



Amylose Rich Starch as an Aqueous Based Pharmaceutical Coating Material - Review

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ABSTRACT

Until about 1950, sugar was the first choice as coating agent for pharmaceutical preparations. As the tablets coating technique was changed from sugar coating to film coating, a number of polymers like Methyl Cellulose (MC), Hydroxy Propyl Methyl Cellulose (HPMC) and Ethyl Cellulose (EC) become the main coating materials in place of sugar. As for as aqueous coating materials are concerned, Sodium Carboxy Methyl Cellulose (Sod. CMC), Polyvinyl Acetate (PA), Polyvinyl Pyrrolidone (PVP), Sodium Alginate, Poly Ethyl Glycol and HPMC etc. are used either alone or in combination. Starch, especially amylose rich starch is known to have good film forming property. Therefore amylose rich starch is now-a-days used as aqueous based coating materials for pharmaceutical coating. It is successfully used for coating in combination with sorbitol and glycerol as plasticizer. A nine months study on prepared films justifies the stability of amylose rich starch. Both the dispersion and solution of amylose rich starch are used for coating purpose. The amylose rich starch composition for this is 70% amylose and 30% amylopectin. Aging problems are overcome by proper type and proper concentration of plasticizer. The coating with amylose rich starch provides safety, economic and ecological benefits.

Keywords: Amylose, Amylopectin, Plasticizer, Sorbitol, Glycerol.

INTRODUCTION

Tablets/Pills, a pharmaceutical well known dosage forms are most widely used to deliver any therapeutically active substances to the human body. Starch, a biopolymer commonly obtained from natural sources having the properties of non-toxicity and bio-degradability. The most common relationship between starch and tablets is as a binder and filler, but now-a-days starch is used as a coating agent for pharmaceutical dosage forms. In the area of food for bio-based packing and edible coating, films that are made of starch are of great interest because of bio-degradable and safe nature of starch. ^[1-2]

The amylose rich starch is used as pharmaceutical coating materials and has good tablet film forming properties. ^[3] HPMC is also used for aqueous coating, but has poor water solubility and the film formed has poor film adhesion and poor mechanical strength. The main work on development of amylose rich starch as an aqueous based pharmaceutical

coating materials is done by Krogers *et al*, during 1999-2003.

HISTORY

One of the earliest coated dosage forms appears in early Islamic drug literature, where coated pills are mentioned by Rhazes. Tablets have to be coated for various reasons like for enteric coating, moisture protective coating, coating for controlled release, taste masking and also for cosmetics and flavors. Abbott laboratories marketed the first film coated pharmaceutical tablets. Dr. Dale Wurster, Professor at the University of Wisconsin, patented an air suspension coater that efficiently applied film coating compositions. ^[4] Mathematical modeling of the aqueous coating process has been accomplished by Reiland *et al*. ^[5]

The possibility of using amylose for the production of self supporting film was recognized by Wolff and co-workers fifty years ago. ^[5] Native starch based coating for pellets and tablets using a warm solution are studies by Palviainen *et al*. ^[6] Studies on the Rubbery starch film during storage, ^[7-8] reported that marked changes are seen in properties. In food applications starch have been made by coating from hot solution or by thermo mechanical processing techniques such as extrusion ^[9] or by compression moulding. ^[10] The considerable interest has been generated in the hydrophilic

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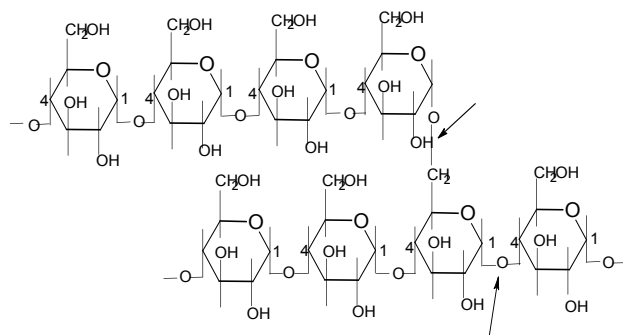
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biopolymer, by the fact that starch, especially amylose rich starch makes strong films with low oxygen permeability.^[11-12] Starch is not soluble in water at ambient temperature. A dispersion of water-insoluble starch, applied at ambient temperature would be desirable for application on pharmaceutical technology.^[13] The films are prepared by different techniques. The different techniques for preparation cast film and sprayed films may nevertheless lead to very different properties of films.^[14]

