

A

Dessertation Report

On

**DISPERSION COATING OF PAPER WITH HYDROCOLLOIDS FOR
THE IMPROVEMENT OF BARRIER AND FUNCTIONAL
PROPERTIES OF PAPER**

*Submitted for partial fulfilment of the requirement
for the award of the degree of*

**MASTER OF TECHNOLOGY
IN
PULP & PAPER TECHNOLOGY**

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation entitled “ **Dispersion coating of paper with hydrocolloids for the improvement of barrier and functional properties of paper**” in partial fulfilment of the requirement for the award of degree of Master of Technology in Pulp and Paper Engineering submitted at Department of Paper Technology, IIT Roorkee, is an authentic record of my own work carried out during the period from June-2018 to May-2019 under the supervision of Dr. Ashish A. Kadam, Assistant Professor, Department of Paper Technology, IIT Roorkee, Dr. Sanjay Tyagi , Scientist , CPPRI and Dr. Ruchir Priyadarshi Head-Biopolymer ,Yash Paper Ltd , Faizabad (U.P).

The matter embodied in this dissertation has not been submitted by me for the award of any other degree.

Date: 19-05-2019

Place: Saharanpur

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This is certify that the above statement made by the candidate is correct to the best of my knowledge.

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Date:

Place:

Dharmendra Kumar



ABSTRACT

Increased environmental concerns over the use of certain synthetic packaging and coatings in combination with consumer demands for both higher quality and longer shelf life have led to increased interest in alternative packaging materials research. The present investigation deals with the preparation of coating formulation from the source of Naturally renewable biopolymers as a coating solution for barrier and functional of paper packaging paper. These biopolymer coatings may retard unwanted moisture transfer in food products, are good grease and oil barriers as well as heat sealable, biodegradable, and have potential to replace current synthetic paper and paperboard coatings. In the present investigation mainly focused on two approach, first Acrylics based water soluble polymer with the addition other coating additive and second Fully Natural bio-based polymer with the addition of some coating additive like plasticizer etc. these approach are used to get the required properties. The various coating formulations are used on laboratory scale to find the suitable materials to fulfilled the required properties for packaging grade paper. Natural renewable biopolymer mainly hydrocolloids are used as a barrier coating solution, these polymers are polysaccharides based like Chitosan, Oxidized starch, Sodium Alginate, carrageenan and protein based Gelatin are used to formulate new pathway for fully bio-based paper coating. The results obtained from laboratory data are found to be very interesting and seems very promising.

Keywords: Dispersion coating, Biopolymer, Base paper, Paper testing.



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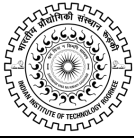
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1 INTRODUCTION

1.1 Background

Paper is widely used in packaging application and is biodegradable and therefore safe for the environment. However paper is hygroscopic and porous, its barrier properties against water vapour, gases and grease are poor. Polyolefin's are generally chosen as paper coating materials to overcome porosity and hygroscopicity of paper. These synthetic polymers fill the paper pores and form a dense layer at the paper surface. Unfortunately these material have poor biobegrability ,recyclability and highly impact on the environmental. To overcome this problem current research was find a new renewable coating material which is a completely biodegradable and environmental-friendly for coating on the paper surface to improve its barrier properties and use as a packaging application.

It has been predicted that the global packaging market will reach \$960 billion by 2018, and the total functional and barrier-coated paper and paperboard market was \$3.9 billion in 2010. Almost two thirds of this value originated from products coated with extrusion polymers or aluminum. However, increasing environmental concerns over the use of nonrenewable oil-based polymers in packaging materials have increased the general interest in using renewable coating components.

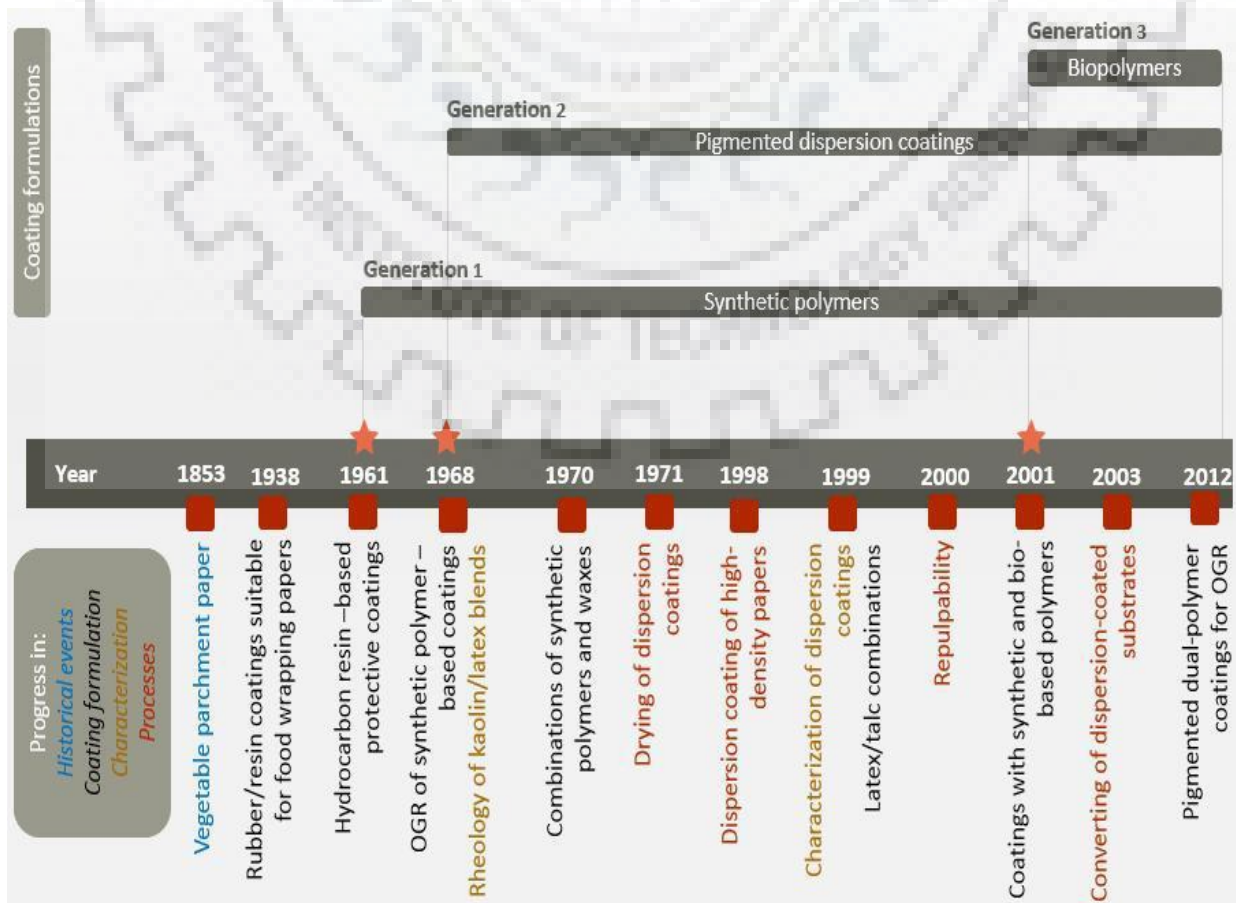


Figure 1: Development of coating formulation.



At the same time, consumer habits have changed worldwide and the demands for cost reduction and a wider utilization of sustainable packaging materials require new barrier solutions especially for short-term uses. Examples of such food products are bakery goods, microwavable instant meals and fast foods.

The first generation of coating dispersions was based on aqueous synthetic polymers, such as hydrocarbon resins for improving water-proof and polyolefin dispersions for improving grease and gas barrier properties . The development has been rapid

The water vapor barrier properties of the latex-based dispersion coatings can for instance be improved by the addition of wax or plate-like fillers such as kaolin. In third generation partial replacement of synthetic polymers with bio-based alternatives, such as modified starches, chitosan, Sodium alginate, Carrageenan, Gelatin and a synthetic-polymer-free combination of starch-plasticizer solution with nano clay are used.

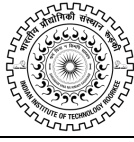
1.2 Objective of the study:

The objective of this work are to investigate home-compostable, environmental-friendly packaging paper with low barrier as grease and water resistance functionality as well as the heat sealability. This paper is meant to be used for the wrapping and bag applications for the food items with low barrier requirement. The particular emphasis in this work has been on the partial or complete replacing of synthetic polymers in the coatings with bio-based alternatives.

The main purpose of the food package is to protect the packed food from outer substances or threats that are considered harmful to the food. Contamination by dirt, gases, migration, aromas, UV radiation, odors and water should be minimized. Besides protecting food from outer threats, the package must also retain the components of the packed food inside the package. Oil and grease resistance is thus an essential material property, and it can also prolong the shelf-life and maintain the quality of the food.

1.2 Outline:

The experimental part give the details of the work carried out. In this experiments discussed the factors that affect the barrier properties of paper mainly water vapor transmission rate ,grease and oil resistance, water absorption as well as heat salability of hydrocolloids-based dispersion coatings filled with nanoclay, and same with acrylics-based polymer. Acrylics-based polymer is also a hydrophilic in nature as same biopolymer (Polysaccharides-based and protein-based) . In this experiment investigations are carried out to find suitable alternative as renewable bio-based polymer mainly hydrocolloids (Polysaccharide based or protein based or combination of both) to coat on the base paper to meet the required functional and barrier properties of paper.



2. Background Literature

2.1 Dispersion Coating:

Barrier polymer dispersion coating is understood to mean the coating technique where latex (that is, an aqueous dispersion of fine polymer particles) is applied to the surface of paper or board as such to form a solid, non-porous film after drying. The target of dispersion coating is to achieve a barrier layer against water, water vapour, grease, oil, gas, etc. by environmentally 'friendly' coating.

Dispersion coatings can be fully recycled, which in fact has been one of the driving forces behind the development of the barrier dispersion coatings. Recycling includes repulping, composting and incineration. Thus dispersion coated barrier products, for example, packaging materials, are more easily re-used than typical extrusion coated applications. In addition, loads to landfills decrease as a result of the composting behaviour of dispersion coated barrier materials.

Polymer dispersions consist mainly of water and polymer. Typically used polymers are modified starch, different acrylates and methacrylates, copolymers of these and natural biopolymers. During the manufacturing process several constituents are added in order to elevate barrier properties or processability. In addition, polymer dispersions may include various amounts of fillers to increase properties such as runnability and cost-effectiveness. Waxes are widely used to hydrophobize the surface.

2.2 Hydrocolloids Coating Materials:

Agar: Agar is a hydrophilic colloid consisting of a mixture of agarose and agaropectin that have the ability to form reversible gels simply by cooling a hot aqueous solution. Agar gel melts on heating and resets on cooling. Typical gel temperatures of agar for 1.5% solution are in the range 35-45 °C. Because of its ability to form very hard gels at very low concentrations it has been used extensively as a gelling agent in the food industry. However, in despite its biodegradability and its enormous gelling power, agar has been few used as edible film and coating due to a poor aging. Indeed, both photodegradation and fluctuations in ambient temperature and humidity alter agar crystallinity, leading to formation of micro-fractures and polymer embrittlement. However, it was reported that agar-based film displays a better moisture barrier properties than starch film . The influence of agar on the structure and the functional properties of emulsified edible films has been recently studied. Gelled agar chains



can stabilize film-forming emulsion to create a macronetwork. This macronetwork entraps flattened lipid particles improving barrier performance by increasing tortuosity.

