

## Design and properties of polysaccharide based: Silica hybrid packaging material

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### Abstract

The purpose of this study was to determine the mechanical, barrier and antifungal properties of silica (extracted from rice husk) incorporated polysaccharide films. The mechanical properties, i.e. tensile strength, elongation at break and moisture content were affected by the addition of silica, which made the otherwise pure and fragile polysaccharide-based films more firm and manageable. The rate of water vapor transmission and water vapor permeability of the films decreased with the incorporation of silica in the biopolymers, which make the polysaccharide films suitable for being used in food industry as packaging material. The Fourier Transform- Infrared (FTIR) spectroscopy analysis of the films displayed interaction between the biopolymer components and silica. The morphology of the films was investigated by Scanning Electron Microscopy (SEM) that indicated silica incorporated films had an overall rough and irregular morphology as compared to pure biopolymer films. The presence of an inhibition zone around the silica incorporated film indicated the inherent antifungal activity of Bio-silica displaying its role as an antifungal agent in preventing fungal food spoilage.

**Keywords:** Polysaccharide films, Water vapor permeability, FTIR, SEM, Antifungal activity, Silica

### 1. Introduction

Today the biggest challenge in our lives is to deal with waste. We are running out of options for its treatment and proper disposal causing pollution and health hazards. The piling waste not only in the non-biodegradable form, but also the food is making the planet inhabitable as well as famished.

Currently, a variety of petroleum based plastic materials (Polypropylene, Polyethylene, Polystyrene, etc.) are dominating the packaging industries owing to their durability, versatility, lightweight and most importantly their cost-effectiveness. This trend is being overcome by the growing concern towards environmental pollution caused by the production as well as the disposal of these materials and the presence of toxic substances that could migrate from the packaging material to the product causing a potential risk to human health while using the product [1]. These concerns have led to the exploration of the vast reserve of renewable sources (plants, animals, microbes, etc.) capable of producing natural polymers which are not only eco-friendly but also cost effective.

Biopolymers are valuable product that is a promising green alternative to synthetic, non-degradable polymers. Renewable natural sources act as raw material for the non-toxic extraction of biodegradable polymers. Biological systems such as micro-organisms, plants and animals can be used to synthesize biopolymers, or they can be produced chemically from biological constituents like sugars, starch, natural fats or oils, proteins, etc. These natural polymers are much more suitable components for food as well as non-food packaging applications due to their qualities of renewability, degradability and edibility [2].

Natural raw materials which are most frequently used in the production of food packaging/ coating materials are carbohydrates, proteins and lipids. However, poor water vapor barrier properties of carbohydrates (polysaccharides) and proteins, and low elasticity of lipids are the main limitations for

their use as commercial packaging materials [3]. Polysaccharide films, because of their hydrophilicity, provide a good barrier to CO<sub>2</sub> and O<sub>2</sub>, retarding the respiration and ripening processes. Whereas their polarity, determines their poor water vapor barrier properties as well as sensitivity to moisture, which may affect their functional properties [4]. Various methods may help in overcoming these problems such as the addition of compounds, composite coatings, and many more.

The compounds being added to the packaging material to improve their properties can again be naturally occurring or artificially synthesized. Various valuable compounds can be extracted from food waste/ by products that enhance/ decrease the required properties. A compound that can absorb water, thereby enhancing the water vapor barrier properties of carbohydrate and protein-based packaging material is silica. Synthetic silica has a lot of uses, which is gradually being replaced by micro/ nano silica extracted from rice husk, in various industries as an anti-caking agent, dehumidifying agent, filler, desiccant etc.

Rice husk i.e., an agricultural byproduct, has an ash content varying from 18-20%, wherein the silica being the major constituent varying from 85-95%. India produces approximately 12 million tons of this unavoidable food waste annually. Two million tons of pure high grade silica can be produced using rice husk as the raw material to meet the high demand of various industries using it. With such a large proportion of silica in the rice husk ash, it is reasonable to use ash as the raw material for the extraction of silica, which has a wide market and also takes care of ash clearance [5]. The ash obtained from the combustion of rice husk, at moderate temperature, contains about 92-97% of amorphous silica and some metallic impurities. This high amount of silica content in rice hulls has a great economic advantage for developing nations that have large quantities of rice hulls readily available and virtually free of cost. This naturally occurring silica in rice

husk is Bio-Silica/ Biogenetic Silica, which is in hydrated amorphous form i.e. silica gel.

Silica has some interesting properties such as its adsorbing nature as well as its inhibitory effect on fungi growth. Surface hydroxyl groups of silica gel are responsible for the adsorption properties of silica gel. Usually silica gel contains silanol groups, which are free standing hydroxyl groups and some hydroxyl groups hydrogen bonded to neighbouring silanol groups [6]. Soluble silica provides resilience to cell walls in plants, which acts as a mechanical barrier against insects. Plants deposit silica at infection sites to inhibit fungus attacks. Apart from providing protection from insects and fungal attacks, silica accumulation in plants can alleviate water stress, salinity stress, nutrient deficiency or toxicity stresses as well as improve erectness of leaves and yield enhancement. Further along, silica is also considered as an environmental friendly element with respect to soils and fertilizers [7].

In this study, an attempt is made to incorporate Bio-Silica in Carbohydrate (Polysaccharide)-based packaging material (films) to enhance their water vapor barrier properties and impart antifungal properties, inherent in silica, which can be utilized by the food industry to preserve hygroscopic food substances. Along with this, it intends to resolve the disposal issue of husk, fruit peels and utilization of broken rice, to manufacture a valuable and cost effective product.

## 2. Materials and Methods

### 2.1 Materials

Rice husk was collected from a rice mill in Uttar Pradesh. Broken rice was procured from a local grocery store in Delhi. Oranges (*Citrus sinensis*) were collected from a local fruit market in Delhi. Guar gum powder was procured from Sisco Research Laboratories (SRL) Pvt. Ltd. All chemicals were of analytical grade and used without any purification. The chemicals used in the process were obtained from Sisco Research Laboratories (SRL) Pvt. Ltd and Himedia, Mumbai, India. Distilled water was used during the entire procedure.