Starch and its constituents

Biopolymer starch is composed of glucose units and having two main constituents are, amylose and amylopectin. Amylose constituent is a linear one, having long chain of α -D glucose units linked together by α -1,4 glycoside linkages (Fig. 1) and only slightly branched.^[15] The amylopectin constitutes α -1,4 linkages of glucose units, interlinked by α -1,6 linkages and having a branched structure.^[16] The starch obtained from different sources has varying quantity of amylose and amylopectin usually 16-28% of amylose content in starch granules, whereas waxy starch solely contained amylopectin.^[17]

Starch obtained from maize, rice and wrinkled pea is known as high amylose starch and contain over 50% of amylose content.^[3] Starch occur in nature in three main crystalline allomorphs designated as A, B and V-type. B-type crystalline is rapidly formed by amylose rich starch films and slowly by the aging of amylopectin rich starch films.^[18] When starch granules are heated in the aqueous environment, granules starts swellings, i.e. *gelatinization*^[19] takes place at about 55-80° and it depends on the type of starch used.^[17] The phenomenon called *pasting*, eventually lead to total disruption of starch granules^[19] and it occurs at temperatures of about 100-160°.^[17] But on cooling starch begins to undergo *retro-gradation*, the starch molecules begin to re-associate in an ordered structure.^[19] The *retro-gradation* of starch can be studied by theological methods, X-ray diffraction, thermal analysis and spectroscopic methods.^[20] The properties of formed gel vary with the concentration of amylose and amylopectin in the starch. The gel formed by amylose rich starch exhibit higher mechanical and thermal resistance and degrades less both chemically and enzymatically as with amylopectin rich gel.^[21]



α -(1,4)-glycosidic bond

Fig. 1: Structure of starch molecule consisting two different types of linkage between glucose units

Formation of starch films

The film of amylose rich maize starch is having the problems of aging and non-user friendly hot coating solution.^[7] These limitations are taken as interest for further study. Stability of films plasticized with glycerol and sorbitol was studied and

also the optimization of the plasticizer content was done. The problems of hot solutions were solved by developing the film forming coating dispersion. Amylose rich starch having amylose content 70% and amylopectin content 30% was used for film preparation and also for coating purpose. The plasticizer sorbitol and glycerol were used and the solvent used was purified water.^[22]

Film formation by amylose rich starch solution

Amylose rich starch solution was prepared by using pressure reactor. Continuous stirring was done at 100 rpm at $160^\circ \pm 1^\circ$ at a pressure of 4 bars and then it was cooled to $95^\circ \pm 2^\circ$.³ The solution formed above has 5% amylose rich starch content and plasticizer added varied mixed with solutions and films were prepared immediately and appearance of the films were tested for 9 months.^[22]

Film formation by amylose rich starch dispersion

Amylose rich maize starch (2% w/w) and purified water were stirred (100 rpm) and heated to 160° in pressure reactor having pressure of 4 bars. The chamber was cooled to 95° and still hot solution was cooled in ice bath to temperature of 10, 40 and 80° then ethanol (1:1) was added with continuous blending. The dispersion formed are referred to as “dispersion 10”, “dispersion 40” and “dispersion 80”.^[13] From these dispersions ethanol and water mixture were removed by filtration the next day and then purified water, sorbitol and glycerol were added to the filtrate, after that it was used for coating and film formation for studies. This method was patented in 2001.

Properties of starch films

It has been reported that there were marked changes in the stress-strain behavior of film formed by thermoplastic barley and oat starches during 2 months of storage.^[8] The stability of starch films are studied by different properties.

