodegradability[13]. Gelatin is unique among hydrocolloids in forming thermo-reversible with a melting point close to the body temperature, which is particularly significant in edible and pharmaceutical applications[14]. However, as animal protein, gelatin is more expensive than plant protein, which to a certain extent inhibits its application as edible film[7]. Thus, the objectives of this work were to prepare composite films based on SP and gelatin, and to utilize effectively the functional merits of SP and gelatin in coating medium corrugated paper board.

MATERIALS AND METHODS

Materials

Corrugated paperboard (basis weight 100g/m^2) was obtained from a Company in October 6th City. Soy protein flour was obtained from Agriculture Research Center, while a commercial gelatin was used for the experimental.

Preparation of coating solutions

Soy protein coating solution was prepared by dissolving 10g of SP flour into 100ml of distilled water at 30°C with stirring. 0.1g polyethylene glycol (molecular weight 2000)\ g SP as a plasticizer was added. The mixture was stirred for 10 min. After that, the solution was strained through nylon cloth to remove small lumps. The pH of SP solution was adjusted to 7, 8 and 11 with NaOH. Gelatin coating solution (10%w\w) was prepared as follows: Gelatin was hydrated at room temperature for 30 min, then dissolving at 50°C in a water bath with mechanical stirring for about 20 min until complete dissolution followed by addition of 0.1 g polyethylene glycol\g gelatin. Very small amount of ethanol was sprayed to eliminate air bubbles. Composite coating solution of SP and gelatin was prepared by mixing equal amounts of the above two solutions (pH of SP solution = 8) and stirred for 5 min.

Paper coating

Paper sheets (20x20cm) were coated by dipping each sheet in coating solutions prepared for one minute and left to dry in air.

Conditioning

Since the physical properties of paper depend on its moisture content, it is necessary to condition the sheets at a definite and constant temperature and humidity if standard test data are required. This is done by exposing the paper to the standard conditions until its moisture content is in equilibrium with that of atmosphere, then testing the property in that atmosphere[15].

Thickness of paper sheets was measured using a hand-held micrometer. Five thickness reading were taken along the length of the strip, mean values were reported.

In accordance with the German Standard Method by means of a Frank 468 tester the tensile strength (TS) of the sheets was measured[16]. For each test, at least five experiments were carried out, and the arithmetic mean of the obtained results was calculated.

Water absorptivity, water permeability and dye uptake of board

Water absorptivity of paper samples was determined according to method of D 570-81 ASTM[15].

Paper sample of known weight was immersed in water for different times. Weight was determined after immersion according to the following equation:

$$\text{Water absorptivity \%} = \frac{W_w - W_i}{W_i} \times 100 \qquad (1)$$

Where w_w is the wet weight and w_i is the initial weight. Water permeability of board was measured according to ASTM D 895 method using Toyoseiki device.

The uptake of the dye by the board was measured by sampling the dye bath before and after dying. The used dye was C.I. Reactive yellow. The dye concentration was measured at the wave length of maximum absorption at λ max. on Shimadzu UV\ vis Spectrophotometer (Shimadzu, Japan). The dye bath exhaustion percent (E%) was calculated from equation 2:

$$E\% = \frac{C_1 - C_2}{C_1} \times 100 \qquad (2)$$

Where, C_1, C_2 are the concentration of dye in the dye bath before and after dyeing, respectively.

Scanning electron microscopy and infrared spectroscopy

Scanning electron microscopy (SEM) of surfaces and cross section of uncoated and coated paperboard test specimens were conducted on JEOL JEM-100 S electron microscope using the gold-sputtering technique. Fourier transform infrared spectroscopy (FT-IR) spectrum of uncoated and coated board by gelatin and soy protein were carried out using JASCO FT-IR type - 6100

RESULTS AND DISCUSSION

Effect of coating materials on surface of corrugated medium

Regarding the effect of soy protein concentration (pH 8), it is found that 5 g SP\100ml H_2O could not generate a homogeneous coating on paper due to the excess amount of water[17] which resulted in a wrinkled paper. Generally coat thickness is influenced by the solid content of coating solution[17], though it is not proportional to the solid content. Both SP and gelatin, as well as the blend of them resulted in a thicker coat due to the higher solid content and corrugation of medium decreased. TABLE 1 indicates that the thickness of coated paper is affected by the type of coating material[18]. Demonstrated through SEM image analysis that WPI coating produced a more homogeneous and smooth coating surface than its uncoated counterpart. In this case, the coating materials acted in a similar way to fillers, like clay. Fillers fill the void areas on the surface of the paper to provide a smooth surface. The smoothness provides for good printing resolution and reduces ink consumption.