Alginate: Alginate is an indigestible biomaterial produced by brown seaweeds (Phaeophyceae, mainly Laminaria) therefore it may also be viewed as a source of dietary fibre. Alginate has a potential to form biopolymer film or coating component because of its unique colloidal properties, which include thickening, stabilizing, suspending, film forming, gel producing, and emulsion stabilizing. An attractive feature of alginate solutions is the gelling capacity in presence of Calcium. Edible films prepared from alginate form strong films and exhibit poor water resistance because of their hydrophilic nature. The water permeability and mechanical attributes can be considered as moderate compared to synthetic films. A mixture of starch and alginate to form edible film has been studied by Wu et al. achieving to improve the mechanical properties of film and coating.

Chitosan: Chitosan is mainly made from crustacean shells, is the second most abundant natural and non-toxic polymer in nature after cellulose. Chitosan shows antifungal and antibacterial properties, which are believed to be originated from its polycationic nature. However, a major drawback of chitosan is its poor solubility in neutral solutions. The required degree of deacetylation to obtain a soluble product must be 80–85% or higher. Chitosan products are highly viscous, resembling natural gums. Chitosan can form transparent films to enhance the quality and extend the storage life of food products. Pure chitosan films are generally cohesive, compact and the film surface has a smooth contour without pores or cracks. Chitosan films such as many polysaccharide based films, tend to exhibit fat and oil resistance and selective permeability to gases but lack resistance to water transmission. Chitosan-based edible films and coatings allowed to extend and preserve shelf life of fresh strawberries, of slices mango fruit.

Carrageenans: Carrageenans are water-soluble polymers with a linear chain of partially sulphated galactans, which present high potentiality as film-forming material. These sulphated polysaccharides are extracted from the cell walls of various red seaweeds. Different seaweeds produce different carrageenans. The positions and numbers of sulfate ester groups are important because they are, together with the anhydrogalactose bridge, responsible for carrageenan functionality and determine a classification in three major types: κ , ι and λ . κ - and ι -carrageenans contain the 3,6-anhydro units and are used as gelling agents because of their property to produce thermoreversible gels on cooling below the critical temperature. λ -Carrageenan, with only sulfated galactose groups and no anhydrogalactose bridge, is a thickening polymer. The use of carrageenan as edible films and coatings already covers various fields of the food industry such as application on fresh and frozen meat, poultry and fish to



prevent dehydration , dry solids foods, oily foods etc. Recently, carrageenan films were also found to be less opaque than those made of starch.

Cellulose derivatives: Cellulose derivatives are polysaccharides composed of linear chains of β (1–4) glucosidic units with methyl, hydroxypropyl or carboxyl substituents. Only four cellulose derivative forms are used for edible coatings or films: Hydroxypropyl cellulose(HPC), hydroxypropyl methylcellulose (HPMC), Carboxymethylcellulose (CMC) or Methyl cellulose (MC). Cellulose derivatives exhibit thermo-gelation therefore when suspensions are heated they form a gel whereas they returns to originally consistency when cooled [34]. The films cast from aqueous solutions of MC, HPMC, HPC and CMC tend to have moderate strength, are resistant to oils and fats, and are flexible, transparent, flavourless, colourless, tasteless, water-soluble and moderate barriers to oxygen. MC is the most resistant to water and it is the lowest hydrophilic cellulose derivatives. However, cellulose derivative films are poor water vapour barriers because of the inherent hydrophilic nature of polysaccharides and they possess poor mechanical properties . A way to improve the moisture barrier would be the incorporation of hydrophobic compounds, such as fatty acids, into the cellulose ether matrix to develop a composite.

Starch: Starch is the major carbohydrate reserve in plant tubers and seed endosperm where it is found as granules, each typically containing large number of amylopectin molecules and less number of amylose molecules . Amylose is responsible for the film-forming capacity of starch. The largest source of starch is corn (maize) with other commonly used sources being wheat, potato, tapioca and rice. Starch is used to produce biodegradable films to partially or entirely replace plastic polymer. The films are transparent , flavourless, tasteless and colourless. However, starch film application are limited by poor mechanical strength. Films from cassava starch had good flexibility and low water permeability, indicating potential application as edible films. Plasticizer is generally required for starch-based edible films to overcome film brittleness. The most commonly used plasticizers for starch films are glycerol and sorbitol. Recently have developed starch films from oxidized potato starch (OPS) with glycerol as a plasticizer at different contents. The OPS films were transparent and flexible with interesting mechanical properties.

Gelatin: Gelatin is prepared by the thermal denaturation of collagen, isolated from animal skin, bones and fish skins. The physical properties of gelatins are related not only to the molecular weight distribution but also to the amino acid composition. Gelatin is readily soluble in water at temperatures above 40°C, forming a viscous solution. Mammalian gelatins commonly have better physical properties and thermostability than most fish gelatins , and this has been related mainly to their higher amino acid content The molecular weight distribution depends mainly on the degree of collagen cross-linking and the extraction procedure . Films



from tuna skin gelatin plasticized with glycerol presented lower water vapor permeability (WVP) compared to values reported for pigskin gelatine.

2.3 Plasticizer:

Dispersion coated paper need to have good elasticity and flexibility, a low brittleness, a high toughness and to prevent cracking during handling and storage. Therefore, plasticizers of low molecular weight are typically added to hydrocolloid film forming solutions to modify the flexibility of coated film. Plasticizers with characteristics such as small size, high polarity, and greater distance between polar groups within a molecule generally impart greater plasticizing effects on a polymeric system. Indeed, they act by increasing the free volume or in other word by decreasing intermolecular attractions between adjacent polymeric chains by reducing hydrogen bonding between polymers chains . Generally, plasticizers are required for polysaccharides or proteins based coated films. Their amount added into hydrocolloid film-forming preparations varies between 10% and 60% by weight of the hydrocolloid. The most commonly used plasticizers are glycerol , sorbitol and water. However, addition of plasticizers may cause significant changes in the barrier properties of the films, e.g. increase film permeability to gases , decrease the ability of the film to attract water or decrease the tensile strength .

2.4 Antimicrobial agent:

Common chemical antimicrobial agents used in food systems, such as benzoic acid, propionic acid, sodium benzoate, sorbic acid, and potassium sorbate, may be incorporated into coated films and coatings to inhibit the outgrowth of both bacterial and fungal cells . In fact, the antimicrobial compounds, when establish contact with food, inhibit the growth of microorganisms present in the surface.



3. Coating Methods

A control coater (RK Print-Coat Instruments Ltd. UK) was used to deposit the coating solutions on the paper at ambient temperature. This automatic machine uses standard wire-wound bars to produce a uniform and coating. Four coat weights were applied: 2, 4, 6 and 8 g/m², where the coat weight was varied by varying the diameter of the wire on the rod. The coating process was performed at a speed of 6 m/min. After wet coating, the papers were dried at 30°C for 24 hr. Before testing, all samples were conditioned for two days in an environmental chamber at 50% RH and 23°C. The coat weight are depends on many factor such as dry solid content of coating solution, wire wound size of the coater Rod, pressure applied during coating and drying condition of coated paper.

Long K Bar

Order Id	Description	Length (cm)	Film Width (cm)	Diameter (cm)	Color Code	Wet Film Deposit
KHC.11.0	Long K-Bar No.0	37.5	25.5	0.9	White	4μm
KHC.11.1	Long K-Bar No.1	37.5	25.5	0.9	Yellow	6μm
KHC.11.2	Long K-Bar No.2	37.5	25.5	0.9	Red	12μm
KHC.11.3	Long K-Bar No.3	37.5	25.5	0.9	Green	24μm
KHC.11.4	Long K-Bar No.4	37.5	25.5	0.9	Black	40μm
KHC.11.5	Long K-Bar No.5	37.5	25.5	0.9	Horn	50μm
KHC.11.6	Long K-Bar No.6	37.5	25.5	0.9	Orange	60μm
KHC.11.7	Long K-Bar No.7	37.5	25.5	0.9	Brown	80μm
KHC.11.8	Long K-Bar No.8	37.5	25.5	0.9	Blue	100μm
KHC.11.9	Long K-Bar No.9	37.5	25.5	0.9	Tan	125μm

Figure 2: Control coater bar specification.

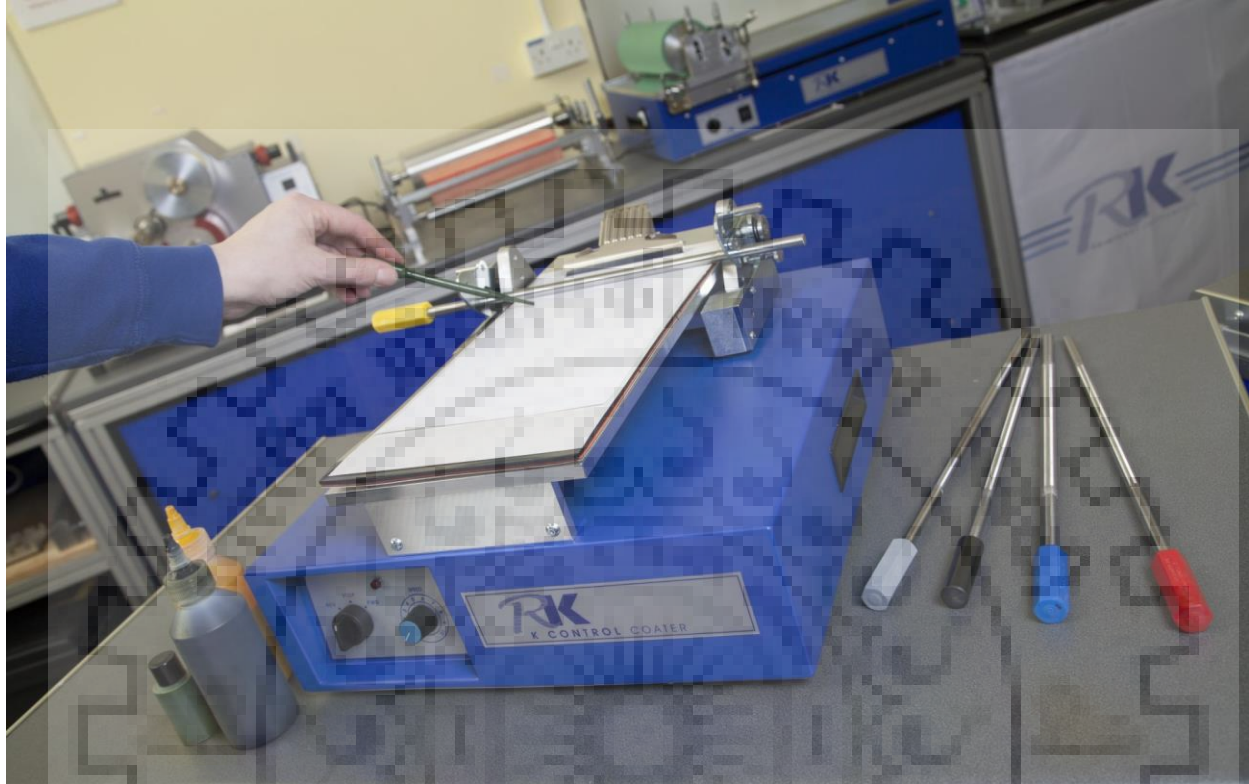


Figure 3 : RK Control Coater





3. Experimental Details

3.1 Pre-coat Formula Preparation:

11gm of oxidized starch powder with 10% moisture content dissolve in hot water(80°C) and cooked 10 minutes at a temp. of 105°C to make a solution of 10.6% DS. After that cool it at room temp. and perform coating experiment.