Stress-strain and mechanical properties

Stress-strain properties of films are a sensitive measure of the aging of starch film.^[7] Amylose rich starch is less sensitive to aging phenomena than amylopectin rich starch.^[18] The changes in elongation are clearly related to the changes in starch structure and B-type crystallinity.^[7] The embrittlement on aging of starch films has been explained by loss of plasticizing water by evaporation, physical aging and glass transition temperature.^[25] So, the films formed by solution and dispersion, both are tested by X-ray diffraction (XRD) and also by material testing machines. Pure amylose and amylopectin films have different mechanical properties, amylopectin films having different mechanical properties, amylopectin films having a more brittle character than amylose films.^[26]

Amylose films have tensile equal to or stronger than the other coating polymers (Table 1), while amylopectin films have lower tensile strength. The amylose and amylopectin films have higher elongation values than other polymers. The pure films having no plasticizer show aging during storage but plasticizer combination of glycerol and sorbitol (at 100% level) is the best and the crystallinity dose not change during storage.^[22] The films formed by dispersion 10, 40 and 80 are tested and films formed by “dispersion 40” have minor changes during the nine months study.^[13]

Permeability properties

Starch films are known as poor water permeable. Plasticizer contents and surrounding air humidity directly affect oxygen permeability and increase with increase in plasticizer content

and high air humidity.^[30] Further some high crystallinity shows reduction in gas (N₂, O₂, and CO₂) and water vapour permeability.^[30-31] For unplasticized films an increase in amylose content leads to a decrease in CO₂ and water vapour permeability and increase in both tensile strength and elongation.^[32-33] For plasticized glycerol films, however the tensile strength increases with amylose content while the elongation decreases.^[33] The measurement of water vapour transmission rate (WVTR) is done by using glass bottles with calcium chloride (CaCl₂) sealed with metal rings.^[28] The measurement water vapour transmission rate values of the amylose rich films were $40 \pm 6 \times 10^{-11}$ g/ms Pa.^[22] The amylose rich starch films plasticized with sorbitol and glycerol (1:1) at 100% level were stable with respect to WVTR, the WVTR did not change the nine months of storage. The films formed by “dispersion 40” were transparent during storage.^[13]

Table 1: Comparison of material properties of films formed by some film forming polymers

Polymer	Elongation (%)	Stress at break (M Pa)	Plasticizer
Amylose ^[27]	31	20	40% glycerol
Amylopectin ^[27]	29	06	40% glycerol
HPMC ^[28]	4-14	-	3% propylene glycol
Eudragit® L ^[29]	1-3	14-25	tri-ethylene citrate
HPMC-AS ^[29]	1-3	5-16	tri-ethylene citrate

HPMC-AS: Hydroxy propyl methyl cellulose acetate succinate; Eudragit® L: Methacrylic acid polymer; HPMC: Hydroxy propyl methyl cellulose

Table 2: Appearance of amylose rich starch film stored for nine months at 25° and 60%RH.^[22]

Plasticizer(s)	Total plasticize contents*		
	50%	100%	120%
Glycerol	Hard and wavy	Glycerol droplet on film surface	-
Sorbitol	Sorbitol crystals on films	Sorbitol crystals on film surface	-
Glycerol : Sorbitol tacky (1:1)	Hard and wavy	Appearance as the initial film	Opal and film

* w/w on the basis of polymer content.

Crystallinity

From calorimetric and X-ray diffraction, Forssell *et al.* concluded that the major changes in the mechanical properties of starch films is due to re-orientation and/or re-crystallization of amylose and amylopectin molecules.^[8] Amylose films (plasticized with 0, 10 and 30% of glycerol) showed a B-type diffraction pattern and no changes in crystallinity were observed during two months storage at RH 0, 54 and 91% at room temperature.^[34] The increasing crystallinity was attributed to the rubbery state of the higher plasticized amylopectin films.^[35] Amylose is responsible for initial re-crystallization of at least the B-type lattice.^[36] The X-ray diffraction pattern of the films formed by dispersion 10, 40 and 80 resembled that of B-type starch. The changes during nine months were measure and studied by XRD, FT-IR (Fourier Transform Infra Red Spectroscopy) and NMR.^[13]

Glass transition Temperature (T_g)

At low enough temperature all amorphous polymers exit in glossy state where no large scale molecule motion can take place, in glossy state polymers as characterized by their hardness, stiffness and brittleness. At T_g polymers undergo

transition, where they change from glass to rubbery elastomer.^[37] Significance decrease in stiffness and increase in molecular mobility takes place at glass transition temperature.^[38] T_g is a characteristic of the polymer, which depends on particular polymer employed, plasticizer added and the amount of plasticizer.^[39-40] Increasing the plasticizer content in films leads to a lower T_g.