Effect of pH of SP coating solution on mechanical properties of corrugated board

Figure 1 illustrates that TS and tear resistance of paperboard coated with SP coating solutions were affected by pH value of this solution. The maximum value

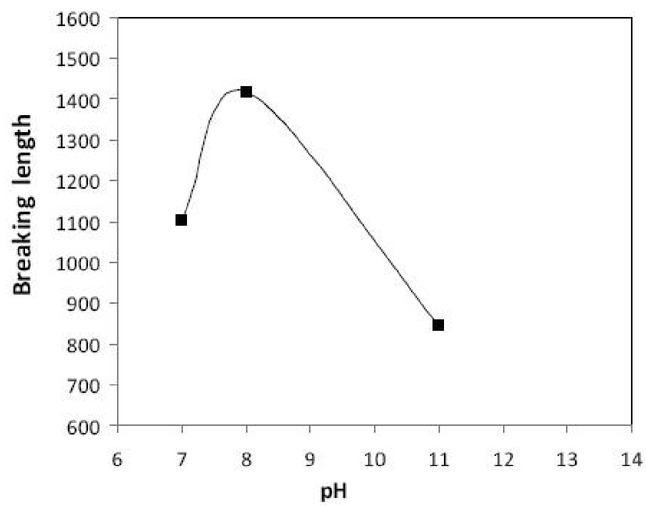

Figure 1 : Effect of pH of SP coating solution on mechanical properties of coated paperboard.

was achieved at pH 8 at which TS reached 1416 compared with 1103 at pH 7[10]. Reported that treatment with alkali and heating\dehydration could modify the physical properties of SPI films. Sensitivity of protein to pH change was usually associated with a high content of ionized polar amino acids[19]. At pH>7, denaturation and dispersion of protein was easily, thus more protein-protein and protein-cellulose interactions would occur. At pH 11 the tensile strength decreased which may be attributed to increasing the amount of sodium hydroxide added to adjust pH value. Sodium hydroxide absorb more water, water acts as a plasticizer besides PEG. TABLE 1 indicates that blends of soy protein (pH8) and gelatin enhance tensile strength of coated

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TABLE 1 : Effect of coating material on mechanical properties and thickness of coated paperboard.

Sample	Breaking length,m	Tear resistance,gm	Thickness increase, µm
Uncoated	1016.6	190	0
Coated by SP¹	968.5	184	56.78
Coated by SP²	1416.7	198	310.21
Coated by SP²+PEG	1300	196	273.33
Coated by gelatin	2676	194	176.67
Coated by gelatin+PEG	2571.12	194	91.67
Coated by SP²+ gelatin+PEG	2693.5	198	198.67

SP¹: 5g SP\100 ml H_2O
SP²: 10g SP\100 ml H_2O

carton.

Effect of plasticizer on mechanical properties of coated paperboard

Plasticizers are one of the basic additives of film forming polymers. They reduce intermolecular force and increase the mobility of biopolymer chains. Addition of a plasticizing agent is necessary in order to overcome the brittleness of film, to improve flow and flexibility, to increase toughness, strength and impact resistance of film coating and to prevent it from cracking during packing and transportation[20,21]. TABLE 1 indicates that adding of PEG 0.1g\g SP or 0.1g\g gelatin reduces TS of coated carton compared to that coated without PEG. Polar groups-OH along plasticizer chains are believed to develop polymer-plasticizer through hydrogen bonds that replace polymer-polymer interaction in the biopolymer films[22]. The hydrogen bonding ability of PEG was affected by factors such as the number of hydroxyl groups per mole, molecular size, solubility and polarity. It was found that hydrogen bonding interactions decreased as the molecular weight of PEG increased[23,24]. In addition, as the molecular weight of PEG increases, its polarity and solubility decreased, causing a decrease in its ability to interact with polymer chains. So, adding of PEG 2000 to SP or gelatin reduces the interaction between cellulose and biopolymer. Also, the plasticizer reduce pH of coating solution approximately by 0.3.

TABLE 2 : Water uptake of coated paperboard

Coated sample	Water uptake, % 2h	Water uptake, % 24h
Uncoated	196.03	204.6
Coated by SP pH7	120.3	139.2
Coated by SP pH8	43.26	77.86
Coated by SP pH11	77.93	91.22
Coated by gelatin	185.36	194.80
Coated by gelatin+SP	210.2	231.1

Swelling properties, water permeability and dye uptake of coated board

TABLE 2 illustrates the hydrophilic nature of cellulose fibers. Coating with SP enhances water absorption of corrugated paperboard. The best result was at pH 8. The water absorption was reduced from 204.6% for uncoated board to 77.86 %. This may be attributed to sulfhydryl and hydrophobic groups. Such groups associated upon drying to form disulfide and hydrophobic bonding forces. Gelatin coating had limited effect on water absorption. This might be ascribed to the fact that gelatin could swell more strongly in water than SP. The water permeability test indicates that uncoated paper board was cut at pressure 0 WG (water gauge), but that coated with SP did not cut at the same pressure and water flow. The board coated by SP and gelatin composite and raising the pressure up to 10 WG showed no water flow. This means that compositing of soy protein and gelatin with cellulose fibers improved water permeability of corrugated carton. The measurements of dye uptake gave 46.8% for uncoated board, 81.4% for board coated with soy protein (pH 8) and 83.7% for board coated by gelatin. This indicates that gelatin trapped more dye than cellulose or SP coated cellulose.