Oxidation, as a chemical way of starch modification, is commonly used to obtain modified starches with low viscosity at high solid concentrations. The oxidized starch has been reported to have excellent film-forming properties. Starch are oxidized to improve their adhesion properties in coating application and it tends to penetrate deeply into the paper structure due to this porosity reduce. It also improve the strength of paper.

The commercial production of oxidized starch generally employs sodium hypochlorite as the oxidizing agent. During oxidation the hydroxyl group of starch molecules are first oxidized carbonyl group then carboxyl group or aldehyde group. The content of carboxyl and carbonyl group in starch molecules indicates the extent of starch oxidation. Oxidized starch are mainly soluble in hot water and it has 70 cp viscosity at 50 C.

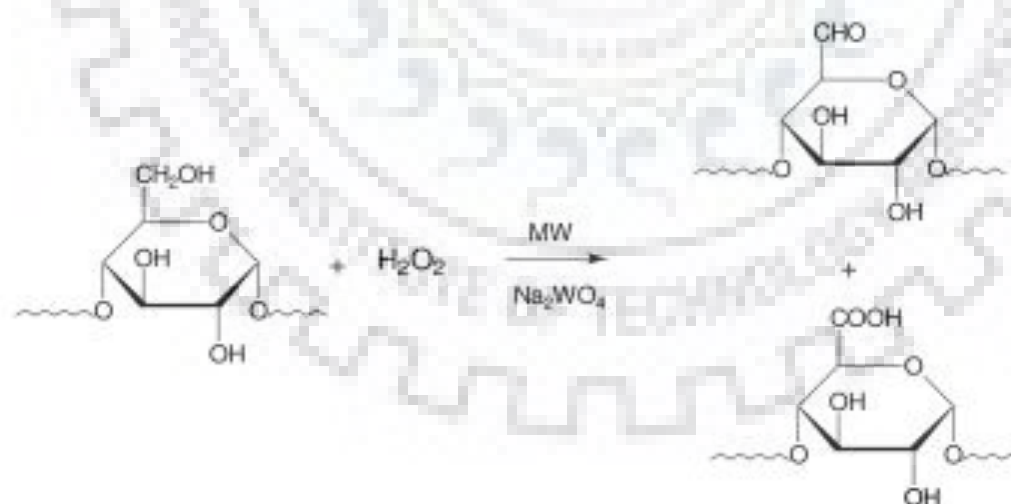


Figure 4: Oxidation of starch to form oxidized starch.



3.2 Pre -Coat Results:

Table 1: Pre-coat results of Oxidized starch, F-00, F-05, and F-08.

KBP paper	Without coat	Oxidized starch	Formula-00	Formula-05	Formula-08
Basis weight	39.76	41.43	46.00	48.50	45.50
Roughness:Bendtsen (ml/min)					
Top side	90-100	100-125	85-90	300-320	60-70
Wire side	500-550	NA	NA	NA	NA
Air permeance:Gurley (sec/100 ml of air)	95	366	764	322	615



3.1 First Stage Barrier coating Formulation:

These materials are mainly Acrylic based polymer used in barrier coating experiments with and without addition of filler Nanoclay, all are provided by Yash Paper Ltd .

Acrylic based polymer is water soluble which is hydrophilic in nature .The addition of nanoclay to the acrylic formulation improved water barrier, which is a very important property for the coating applications. The improvement in properties of the coating was more pronounced in the case of the additive based on nanoclay, due to its higher aspect ratio.

Formula-00:

Table 2: Four coating formulation from Formula-00 coated on KBP paper.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	A-00	F-00	0	6±0.3
2.	B-00	OS/F-00	1.5±0.2	6±0.3
3.	C-00	OS/F-00 + Nanoclay (5%)	1.5±0.2	6±0.3
4.	D-00	OS/F-00 + Nanoclay (10%)	1.5±0.2	6±0.3

F-00 - Formula-00, OS - Oxidized Starch (pre-coat).

Coating conditions (Dry solid weight):

A-00: 50% , B-00: 50% , C-00: 41.61% , D-00: 35.7%



Results:

Table 3: Cobb Value , KIT , Heat seal strength and WVTR results for Formula-00 formulation.

S.No.	Sample	Cobb (30 min)	KIT Value	Heat Seal Strength (N/m)	WVTR (g/m ² per day)
1.	A-00	74.2 ± 2	1	165.6	153.45
2.	B-00	52.0 ± 1.5	6	114.0	142.78
3.	C-00	51.3 ± 1.2	5	179.6	140.11
4.	D-00	46.3 ± 0.5	5	197.6	124.00

Formula-05:

Table 4: Four coating formulation from Formula-00 coated on KBP paper.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	A-05	F-05	0	7±0.3
2.	B-05	OS/F-05	1.5±0.2	7±0.3
3.	C-05	OS/F-05 + Nanoclay (5%)	1.5±0.2	7±0.3
4.	D-05	OS/F-05 + Nanoclay (10%)	1.5±0.2	7±0.3

Coating conditions (Dry solid weight):

A-00: 50% , B-00: 50% , C-00: 41.61% , D-00: 35.7%



Results :

Table 5: Cobb Value , KIT , Heat seal strength and WVTR for Formula-05 formulation.

S.No.	Sample	Cobb (30 min)	KIT Value	Heat Seal Strength (N/m)	WVTR
1.	A-05	68.6 ± 1.5	1	164.8	176.44
2.	B-05	63.2 ± 0.5	4	162.3	159.15
3.	C-05	60 ± 1.3	5	107.2	152.00
4.	D-05	53.1 ± 0.4	5	128	151.71

Formula-08:

Table 6: Four coating formulation from Formula-08 coated on KBP paper.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	A-08	F-08	0	6±0.3
2.	B-08	OS/F-08	1.5±0.2	6±0.3
3.	C-08	OS/F-08 + Nanoclay (5%)	1.5±0.2	6±0.3
4.	D-08	OS/F-08 + Nanoclay (10%)	1.5±0.2	6±0.3

Coating conditions (Dry solid weight):

A-00: 50% , B-00: 50% , C-00: 41.61% , D-00: 35.7%



Results :

Table 7: Cobb Value , KIT, Heat seal strength and WVTR for Formula-08 formulation.

S.No.	Sample	Cobb (30 min)	KIT Value	Heat Seal Strength (N/m)	WVTR (g/m ² per day)
1.	A-08	46.2 ± 1.2	5	166.8	146.21
2.	B-08	40.8 ± 0.5	7	122	132.45
3.	C-08	38.2 ± 1.4	6	112	128.65
4.	D-08	45.3 ± 0.5	6	93	122.10

Test Method Standards:

Cobb (30 min) -	TAPPI T 441
KIT Test -	TAPP T 559 cm-12
Heat Seal Test -	ASTM F88
WVTR-	TAPPI T448 om-17



Cobb value: (gram of water absorbed per meter square of paper in 30 minutes):

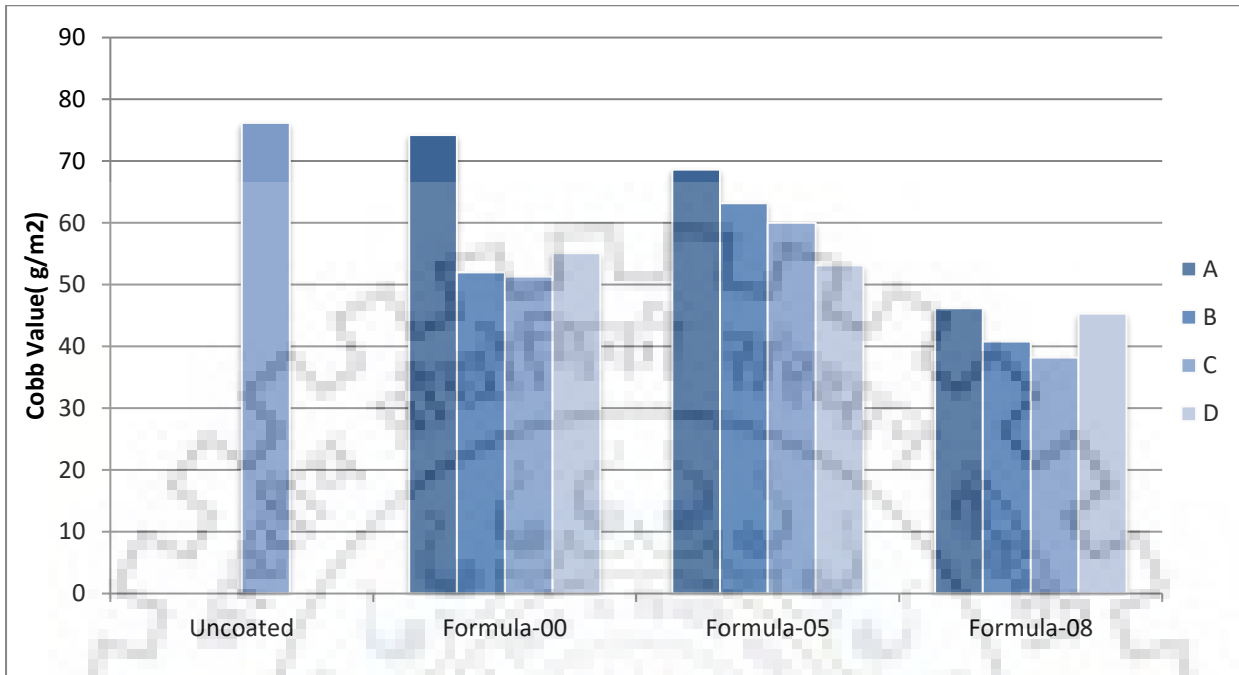


Figure 5: Comparison of Uncoated paper with all three formulation for their Cobb value.