### 2.2 Starch extraction from broken rice

Broken rice was finely ground into rice flour. The rice flour was dispersed in distilled water and the pH was adjusted to 10 with 1N NaOH. The dispersed rice flour was centrifuged for 30 minutes after incubation of 1 hour with continuous stirring. The residue was extracted with distilled water for 24 hours at 4°C and centrifuged for 30 minutes. The residue obtained was further extracted with 2% NaCl for 24 hours at 4°C and centrifuged for 30 minutes. The leftover residue was extracted with 0.1N NaOH twice for 48 hours at 4°C. Extracted residue was centrifuged for 30 minutes and the white starch layer was collected. The collected starch layer was re-suspended in 80% ethanol and stirred. The starch-ethanol solution was heated in a water-bath at 80°C for 1 hour. The solution was allowed to settle for 4 hours at 4°C. The residue was collected and freeze dehydrated to obtain starch powder [8].

### 2.3 Pectin extraction from citrus (orange) peels

The peels were separated from the fruits which were collected, washed and cut into small pieces. The cut peels were blanched in boiling water and filtered using muslin cloth. The insoluble part was treated with warm, absolute ethanol for 30 minutes and washed. The washed insoluble part was hand-pressed and

dried at 60°C till weight was constant. The dried insoluble material was powdered and stored. Distilled water was added to peel powder and citric acid was added to maintain pH=1.5. Pectin extraction was done in a water-bath at 80°C for 1 hour and filtered. The residue was cooled to room temperature. The residue was coagulated with equal volume (1:1) of 99.1% ethanol at 4°C for 3 hours. The precipitate formed was recovered by filtration and washed with 55% and 75% ethanol [9]. The pectin yield (in %) was calculated by:

$$\% \text{ yield} = \left\{ \frac{\text{Amount of pectin extracted (in g)}}{\text{Initial amount of peel}} \right\} \times 100.$$

## 2.4 Preparation of films

### 2.4.1 Preparation of starch (control) and silica incorporated starch films

Control films were prepared, in triplicates. Distilled water was added to 2 g of extracted starch powder. The solution was heated at 85°C for 45 minutes with occasional stirring. 3:1 mixture of sorbitol: glycerol at 40% (w/w starch) was added as plasticizer. The solution was again heated at 85°C for 45 minutes. The solution was cooled to room temperature before casting on a pre-dried glass tray. Subsequently, the films were dried for 24 hours at room temperature. After peeling the films from the glass tray, the resultant free-standing films were conditioned in a desiccator at room temperature. Conditioned films were used for mechanical, barrier and morphological analysis [10].

Silica incorporated starch films were prepared similarly as the control films with the addition of 0.1g silica to the film solution, after plasticizer addition and heating, and then cooled to room temperature before casting on a pre-dried glass tray.

### 2.4.2 Preparation of pectin (control) and silica incorporated pectin films

Pectin films were prepared, in triplicates, where in distilled water was added to 0.5 g of extracted pectin powder. The solution was heated at 85°C for 20-30 minutes while stirring. 3:1 mixture of sorbitol: glycerol was added as plasticizer. The solution was again heated at 85°C for 45 minutes and, thereafter, cooled before casting in 90 mm pre-dried petri plates. The films were dried for 24 hours at room temperature. After peeling the films from the petri plates, the films were conditioned at room temperature in a desiccator and were further used for mechanical, barrier and morphology analysis [11].

Silica incorporated pectin films were prepared in the same manner as the control films with an additional step of adding of 0.1g silica to the film solution, after plasticizer addition and heating, and then cooled to room temperature before casting in 90mm pre-dried petri plates.

### 2.4.3 Preparation of guar gum (control) and silica incorporated guar gum films

Films were prepared, in triplicates, with the addition of distilled water to 1 g of guar gum powder. Glycerol was added, as plasticizer, along with potassium sorbate, after heating at 85°C for 15 minutes. The solution was again heated at 85°C until the consistency was viscous, then, cooled before casting on a pre-dried plastic sheet and dried for 24 hours at room temperature. After peeling the films from the plastic sheet, the resulting films were conditioned in a desiccator at room

temperature and thereafter, used for mechanical, barrier and morphology analysis [12].

Silica incorporated guar gum films were prepared in the similar manner as the control films with the addition of 0.1g silica to the film solution, after plasticizer addition and heating, cooled to room temperature before casting on a pre-dried plastic sheet.

### 2.5 Film Thickness

A digital caliper micrometer was used to measure the film thickness [13].

### 2.6 Moisture content of the film

The moisture content of the films was measured by placing samples on pre-dried petri dishes, in triplicates, for drying in a forced draft oven at  $105 \pm 2^\circ\text{C}$  for 24 hours until a constant mass was observed [14].

### 2.7 Film solubility in water

The solubility of films in water was obtained using the dried samples (as obtained from 2.6) [15]. Dried samples were weighed into centrifuge tubes with 40 mL deionised water. The tubes were kept in a shaker incubator after sealing at  $30^\circ\text{C}$  for 24 hours. Pre-dried and weighed filter papers were used for the separation of films from water. The filter papers with the film residues were dried at  $105 \pm 2^\circ\text{C}$  for 24 hours and the final dry weight of the filter papers was measured. The test was executed in triplicates for each film and the solubility was calculated as equation (1):

$$\text{Solubility (\%)} = [(\text{Film initial dry weight} - \text{Film final dry weight}) / \text{Film initial dry weight}] \times 100 \quad (1)$$

### 2.8 Film Tensile Properties

Evaluation of tensile properties of the films was done using rectangular strips of film samples (60 x 10 mm) [16]. The ends of the strip were mounted between the tensile grips (40 mm apart) on a TA-XT2 Texture Analyzer (Stable Micro Systems). The tensile strength and elongation at break (ELB) were obtained using equations (2) and (3), respectively:

$$\text{Tensile Strength} = \text{Force} / \text{Area} \quad (2)$$

$$\text{EAB} = (\text{Change in length at breaking point } (\Delta l) / \text{Original length}) \times 100 \quad (3)$$

EAB is elongation at break, and ( $\Delta l$ ) is the difference between the original distance between the grips holding the specimen before and after the break of the sample.