Microstructure of coated papers and infrared spectroscopy

Since our first objective was to deposit a thin but continuous layer of coating material on the surface of the paper which is a porous with rough surface material, SEM micrographs (Figure 2) was studied to show that effect. Surface images illustrated in figure 2 show that the coating layer is difficult to differentiate from paper, especially when the two materials interpenetrate each other. Cross section of uncoated (C) and coated paper by soy protein (D) and paper coated by gelatin (E) is illustrated in (Figure 3) It is clear that paper coated by gelatin is homogeneous and regular. The typical FT-IR spectrum of uncoated and coated board by gelatin and soy protein mixture (1;1) is shown in (Figure 4 a, b).

The band at 1057 cm^{-1} is due to the presence of methoxyl groups which the characteristic groups of lignin.(C-O deformation)

The band at 1428 cm^{-1} is attributed to aromatic C-H and CH_2 in methyl or methylene groups

The band at 1379 cm^{-1} is bending vibration of OH

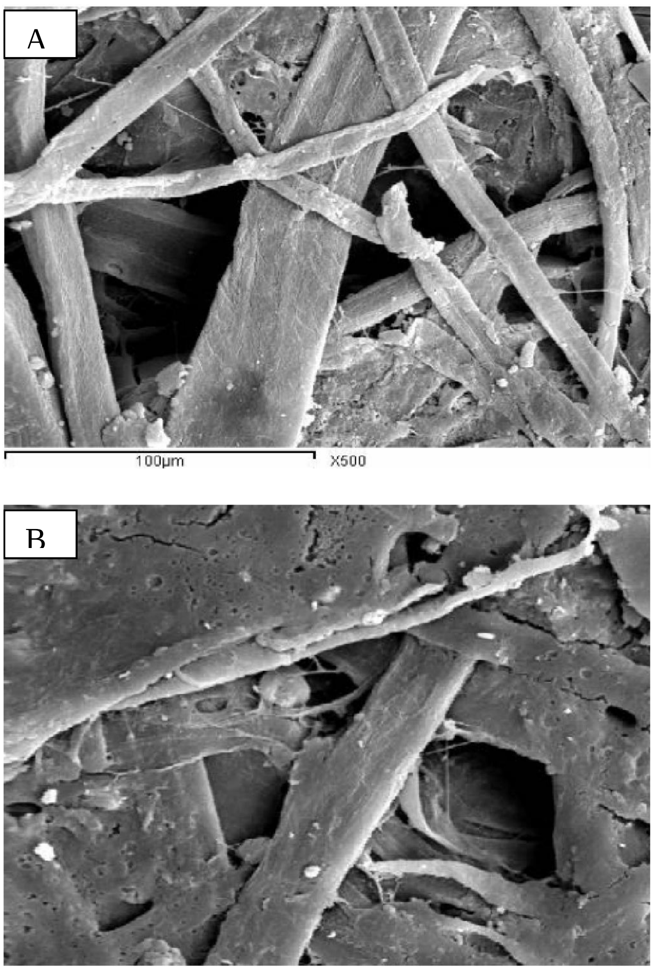

Figure 2 Surface Scanning Electron Micrographs (magnification x 500)
A- uncoated paperboard,
B- paperboard coated by 10% SP