KIT No: (Grease and oil repellency test)

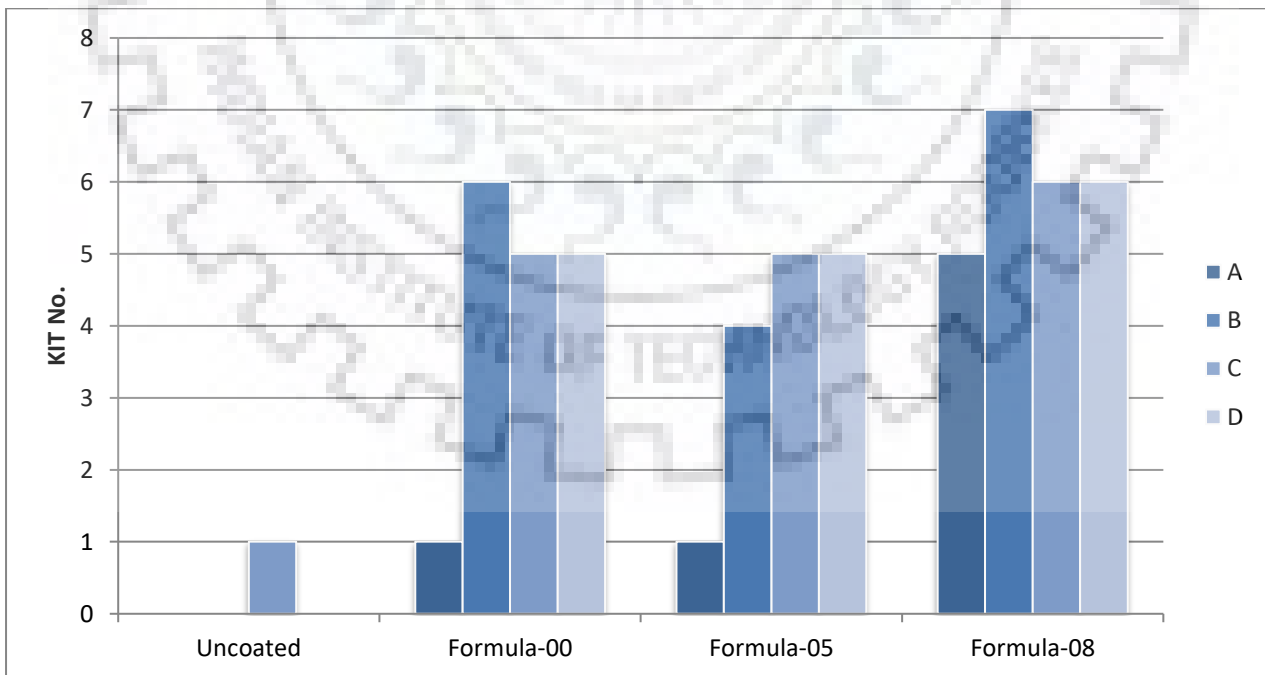


Figure 6: Comparison of Uncoated paper with all three formulation for their KIT no.



Heat Seal Strength (N/m): Comparison seal strength of F-00,F-03 and F-05.

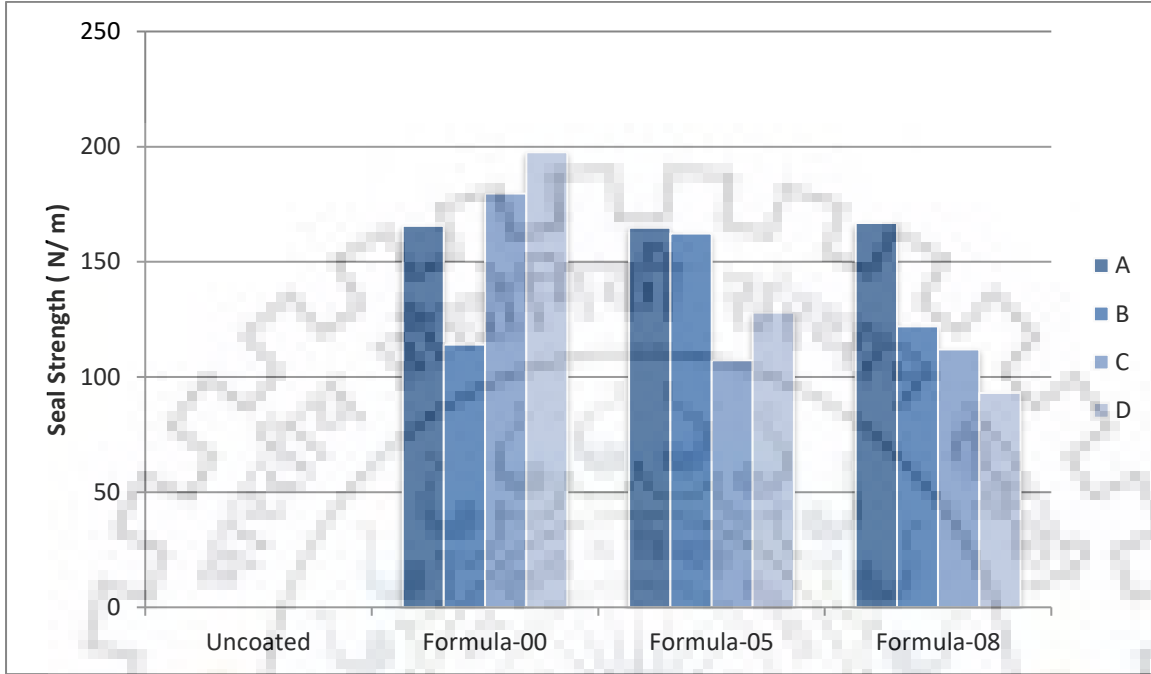


Figure 7: Comparison of Uncoated paper with all three formulation for their Seal strength.

WVTR (g/m² per day): Comparison WVTR of F-00,F-03 and F-05.

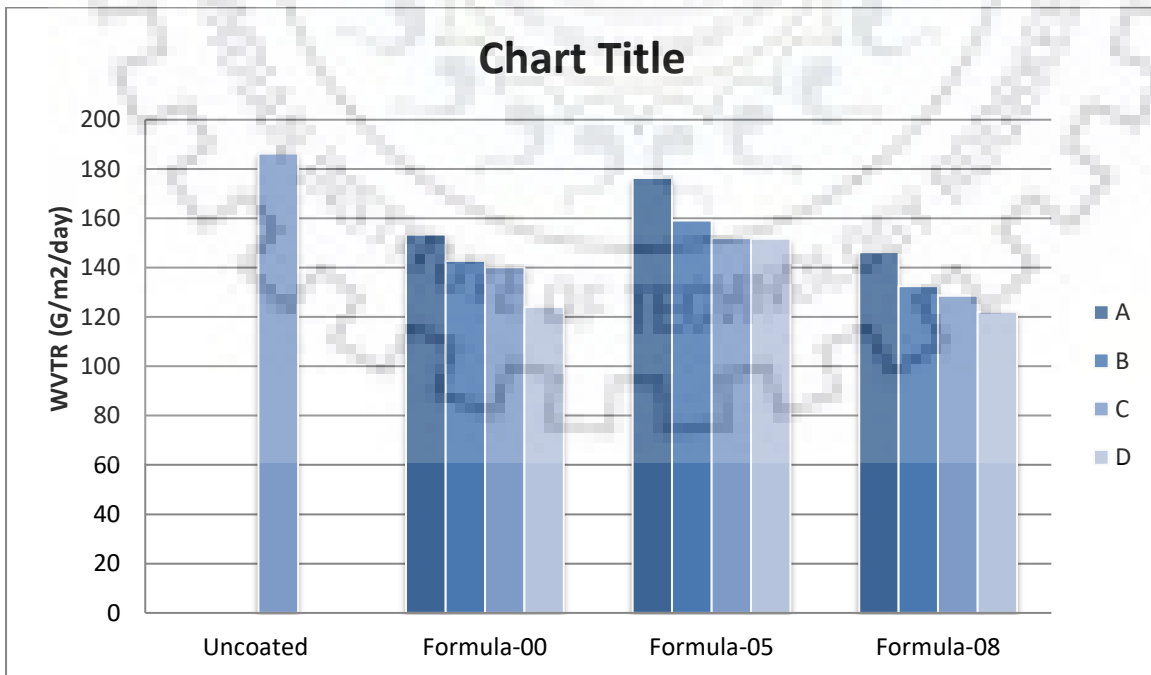


Figure 8: Comparison of Uncoated paper with all three formulation for their WVTR.



3.1 Second Stage Barrier coating Formulation:

3.1.1 Chitosan based barrier coating:

Materials: Chitosan powder with a molecular weight of 900 kDa and degree of deacetylation of 90.2%, Acetic acid and glycerol were from Himedia. Gelatin was also purchased from Himedia Chemicals. Nanoclay from Yash Paper.

Preparation of Coating Solutions: First, chitosan based coating solution was prepared by dissolving 1.5% (w/v) chitosan in 1% (v/v) acetic acid at pH 4 under constant stirring via the use of a magnetic stirrer at 700 rpm at room temperature for 6 h. Glycerol was added to the solution 25% (w/w chitosan).

Gelatin solution at 10%(w/v) concentration was prepared by dissolving 1 g of gelatin powder in 10 mL of deionized water and then heating at 70°C for 30 min.

After preparing the chitosan-glycerol mixture, the gelatin solution was added at 10% (w/v) to obtain the chitosan-glycerol-gelatin coating solutions. The resulting solution was stirred at 500 rpm at room temperature for 1 h.

After that Nanoclay dispersed solution (10% DS) was added in the two different composition (10% and 20% w/w of total polymer) in the solution.

Table 8: Chitosan Based four coating formulation.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	Ch-1	Chitosan/Glycerol/Gelatin	0	7.5±0.2
2.	Ch-2	OS+Chitosan/Glycerol/Gelatin	2.5±0.2	8 ± 0.2
3.	Ch-3	OS+Chitosan/Glycerol/Gelatin+ Nanoclay (10%)	2.5±0.2	8 ± 0.2
4.	Ch-4	OS+Chitosan/Glycerol/Gelatin+ Nanoclay (20%)	2.5±0.2	8 ± 0.2

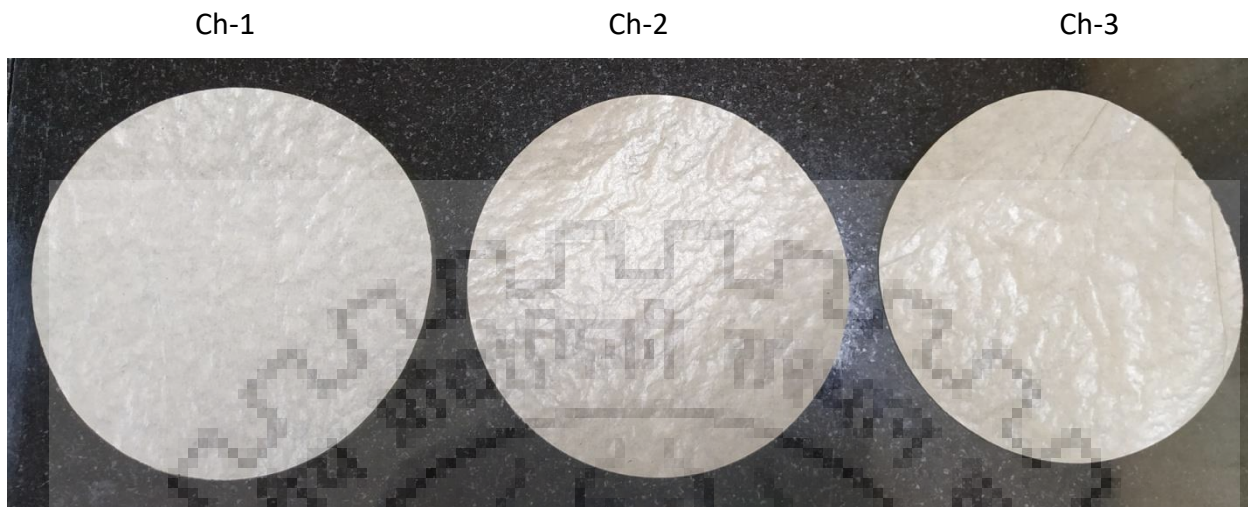


Figure 9: Coated sample of chitosan based coating.