### 2.9 Water Vapour Permeability (WVP)

Water vapor permeability was obtained by mounting the petri dishes, containing 5 mL deionized water, with circle of film samples (approx. 60 mm diameter and 28 cm<sup>2</sup> area) [17]. The edges of the films were sealed with parafilm and reinforced with tape. The entire apparatus was weighed, placed in an oven for 24 hours at  $30 \pm 3^\circ\text{C}$ . Thereafter, changes in their weight were observed. Each film preparation was assessed in triplicates. Water Vapour Transmission Rate (WVTR) and Water Vapour Permeability (WVP) were calculated using equations (4) and (5), respectively.

$$\text{WVTR (g/h m}^2\text{)} = (G/t) / A \quad (4)$$

$$\text{WVP (gmm/ (m}^2\text{ h) kPa)} = (\text{WVTR} \times X) / \Delta P \quad (5)$$

Where, G is the change in weight from the straight line (g), t is the time period during which G occurred (h), G/t signifies the slope of the straight line (g/h) and A is the petri dish mouth

area, (m<sup>2</sup>). X is the film thickness (in mm) and  $\Delta P$  is the water vapor pressure difference across the film.

### 2.10 Film Morphology

The morphology of film samples was analyzed by Scanning Electron Microscopy (SEM, RES Pvt. Ltd.). The samples were placed onto a specimen stub with the help of an adhesive (carbon) coating under high vacuum.

### 2.11 Fourier Transform Infrared (FTIR) analysis

Functional groups in the film samples were determined using a Thermos Scientific FTIR Nicolet 6700 equipped with attenuated total reflectance (ATR) accessory. The spectra were recorded in the range 400 to 4000 cm<sup>-1</sup>.

### 2.12 Antifungal activity analysis

Fungal culture plate preparation: The bread was kept in damp conditions sealed in a plastic bag until fuzzy (blue green molds) growth was observed. The area of bread, having blue-green fuzzy growth was isolated and placed onto the malt extract agar plates, before incubating at  $30^\circ\text{C}$ .

The antifungal property of the films was tested on Malt Extract Agar (MEA) plates against molds (*Penicillium spp.*) isolated from bread using disc diffusion method. Malt extract agar plates were prepared, labelled and two isolated mold sections were placed onto each plate from the previously prepared culture plates. Small discs of films, both with silica and without silica were placed on the plates and sealed with parafilm before incubating at  $30^\circ\text{C}$ . The plates were regularly observed for mold growth and inhibition zone.

## 3. Results and Discussion

### 3.1 Starch extraction from broken rice

The extracted starch was in the form of a white paste, which was then dehydrated to obtain starch powder as shown in Fig.1. About 17 g of rice starch was extracted from 100 g rice flour.



Fig1: Starch extracted from Rice flour

### 3.2 Starch film preparation

The control film, which included only starch were either very brittle or sticky, hence could not be peeled off easily from the glass tray. However, films containing starch and silica (0.1g), with a thickness of 0.1 mm were better in consistency than the control films, as they got easily peeled off from the glass tray, though with some breaks in between as shown in Fig. 2.



**Fig 2:** Starch- Silica Film

**3.3 Pectin extraction from citrus (orange) peels**

The extracted pectin, after ethanol purification, had fibrous gel-like consistency and was bright yellow in colour. Though, after drying for 24 hours at 40°C and grinding, yellowish-brown pectin powder was obtained as shown in Fig 3.



**Fig 3:** Pectin extracted from citrus peels

The % yield of pectin from citrus peels was found out to be 16.6%.

**3.4 Pectin film preparation**

The control film, of thickness 0.1 mm, included only pectin with plasticizers as in Fig. 4, whereas silica (0.1g) incorporated pectin film, with thickness 0.1 mm, is shown in Fig. 5.



**Fig 4:** Control (Pectin) film



**Fig 5:** Pectin- Silica film

**3.5 Guar gum film preparation**

The control film (thickness 0.1 mm) included only guar gum with plasticizers as in Fig. 6, whereas silica (0.1g) incorporated guar gum film (thickness 0.1 mm) is shown in Fig. 7.



**Fig 6:** Control (Guar gum) film



**Fig 7:** Guar gum- Silica film

**3.6 Mechanical properties of films**

The maximum stress that a film can endure being stretched before tearing or deforming is its maximum tensile strength. The free volume between the polymer chains is enhanced with the addition of plasticizers resulting in greater chain mobility and, ultimately, film flexibility. Therefore, the resilience of a plasticized polymer would be less and distort at a lower force than a polymer without plasticizer. As a result, lower tensile strength is anticipated with plasticizer addition. On the other hand, with the addition of plasticizer, higher elongation is probable.

The observed mechanical properties of Starch, Pectin and Guar gum films with and without silica, are shown in Tables 1, 2 and 3, respectively.

**Table 1:** Mechanical properties of Starch films

Film	Thickness (mm)	Moisture (%)	Solubility (%)	Tensile Strength (N/ mm <sup>2</sup> )	EAB (%)
With 0.1g Silica	0.1	18.412 ± 0.920	157 ± 7.85	0.270 ± 0.004	59.308 ± 2.96

The tensile strength of Rice starch film incorporated with silica was found to be  $0.270 \pm 0.476$  N/ mm<sup>2</sup>.

**Table 2:** Mechanical properties of Pectin films

Film	Thickness (mm)	Moisture (%)	Solubility (%)	Tensile Strength (N/ mm <sup>2</sup> )	EAB (%)
Control	0.1	19.117 ± 0.955	12 ± 0.600	1.158 ± 0.057	28.58 ± 1.42
With 0.1g Silica	0.1	23.668 ± 1.183	34 ± 1.700	1.49 ± 0.074	14.616 ± 0.730

The tensile strength of the silica incorporated pectin film increased as compared to that of control film, whereas EAB of silica incorporated pectin film decreased than that of control film. This change can be attributed to the addition of silica in the films which absorbs water in the films, thereby restricting

the flexibility of the films, making the silica incorporated pectin films more resilient to breakage as compared to the control films which were more like fragile gels due to their hydrophilic nature.