bonds

The band at 1648 cm^{-1} is attributed to aromatic stretching

The bands at 2918 cm^{-1} confirmed C-H stretching

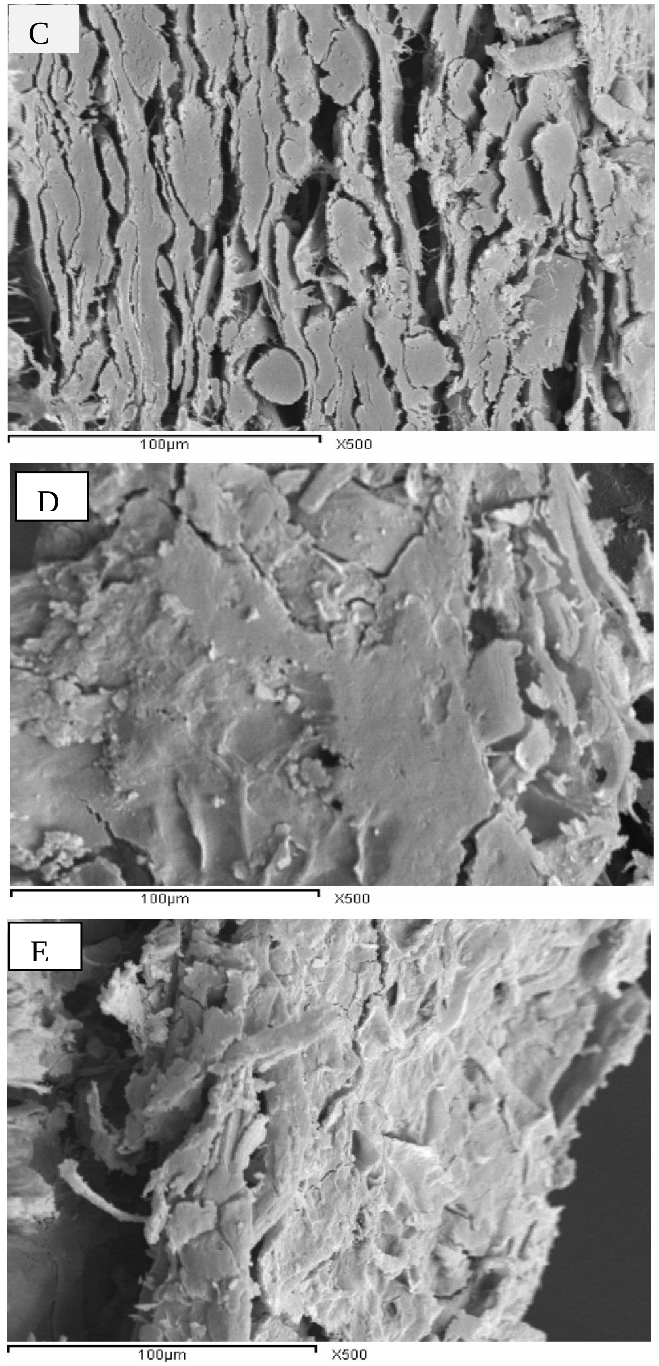

Figure 3: Optical micrographs of cross-sections of uncoated and protein-coated paperboard

vibration of $-CH_3$ groups

The broad band at 3405 cm^{-1} is due to bonded intermolecular polymeric O-H.

The coating process did not affect characteristics band spectra of carton. Small frequency shift was observed. The protein used in coating did not react with cellulose when added on the surface. The intensity of bands in case of carton coated by protein. was greater

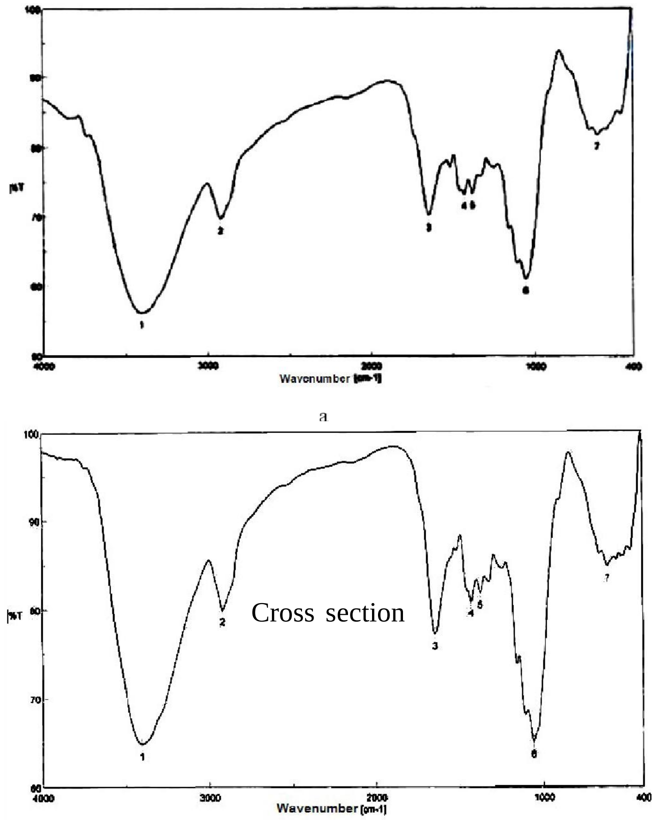

Figure 4: FT-IR spectrum of uncoated (a) and coated (b) paperboard

than the uncoated carton.

CONCLUSION

Corrugated paperboard is widely used in packaging. Most of this fiber board was made from recycled fibers. Soy protein, as well as gelatin could be used as an excellent coating material for corrugated carton. The hydrophopic nature of soy protein enhances water resistance of coated carton. Also, plasticizer and pH value of SP have a significant effect on mechanical properties of such carton. Blend of soy protein and gelatin (1:1) prevents water flow from coated carton. Such properties are often required in food packaging.

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