Results:

Table 9: Cobb value, KIT, Seal Strength and WVTR results for Chitosan based four coating formulation.

S.No.	Sample	Cobb(30 min)	KIT Value	Heat Seal Strength (N/m)	WVTR (g/m ² per days)	Tensile Index (Nm/g)
1.	Ch-1	56.4	11	NA	186.18	29.64
2.	Ch-2	52.2	11	NA	180.80	28.36
3.	Ch-3	49	10	NA	145.71	27.61
4.	Ch-4	43.5	10	NA	132.94	26.84



3.1.2 Modified starch based barrier coating:

Materials: Oxidized starch powder with a molecular weight of 650g/mol from CPPRI . Citric acid and glycerol were purchased from Himedia Chemicals and Nanoclay from Yash Paper Ltd.

Preparation of Coating Solutions: Oxidized starch based coating solution was prepared by dissolving 10% (w/v) oxidized starch in distilled water(80°C) and constant stirring via the use of a magnetic stirrer at 500 rpm for 30 min. maintain at 80°C temperature and then cool it at room temperature. To improve the film formation and materials properties of starch, plasticization and chemical modification e.g. cross-linking of the starch is required. Plasticizer such as Glycerol, and cross-linking agent Citric acid with three carboxylic group were used. After solution comes at room temperature citric acid 10% w/w of starch and Glycerol 25% w/w of starch were added and resulting solution was stirred for 1 hr at room temperature.

After that Nanoclay dispersed solution (10% DS) was added in the two different composition (10% and 20% w/w of total polymer) in the final solution.

Table 10: Modified Starch based four coating formulation.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	St-1	Starch/Glycerol/Citric acid	0	9 ± 0.2
2.	St-2	OS+ Starch/Glycerol/Citric acid	2.5±0.2	9.5 ± 0.2
3.	St-3	OS+ Starch/Glycerol/Citric acid + Nanoclay (10%)	2.5±0.2	9.5 ± 0.2
4.	St-4	OS+ Starch/Glycerol/Citric acid + Nanoclay (20%)	2.5±0.2	9.5 ± 0.2



St-1

St-2

St-3



Figure 10: Coated sample of modified starch based coating.

Results:

Table 11: Cobb value, KIT, Seal Strength and WVTR for Modified starch based four coating formulation.

S.No.	Sample	Cobb (30 min.)	KIT Value	Heat Seal Strength (N/m)	WVTR (g/m ² per day)	Tensile Index (N-m/g)
1.	St-1	46.8	11	166.5	156.2	24.70
2.	St-2	47	11	170	159.77	25.34
3.	St-3	38.5	11	125	142.44	28.34
4.	St-4	38	10	112	124.33	27.82



3.1.3 Sodium alginate based barrier coating:

Materials: Sodium alginate (viscosity 15–25 mPa-s 1% (w/w) in water at 25°C) was purchased from Himedia. Nanoclay from Yash Paper Ltd. Glycerol was also obtained from Himedia Chemicals.

Preparation of Coating Solutions: A sodium-alginate coating solution with a solid content of 4% (w/w) was prepared by dissolving sodium-alginate powder in deionized water at a neutral pH. The sodium-alginate powder was added to water in 1.5% (w/w), stirred at 400 rpm, and the aqueous solution was heated for 6 hr at 75°C. After this time, sodium alginate was completely dissolved, resulting in a homogenous coating solution. After complete dissolution, glycerol 25% (w/w of SA), as a plasticizer, was added to enhance flexibility, decrease brittleness.

After preparing the Sodium alginate-Glycerol mixture, Nanoclay dispersed solution (10% DS) was added in the two different composition (10% and 20% w/w of total polymer) in the solution and stirred the resultant solution at room temperature for 1 hr.

Table 12: Sodium Alginate based four coating formulation.

S.No.	Sample	Coating formulation	Pre-coat weight(g/m ²)	Coat weight (Pre-coat+Barrier coat) (g/m ²)
1.	Sa-1	SA/Glycerol	0	6.5 ± 0.2
2.	Sa-2	OS+ SA/Glycerol	2.5±0.2	7.5 ± 0.2
3.	Sa-3	OS+ SA/Glycerol + Nanoclay (10%)	2.5±0.2	7.5 ± 0.2
4.	Sa-4	OS+ SA/Glycerol + Nanoclay (20%)	2.5±0.2	7.5 ± 0.2



Figure 11: Coated sample of sodium alginate based coating.

Results:

Table 13: Cobb value, KIT, Seal Strength and WVTR results for sodium alginate based four coating formulation.

S.No.	Sample	Cobb(30min.)	KIT Value	Heat Seal Strength (N/m)	WVTR	Tensile Index
1.	Sa-1	62.4	8	NA	183.44	24.67
2.	Sa-2	68	9	NA	174.11	23.98
3.	Sa-3	53	9	NA	152.32	29.20
4.	Sa-4	54.6	9	NA	152.00	27.21



3. Results and Discussions

3.1 Cobb Test (Water Absorptions):

The barrier performance of the coated paper was evaluated by measuring the water resistant properties (Cobb test) of the paper. The Cobb test was conducted according to the standard TAPPI T441 om-98 under a water pressure of 100 mm within 30 min. According to this test higher the Cobb data, the faster the water absorption rate of the paper. All the data obtained from Cobb test are in gram of water absorbed per meter square of paper in 30 min. In the case of uncoated paper cob value are 25 g/m² which is similar to the chitosan coated paper 1. Chitosan coating on base paper did not provide much barrier against water similarly The Cobb value obtained with alginate-coated paper was slightly lower when compared with uncoated paper. The effect of nano clay are very significant in case of starch based coating, it reduced the water uptake in paper by hydrophobized the coated surface of the paper.

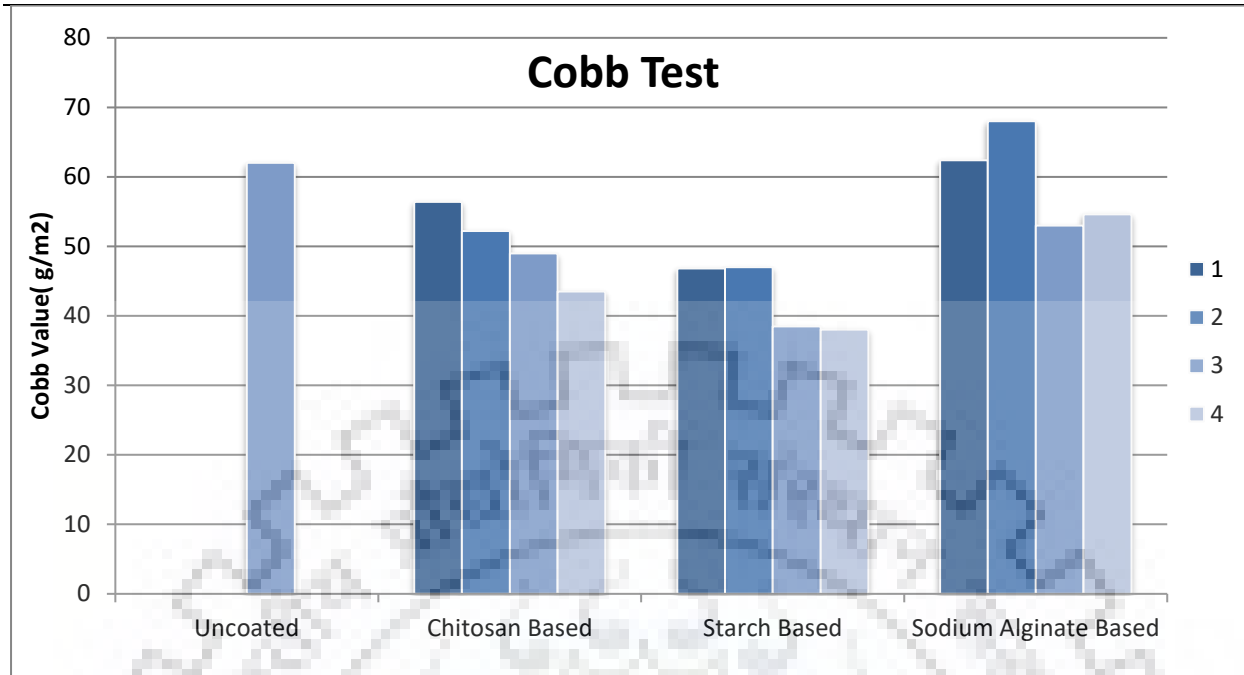
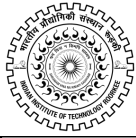


Figure 12: Comparison of Uncoated paper with chitosan based ,modified starch based and sodium alginate based coated paper for their Cobb value.

3.1 Grease Barrier (KIT test):

The barrier performance of the coated paper was evaluated by measuring the repellency of paper to grease oil and wax (KIT test) from the surface of the paper. The KIT test was conducted according to the standard TAPPI T559 cm-12 from the Flourochemical agent. These testing procedure were accomplished by testing samples with a series of numbered reagents (varying in surface tension and viscosity) held in bottles in a specially designed kit. The highest numbered solution (the most aggressive) that remained on the surface of the paper without causing failure was reported as the “kit rating” . According to this test higher the KIT number, better resistance against the grease and oil on the coated paper. In the case of uncoated paper kit number are 1 indicate a very poor grease barrier .g/m² which is similar to the chitosan coated paper 1 .Chitosan coating on base paper did not provide much barrier againt water similarly The Cobb value obtained with alginate-coated paper was slightly lower when compared with uncoated paper .The effect of nano clay are very significant in case of stach based coating ,it reduced the water uptake in paper by hydrophobized the coated surface of the paper .The KIT result for bio-based polymer coating are excellent that showing from below figure by the addition of nanoclay the KIT number are slightly reduced due to their occupied interspaced between the polymer matrix . Hence KIT results showing this bio-polymer based coatings are sufficient for packaging grade paper due to its barrier properties against oil and grease.