**Table 3:** Mechanical properties of Guar gum films

Film	Thickness (mm)	Moisture (%)	Solubility (%)	Tensile Strength (N/ mm <sup>2</sup> )	EAB (%)
Control	0.1	19.327 ± 0.966	29.8 ± 1.49	6.336 ± 0.316	94.652 ± 4.735
With 0.1g Silica	0.1	24 ± 1.20	76.11 ± 3.804	3.658 ± 0.182	32.124 ± 1.60

The tensile strength and EAB of silica incorporated guar gum film decreased when compared to the control film, probably because of the cumulative effect of plasticizer as well as silica. Plasticizer made the film flexible, making the control film stickier whereas the addition of silica in guar gum film restricted their flexibility and made them less sticky.

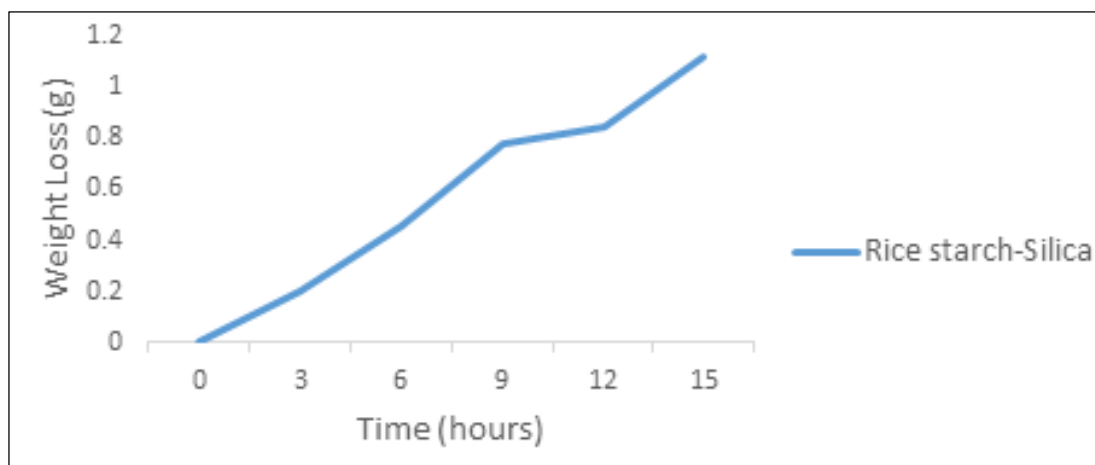
The moisture content of all the three films, i.e. Starch, Pectin and Guar gum incorporated with silica is higher compared to the control films probably because of the presence of silica that must have absorbed moisture from the biopolymer structure as well as the surroundings.

Solubility of the films incorporated with silica was significantly increased when compared to control films due to the interaction of polymeric structure and adsorbed water molecules [18].

### 3.7 Barrier properties of films

The main purpose of food packaging is often to avoid or at least lower the migration of moisture between two components of an assorted food product or the food and the surrounding atmosphere, as a result, the water vapor permeability (WVP) of the film should be as low as possible [19]. Pores in the macromolecule structures filled with microparticles can reduce gas permeability as well as water vapour permeability. Introduction of microparticles decreased water vapor permeability (WVP) of films [20].

The observed water vapour loss through starch, pectin and guar gum films are shown in Fig. 8, 9 and 10, respectively.

**Fig 8:** Water vapor loss through Starch films

The WVP of silica incorporated starch film could not be compared with the starch (control) film as the control film was too sticky and could not be prepared.