Starch film stability and factors affecting stability

Forssell *et al.* and Van Soest *et al.* studied changes in the mechanical properties of rubbery starch films during storage.^[7-8] When increase in tensile strength takes place, elongation decreases. During storage some changes accruing in starch films are: change in water content, T_g and crystallinity.^[7, 25] Changes in the mechanical properties are studied by calorimetric and X-ray diffraction technique by Forssell *et al.* conclude that the changes are due to crystallization of amylopectin and amylose molecules. From Atomic Force Microscope (AFM) friction measurement, Kuutti *et al.* conclude that plasticizer i.e., glycerol was migrating to the surface during aging.^[41] For amylopectin films having 30% glycerol stored at 91% RH, the crystallinity increase from 10 to 19% within one month. The increasing crystallinity during one month was attributed to rubbery state of highly plasticized amylopectin films.^[35] But the amylose films plasticized with 0, 10 and 30% of glycerol showed a B-type diffraction pattern and no change in crystallinity occurred during two months of storage.^[22]

Drying temperature

Drying temperature affects the crystal type for amylose rich starch, lower drying temperature leads to B-type pattern, where ad temperatures above 80° produce an A-type pattern.^[42] Drying temperature also affects the degree of crystallinity. Room temperature (20°C) leads to higher crystallinity than formed at an elevated temperature (68°C).^[43] In coating with amylose starch solution, increase in temperature from 40 to 70° results in decrease in surface roughness. Thus higher temperature up to 70° seems to produce better quality and a smoother coating. But at temperature below 30°C the tablets prove to over wet, which results in rougher film coating.^[13]

Air humidity

Increase in air humidity, increase the crystallinity of amylopectin film and starch films.^[43] But air humidity has no effect on the crystallinity of amylose films.^[27, 44]

Spray rate

As the atomizing air pressure increases it increase the surface area available for evaporation.^[45] Increase viscosity of the coating liquid also caused an increase in roughness.^[46] The increase in roughness is due to the fact that higher viscosity leads to higher contact angles.^[47] Adhesion of polymer to substrate increased with the roughness of substrate.^[48]

Plasticized films and amount of plasticizer

Plasticizers are added to polymers to increase the ductility of material. Glycerol, sorbitol, glucose, fructose, xylose, diacetate glycol, polyethylene glycol (PEG 200) and glycerol diacetate are materials used as plasticizes in starch films.^[24, 27, 31, 39-40] At low plasticizer content the plasticizer (glycerol, sorbitol) does not show the classical effects on starch film elongation.^[23-24] The elongation starts to increase by increasing the plasticizer content i.e. 15% for glycerol and 27% for sorbitol. But tensile strength of films decreases with

increase in plasticizer content.^[22] Starch requires a plasticizer content of roughly 20% to avoid the anti-plasticization effect.^[23] The plasticizer content suitable for coating for cast and sprayed films are different i.e. from 66-100%. Amylose rich starch films plasticized with glycerol and sorbitol with different concentrations are studied. The films plasticized with sorbitol and glycerol (1:1) as 100% of the polymer weight is the best and does not show change in appearance during nine months study (Table 2).^[14, 24]

In plasticized films with glycerol, however the tensile strength increases with amylose content but elongation decreases. Amylose content about 30-40% shows homogenous films, but higher amylopectin content increases the possibility of phase separation.^[49] High amylose content does not affect the mechanical properties but tensile strength and elongation reach a plateau.^[22] The amylose rich starch having 30% amylopectin and 70% amylose is the best.^[3]

The studies on starch as an aqueous film coating material shows that starch having a proper amylopectin and amylose ratio, plasticized with sorbitol and glycerol in proper amounts produced a film of good quality. The studies prove amylose rich starch as a powerful coating material, as it is economical, biodegradable and safe. The problem of handling hot solution was solved by using ambient temperature dispersion. Little work has been done on amylose rich starch; the need is to explore the utility of amylose rich starch as an aqueous based coating material.

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