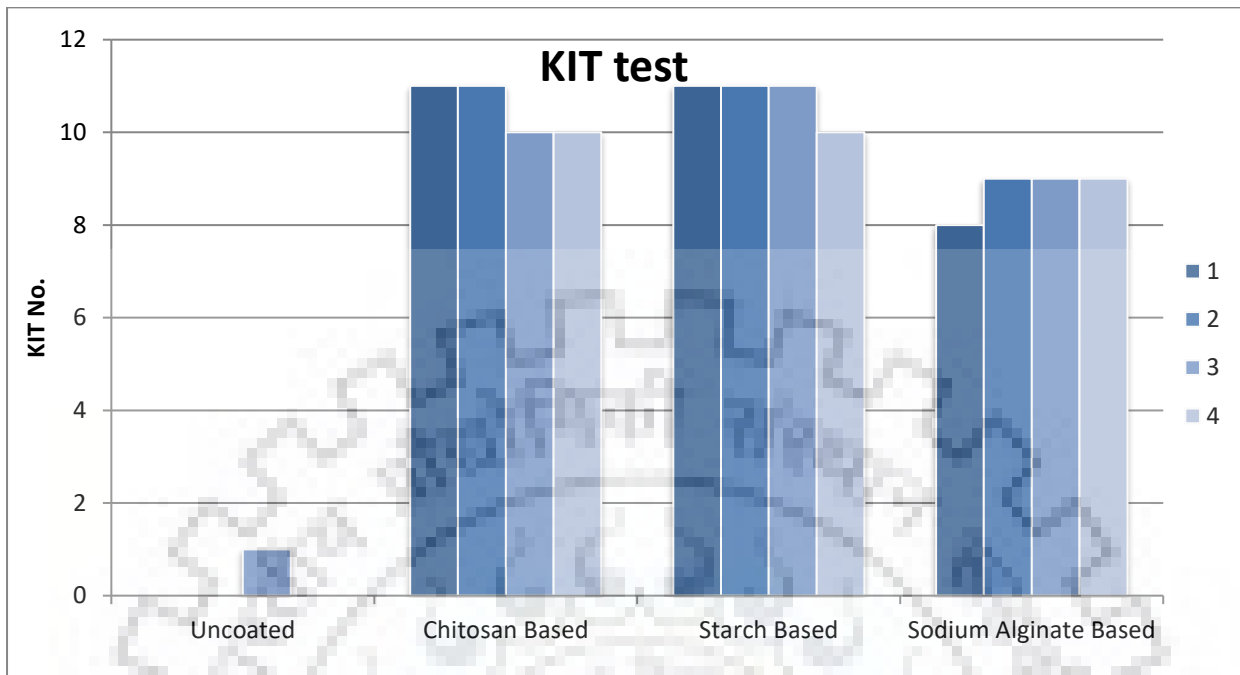
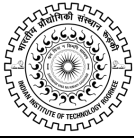


Figure 13: Comparison of Uncoated paper with chitosan based ,modified starch based and sodium alginate based coated paper for their KIT no..

3.1 Heat Sealability:

The heat seal performance of the coated paper was evaluated according to the ASTM Standard Test Method F88 (ASTM, 2005) with some modification. A coated sample was cut into a 10×2.5 cm strip, which were then placed on top of a 10×2.5 cm strips as shown in Figure 2. A 0.5 cm width of the seal area was heat-sealed at 100-200 oC for 10 s using an impulse induction heat sealer. Seal strength of the heat-sealed film was determined by the same texture analyzer according to the ASTM Standard Test Method F88 . Each leg of the sealed film was clamped to the texture analyzer and held perpendicularly to the test direction. The maximum force required to cause seal failure is reported as the seal strength in N/m:

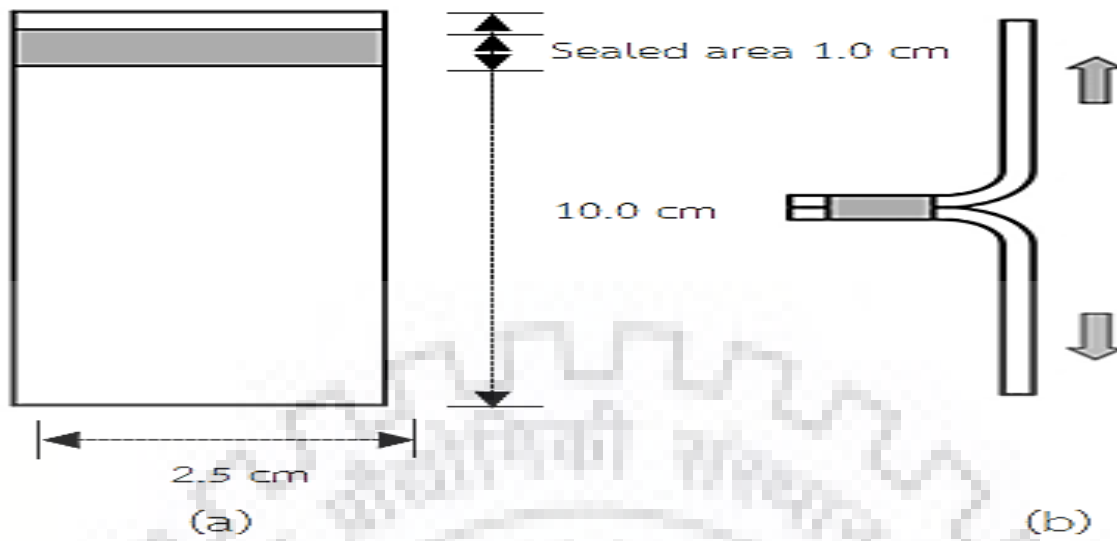


Figure 14: Heat seal test specifications.

The seal strength results showing below are good for modified starch cross-linked with citric acid. In case St-2 seal strength are maximum as compare to others three formulation coating .

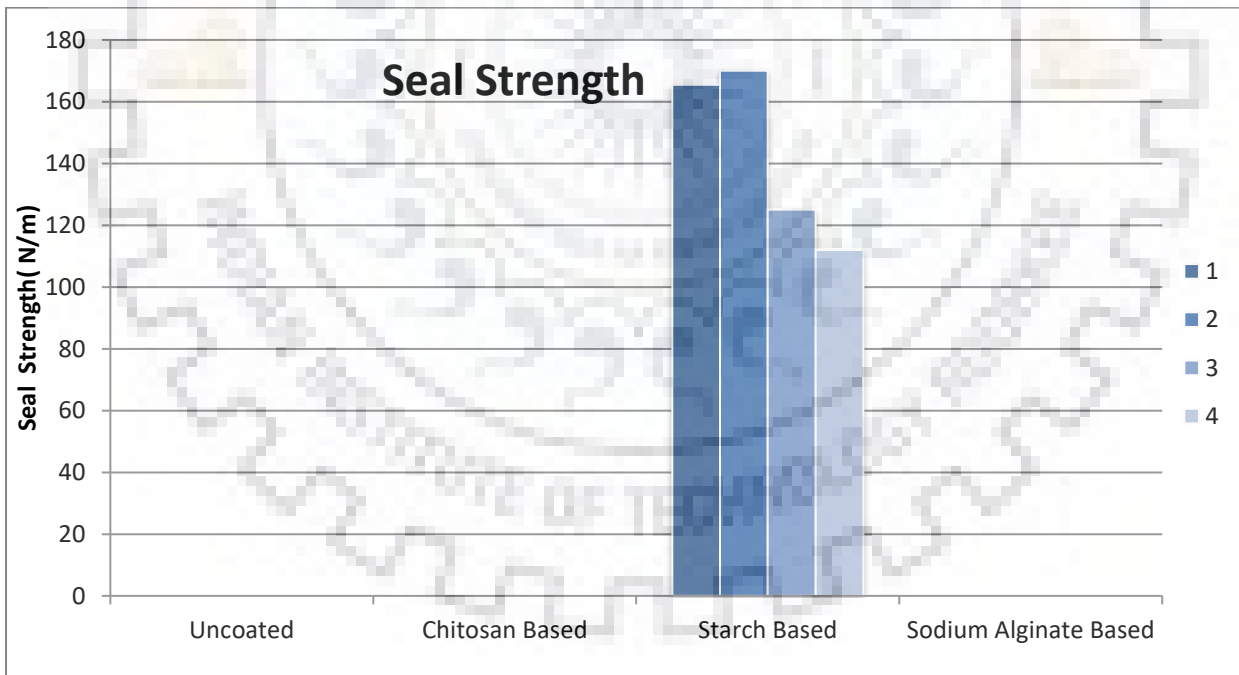


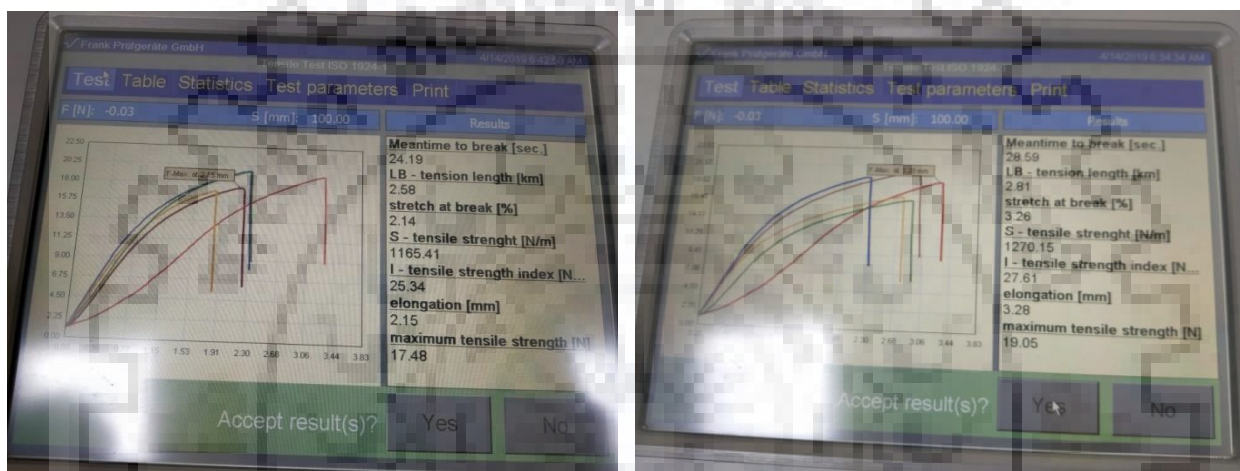
Figure 15: Comparison of Uncoated paper with chitosan based , modified starch based and sodium alginate based coated paper for their Seal strength.



3.1 Tensile Strength :

Tensile strength (TS) are the most commonly reported responses to describe mechanical properties of the packaging grade papers. Here as a wrapping paper mechanical strength and flexibility are required to maintain packaging integrity during shipping, handling, and storage. In general, the mechanical properties of the coated paper are mainly dependent on the base paper and coating weight.

Figure 16: Horizontal tensile test digital panel results.