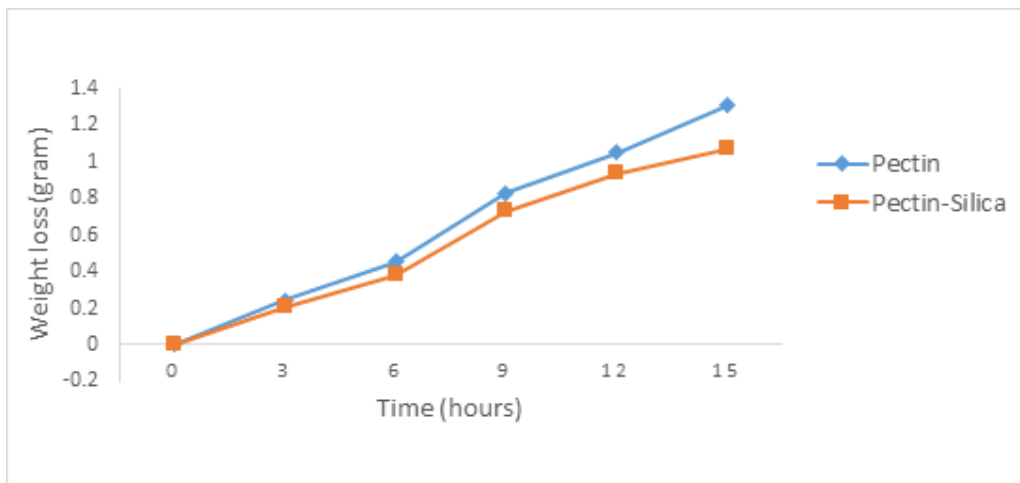


Fig 9: Water vapor loss through Pectin films

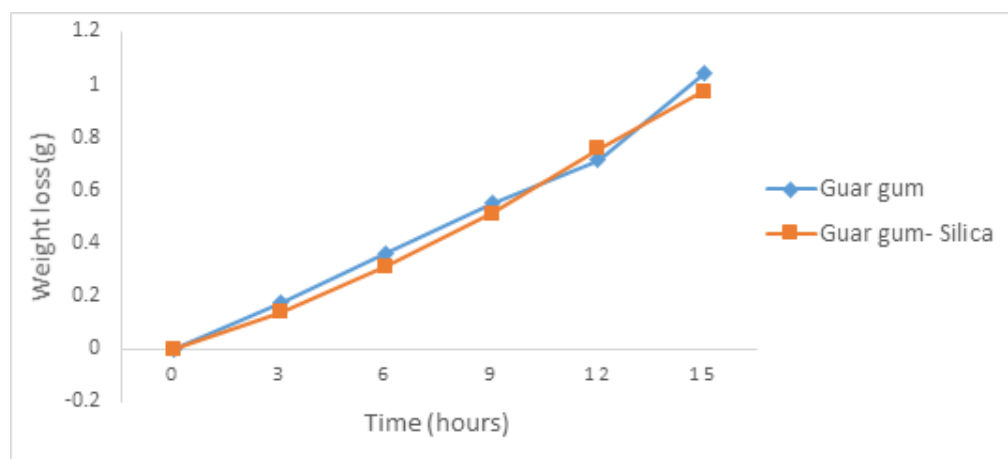


Fig 10: Water vapor loss through Guar gum films

The WVTR of the silica incorporated film was lower as compared to the control film in Fig.9, 10. Addition of silica to pectin reduces water transmission through the film, presumably by entrapping the excess moisture.

The barrier properties of starch, pectin and guar gum films are given in Tables 4, 5 and 6, respectively.

Higher values of water vapor permeability may be explained with the use of plasticizing agent, the presence of glycerol molecules between the polymer chains causes the spacing in-between to increase, thereby, facilitating diffusion of water vapor through the film [21].

Table 4: Barrier properties of Starch films

Film	WVP (gmm/ m <sup>2</sup> h kPa)
With 0.1g Silica	2.68 ± 0.134

The mechanical properties of thermoplastic starch materials are affected due to the moisture sensitive property of starch biopolymer. Consequently, any improvement in reducing moisture sensitivity and increasing water resistance of thermoplastic starch material is important [22]. Understanding of solute and polymer interactions and mass transfer mechanisms in biodegradable films is dependent on the results of water vapor permeability (WVP). The driving force of water transfer through films is the change in water chemical potential, as per the thermodynamics of irreversible processes. The results of the water chemical potential difference are proportional to the

water vapor concentration difference between the two faces, when this process occurs at constant temperature and pressure [18, 23]. This resultant WVP value was due to the occurrence of cross-linking of a hydrophilic group (OH) of starch with silica [24].

Table 5: Barrier properties of Pectin films

Film	WVP (gmm/ m <sup>2</sup> h kPa)
Control	3.229 ± 0.161
With 0.1g Silica	2.733 ± 0.136

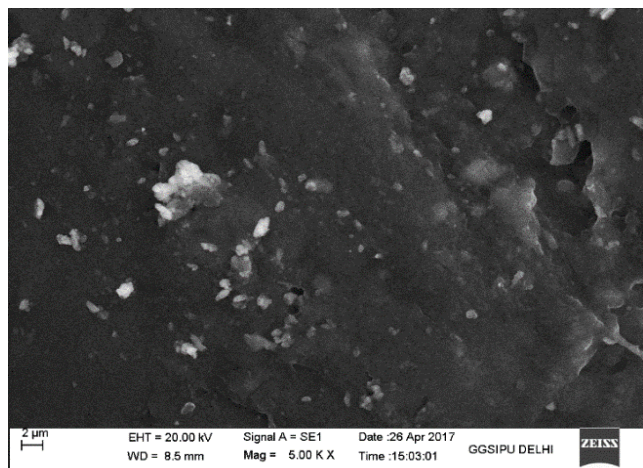
Table 6: Barrier properties of Guar gum films

Film	WVP (gmm/ m <sup>2</sup> h kPa)
Control	1.214 ± 0.060
With 0.1g Silica	1.195 ± 0.059

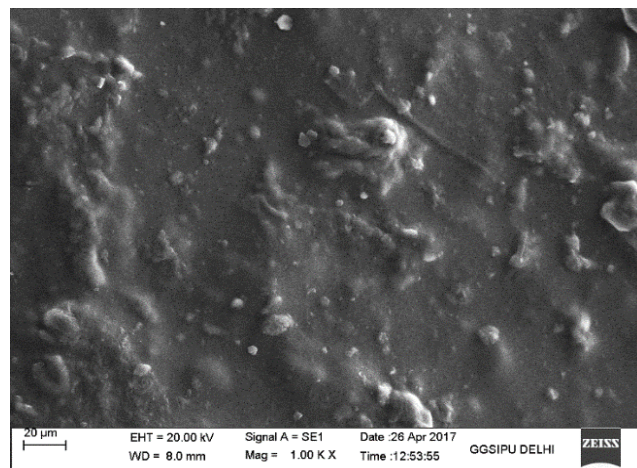
Lower WVP values of starch, pectin and guar gum films incorporated with silica may be due to the interaction between the silica microparticles and the biopolymer film structure [10].

### 3.8 Scanning Electron Microscopy (SEM) analysis

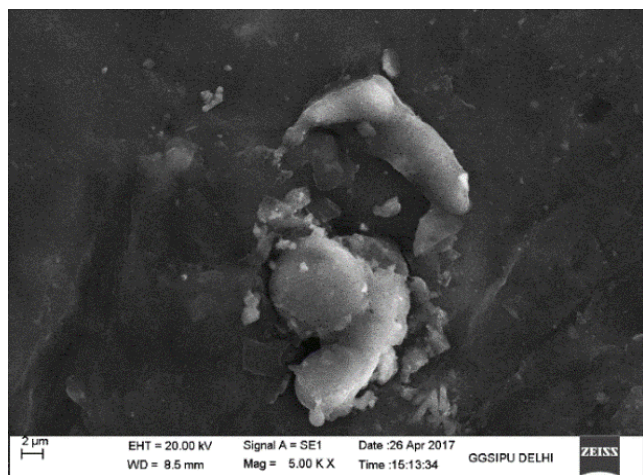
Fig. 11 and 12 show the morphology of starch powder and silica incorporated starch films, Fig. 12 and 13 depict the morphology of pectin and silica incorporated starch films and Fig. 14 and 15 show the morphology of guar gum and silica incorporated guar gum films.