St-2

Ch-3

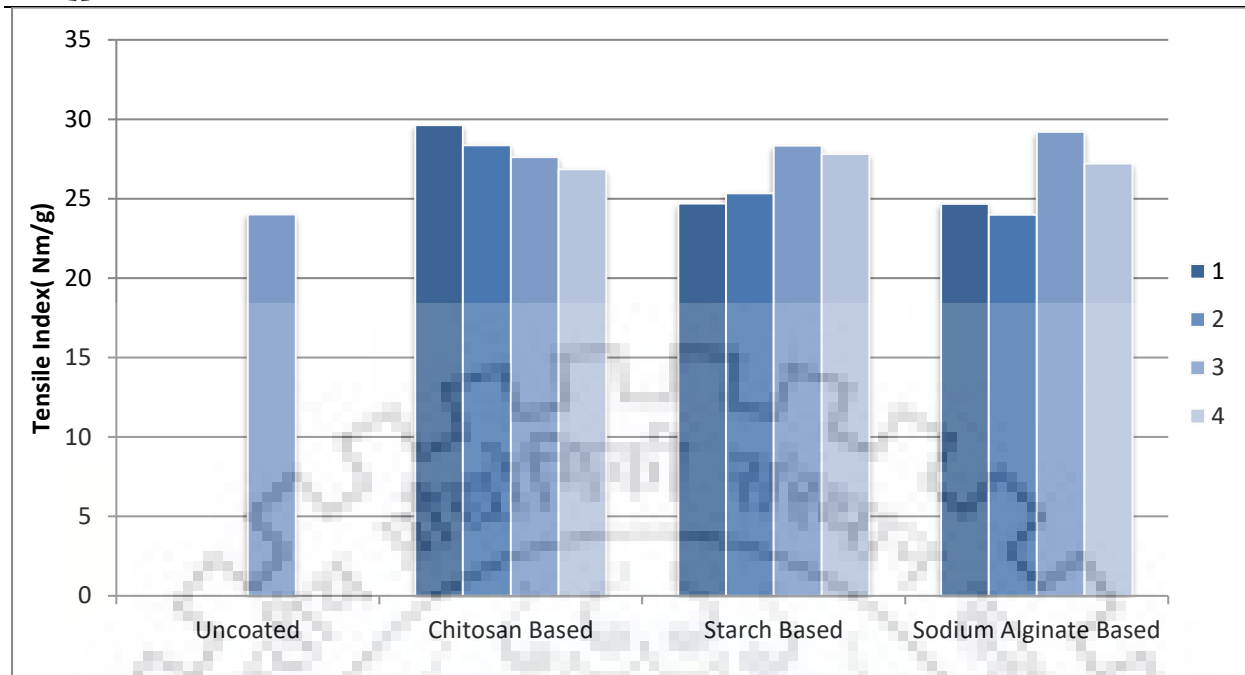


Figure 17: Comparison of Uncoated paper with chitosan based ,modified starch based and sodium alginate based coated paper for their Tensile Index

3.1 Water Vapor Transmission Rate (Moisture Barrier) :

WVTR (water vapor transmission rate) is the steady state rate at which water vapor permeates through a coated paper at specified conditions of temperature and relative humidity. Values are expressed in $\text{g}/\text{m}^2/24 \text{ hr}$ in metric (or SI) units. Testing condition for this coated paper has standardized to 29°C and 50% RH, which is the most common set of conditions reported for wrapping and packaging grade paper. WVTR is the standard measurement by which coated paper are compared for their ability to resist moisture transmission. Lower values indicate better moisture protection. Only values reported at the same temperature and humidity can be compared, because transmission rates are affected by both of these parameters.

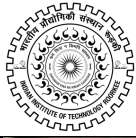


Figure 18: First day WVTR test.



Figure 19: Sixth day WVTR test.

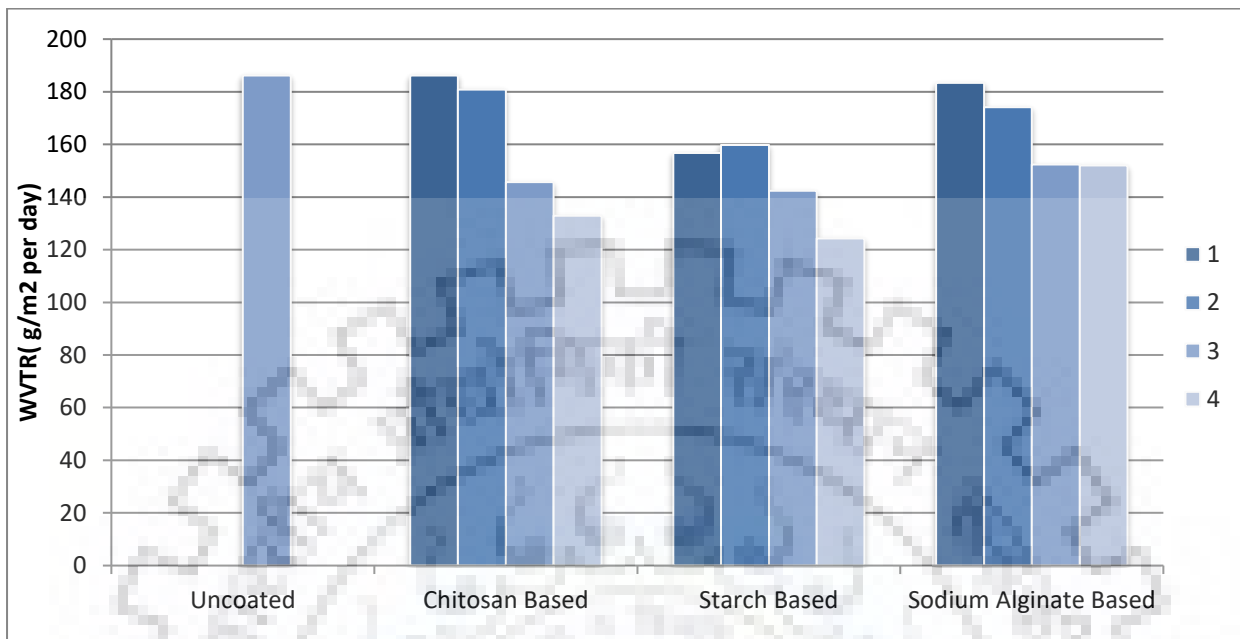
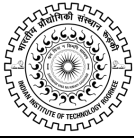


Figure 20: Comparison of Uncoated paper with chitosan based ,modified starch based and sodium alginate based coated paper for their WVTR.

3.1 FE-SEM:

FE-SEM is a versatile, non-destructive technique that reveals detailed information about the morphology and surface texture of the composition of natural and manufactured materials. In this test surface morphology of coated paper are observed to identified the coating layer and compositon.

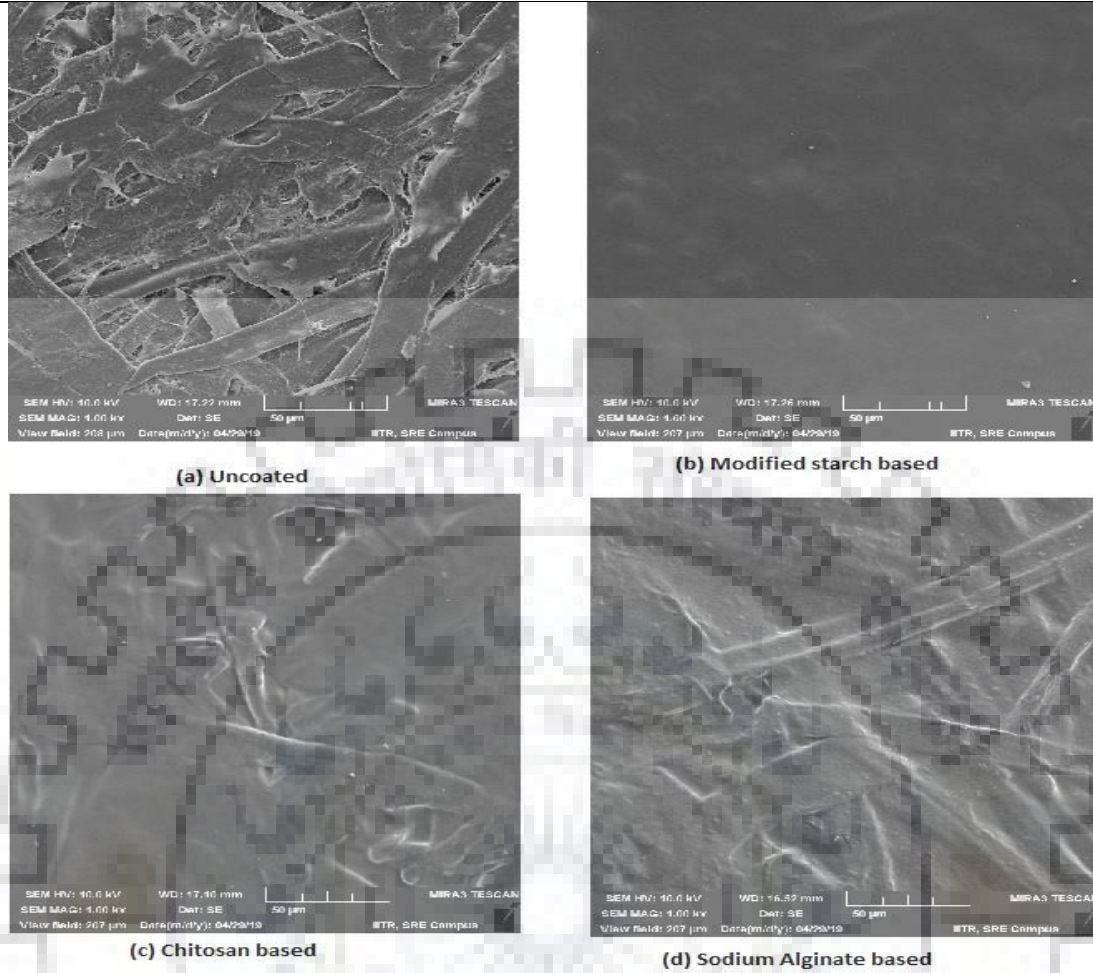
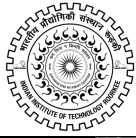


Figure 21: FE-SEM image of surface area of uncoated and coated paper , (a) Uncoated (b) Modified starch based coating (c) Chitosan based coating and (d) Sodium alginate based coating.