**Fig 11:** Morphology of starch powder



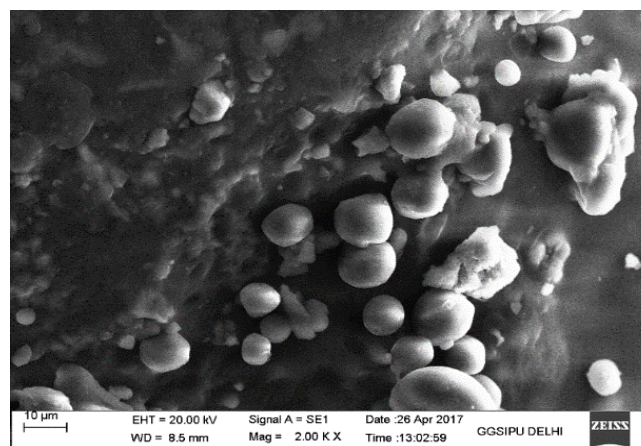
**Fig 14:** Morphology of Silica incorporated Pectin film



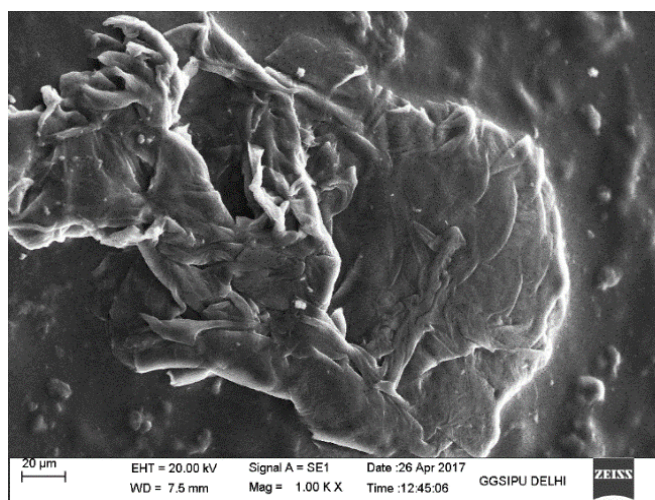
**Fig 12:** Morphology of Silica incorporated starch film

The spherical masses contain interlinking cavities due to the presence of open spaces, which provide extensive porosity capable of being filled and to transport material within the spheres [25]. The silica particles would probably be embedded into the open spaces in the irregular starch structure disrupting the biopolymer structure.

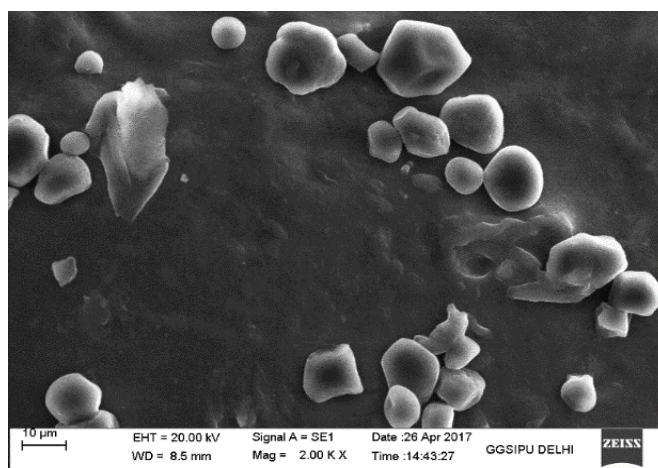
The control (Pectin) film has a dense network as seen in Fig. 13. Addition of silica to pectin film transforms the compact network into fragmented material comprising of thin platelets as seen in Fig. 14. The results are quite similar to a study conducted wherein it was also revealed that cellular permeable materials are obtained at intermediate silica–pectin ratio, due to the presence of silicates which seem to disturb the polymer arrangement to a significant amount [26].



**Fig 15:** Morphology of Guar gum (control) film



**Fig 13:** Morphology of Pectin (control) film



**Fig 16:** Morphology of Silica incorporated Guar gum film

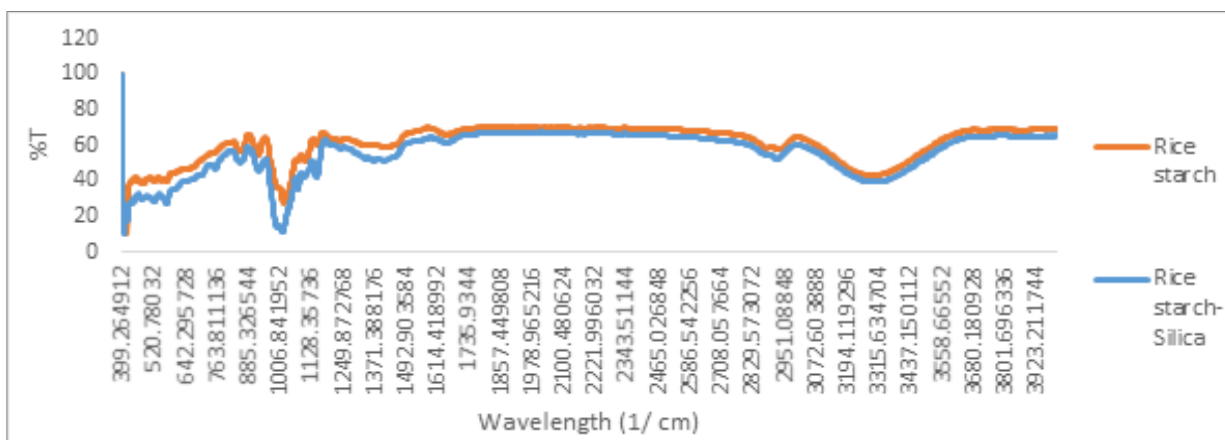
As seen in Fig. 15, guar gum exists in a granular form and there was no cross linking observed between the granules. Normal guar gum particles are small, having a rough surface morphology [27, 28]. Rough surfaces lead to enhancement of the overall surface area, thereby increasing the adsorption sites, which help in attaining a highly viscous aqueous solution. In Fig. 16, particles of various sizes can be seen that further enhanced the rough morphology of the film, and in turn the water absorbency. Similar observations have been reported [28]. Due to intercalation of the silica particles, the interlayer space increases resulting in improved water absorbency [29, 30].

### 3.9 Fourier Transform- Infrared (FTIR) analysis

FTIR spectra of Starch, Pectin and Guar gum films are shown below in Fig. 17, 18 and 19.

**Table 7:** Characteristic modes of vibrations and their wavenumbers for starch<sup>[31]</sup>

Wavelength (cm <sup>-1</sup> )	Functional groups
3295	O-H stretching
2933	C-H stretching of CH <sub>2</sub>
1630	O-H bending (water absorption band)
1455	CH <sub>2</sub> bending in plane
1340	C-O-H bending
1388	CH bending in plane
1150	C-O stretching of C-O-C
1100	C-O-H stretching
1030	C-O stretching in C-O-H and C-O-C in the anhydrous glucose ring
930	C-O-C ring vibration
851	C(1)-H( $\alpha$ ) bending
760	C-O-C ring vibration

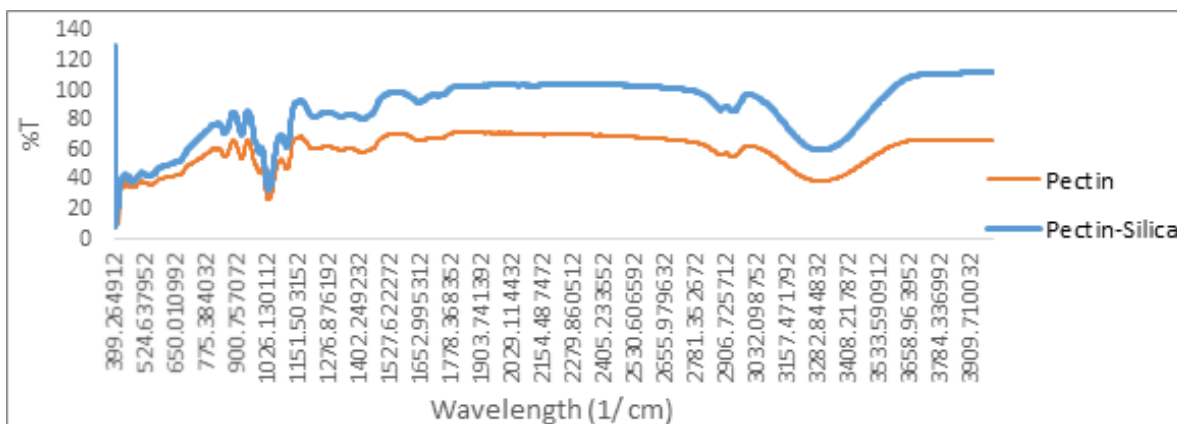


**Fig 17:** FTIR spectra of Rice starch powder and Silica incorporated Rice starch film

In Fig. 17, the band indicating OH stretching of rice starch films is at 3332.99 cm<sup>-1</sup>. The peak at 2931.77 cm<sup>-1</sup> co-relates to the C-H stretching vibration. One distinctive band occurring at 1647.209 cm<sup>-1</sup> is probably due to the bound water existing in the starch molecules. Similar observations have been reported [24].

The swollen particles are enriched in amylopectin since the amylose molecules diffuse out, as starch is gelatinized. A continuous phase outside the granule is formed after dissolution. Silica interacts with heat liberated amylose and amylopectin molecules, when it is added into starch suspensions after being heated [32].

In Fig. 17, the bands in the starch film spectra remain at the same location when compared to the silica added starch film. The bands are sharper, but less intense. The band at 1090 cm<sup>-1</sup> vanishes, in the silica incorporated film and forms a shoulder suggesting disintegration of the configuration of starch backbone. The Si-O and O-Si-O modes dominate the FTIR spectra and a strong in-plane vibration of the - Si-O band appears at 590 cm<sup>-1</sup> (605 cm<sup>-1</sup> in Fig. 16). It is possible that the appearance of this band indicates starch silylation, ultimately resulting in the formation of the C=O-O-SiO<sub>2</sub>Na moieties [32].



**Fig 18:** FTIR spectra of Pectin and Silica incorporated Pectin film

The pectin film spectra displays a wide band at  $3305.95\text{ cm}^{-1}$  analogous to OH stretching of the polymer hydroxyl groups. The bands at  $950$  and  $830\text{ cm}^{-1}$  are comparable to the bending vibration of the hydroxyl group. Whereas a series of peaks at  $2981.94$ ,  $2945.30$ , and  $2881.65\text{ cm}^{-1}$  conform to the symmetric and asymmetric stretching vibration  $\text{CH}_2$  and  $\text{CH}_3$ .

A band at  $1750\text{ cm}^{-1}$  is apparently consistent with the carbonyl vibration band of acetyl groups<sup>[28]</sup> whereas a vibration band at  $1650\text{ cm}^{-1}$  is attributed to adsorbed water. In Fig. 18, the two groups of overlapping bands observed between  $1450$  and  $1250\text{ cm}^{-1}$  and between  $1200$  and  $1000\text{ cm}^{-1}$  are thought to be the 'fingerprint region' of the pectin. The former band includes the

bending vibration of  $\text{CH}_2$  and  $\text{CH}_3$  groups as well as the (COC) of the methyl ester groups, whereas the latter comprises the (COC) of the polymer backbone as well as the (CC) (CO) bands<sup>[26]</sup>.

They also reported an intense band appears at  $950\text{ cm}^{-1}$  analogous to the Si-OH group. The indicator of the extent of silica condensation i.e. the Si-O-Si bending vibration mode is found at  $800\text{ cm}^{-1}$ . The band, conforming to the bending vibration modes of the  $\text{SiO}_4$  tetrahedron can be seen at  $470\text{ cm}^{-1}$ <sup>[26]</sup>. These bands are also seen in silica incorporated pectin film curve (Fig. 18).

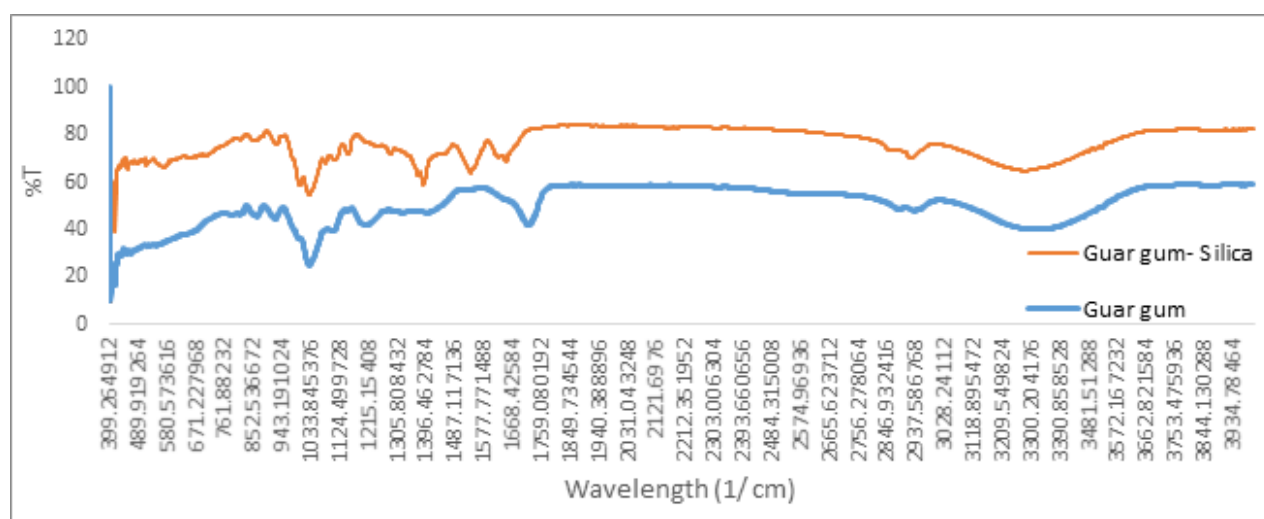


Fig 19: FTIR spectra of Guar gum and Silica incorporated Guar gum film

The FTIR-ATR spectrum of the pure guar gum film shows (Fig. 19) absorption bands at around  $3346.49\text{ cm}^{-1}$  and  $2920.22\text{ cm}^{-1}$  indicating OH stretching vibrations and C-H stretching vibrations, respectively. Along with these, absorption bands for the in-plane bending of OH group and a strong band, i.e. C-O stretching vibration of alcoholic group are also present in guar gum film at around  $1423.55\text{ cm}^{-1}$  and  $1249.98\text{ cm}^{-1}$ , respectively. Similar observations have been made<sup>[33]</sup>.

The presence of new bands in the silica incorporated guar gum film curve between  $1250$  to  $1650\text{ cm}^{-1}$  indicate the interaction of silica with the guar gum polymer structure.

### 3.10 Antifungal activity analysis

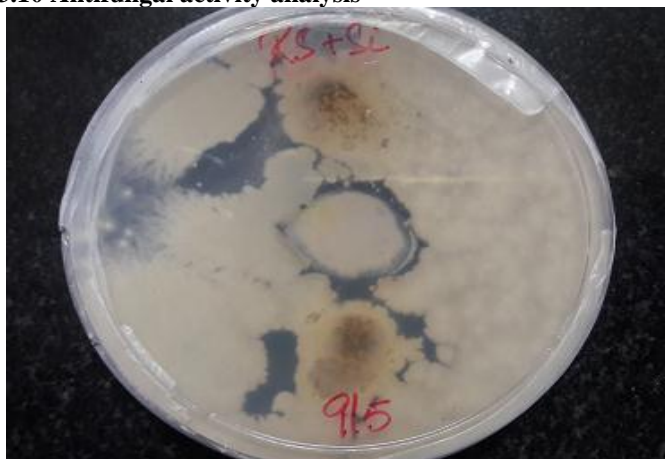


Fig 20: Antifungal activity in Rice starch-silica

The inhibition zone was observed in all the plates, though only a few plates had a clear inhibition zone, like in Fig. 20 i.e. plate with starch-silica film. This result can be attributed by the addition of silica retarding fungal growth either by biochemical or physical mechanisms when host-pathogen interaction takes place like silicon application induces the production of antifungal compounds after pathogen penetration of the epidermal cells<sup>[34]</sup>. The complete functioning of silicon towards retarding growth of fungi is still unknown both in plant systems as well as in-vitro. A similar investigation was conducted wherein inhibition of fungal growth was reported with the use of potassium silicate<sup>[35]</sup>. Further study of the antifungal activity of the silica incorporated films is required before its commercial use as packaging material.

### 4. Conclusion

The incorporation of silica into natural polymers is a prolific approach to formulate novel hybrid structures with prospective significant functions in the fields of biotechnology, medicine, environmental sciences as well as food sector. Due to weak interactions between the mineral and organic components, mechanical properties of the polymer are not greatly enhanced, however, they have a considerable effect on the material's water stability, which is dependent on the silica particle size, source and its distribution in the biopolymer structure. The inherent antifungal properties of silica gel also widen the scope of applications, especially in the food processing sector.

In the present study, polysaccharide (starch, guar gum and pectin) films consisting of silica derived from rice husk have been prepared. The mechanical properties of the silica

incorporated films were better than pure polysaccharide films. With the addition of silica, the films were more resilient to breakage. A significant increase in the moisture content and solubility of films indicate that the films are water soluble and hence, can be useful as edible packaging. These observations (moisture content and solubility of films) could be possible because of the numerous potential intermolecular interactions in the structure of the films. Barrier properties, i.e. water vapour transmission rates and water vapor permeability of polysaccharide films were reduced, owing to the enhanced rough morphology in the presence of extracted silica in the biopolymer structures. Differences in the properties of the control and silica incorporated polysaccharide films are dependent upon the particle size of silica as well as the biopolymer and the interaction between the two i.e. silica and the biopolymer. The inhibition of fungal growth by starch-silica film further augments its role in food preservation, though further extensive toxicity studies are required for the same.

Such films are a potential way to keeping the food quality intact and safe from fungal spoilage while simultaneously cutting down on plastic and agricultural waste.

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