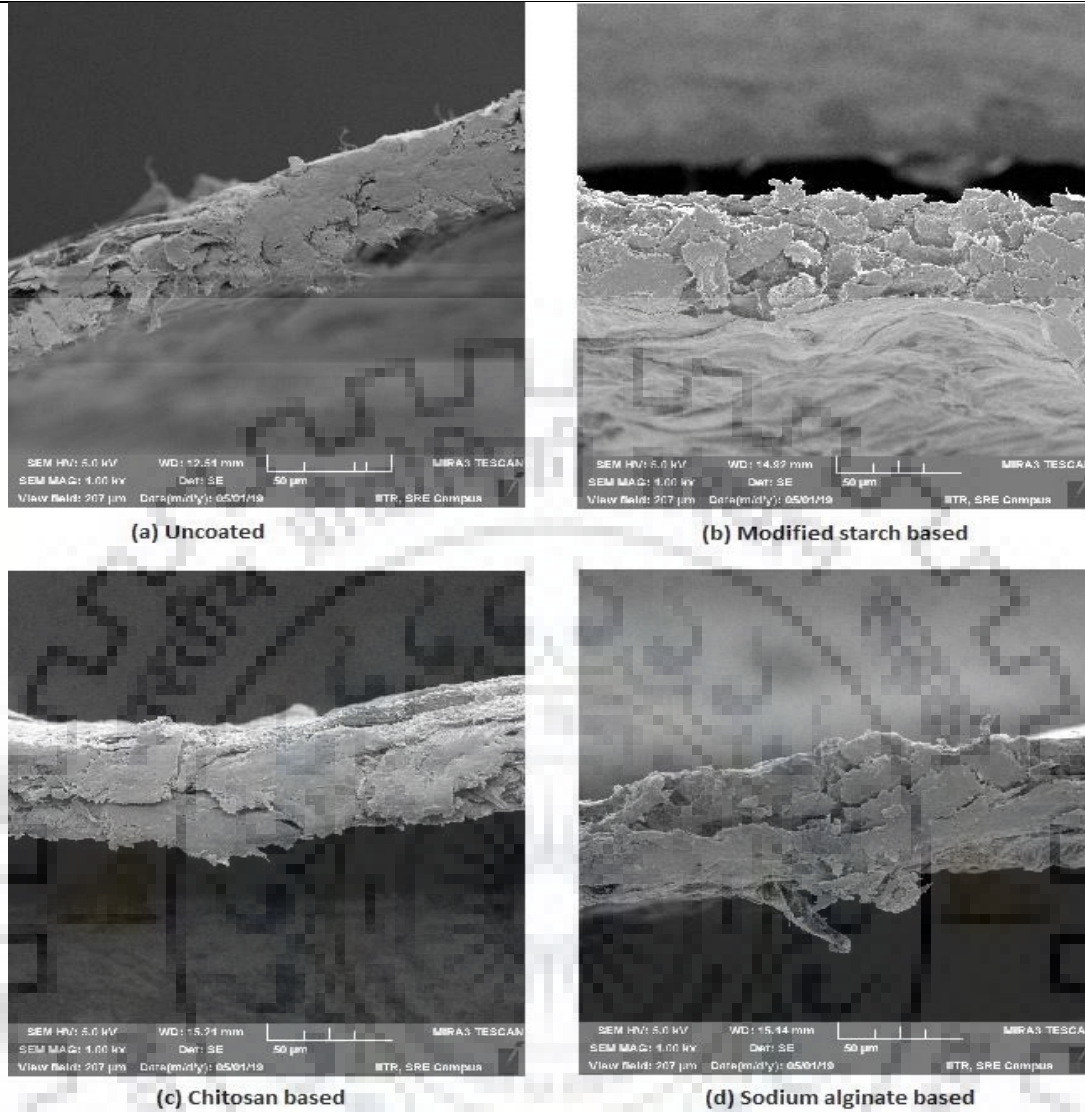
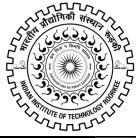


Figure 22: FE-SEM image of cross-sectional area of uncoated and coated paper , (a) Uncoated (b) Modified starch based coating (c) Chitosan based coating and (d) Sodium alginate based coating.



3.1 FT-IR:

Fourier Transform Infrared (FTIR) Spectroscopy is used to perform qualitative and quantitative analysis of organic compounds and to determine the chemical structure of many inorganic compounds. The FTIR microscope permits analysis of coated samples, chemical bonds absorb infrared (IR) energy at specific frequencies (wavelengths), the basic structure of compounds can be determined by the spectral locations of their IR absorptions. The plot of a compound's IR transmission versus frequency is its "fingerprint," which when compared to reference spectra identifies the material.

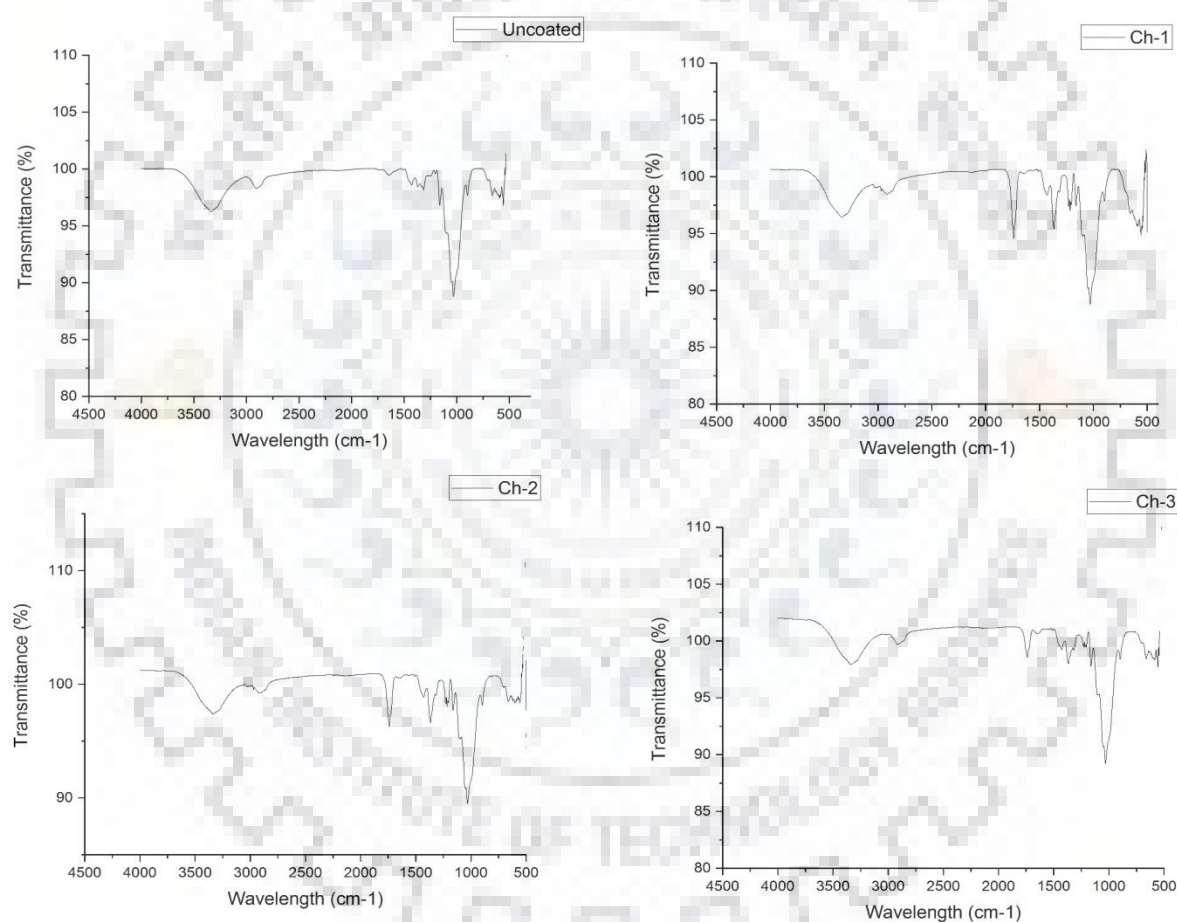


Figure 23: FT-IR peak showing for the uncoated paper and three different coating formulation from chitosan based coating paper.

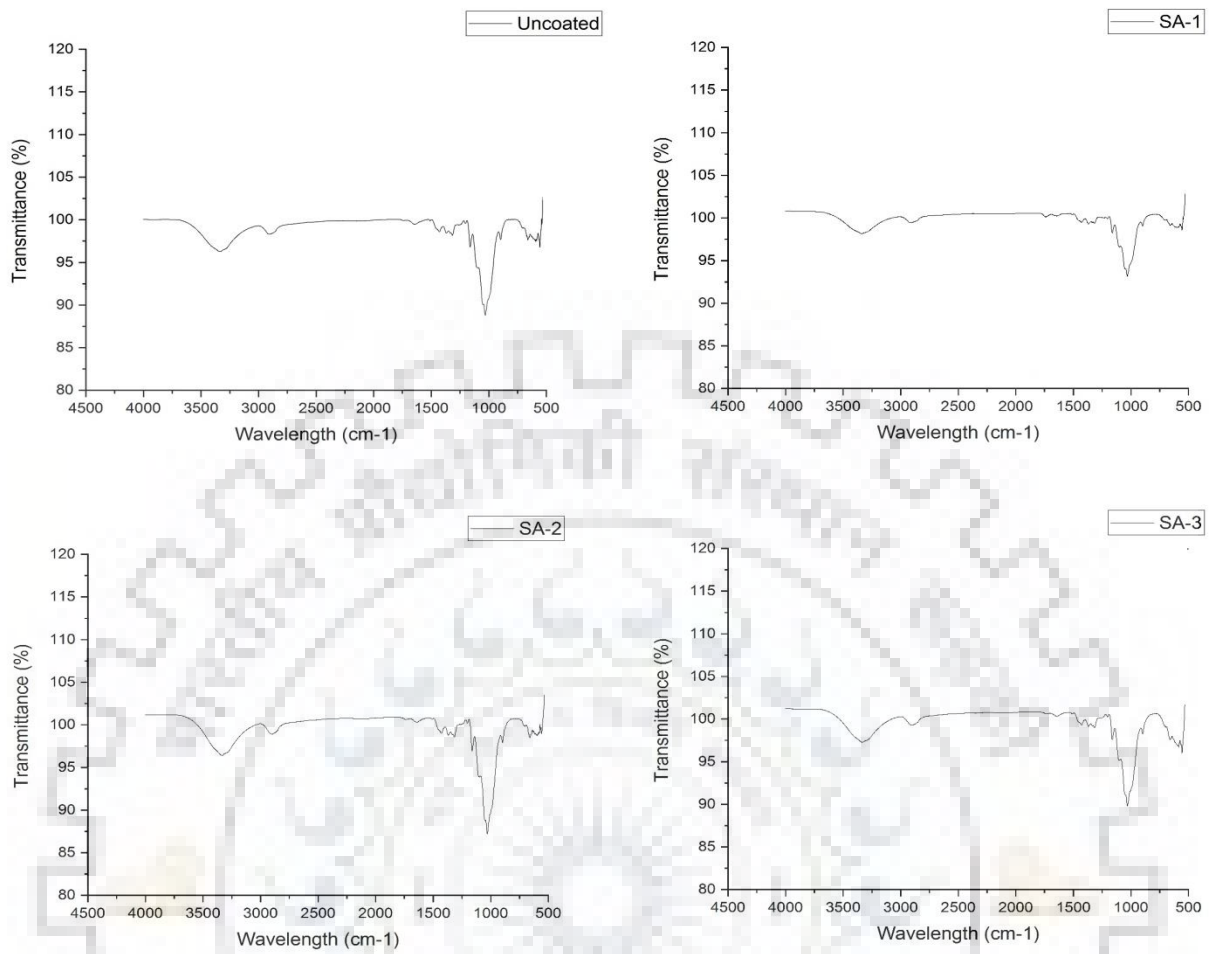


Figure 24: FT-IR peaks showing for uncoated paper and three different coating formulation from sodium alginate based coating paper.

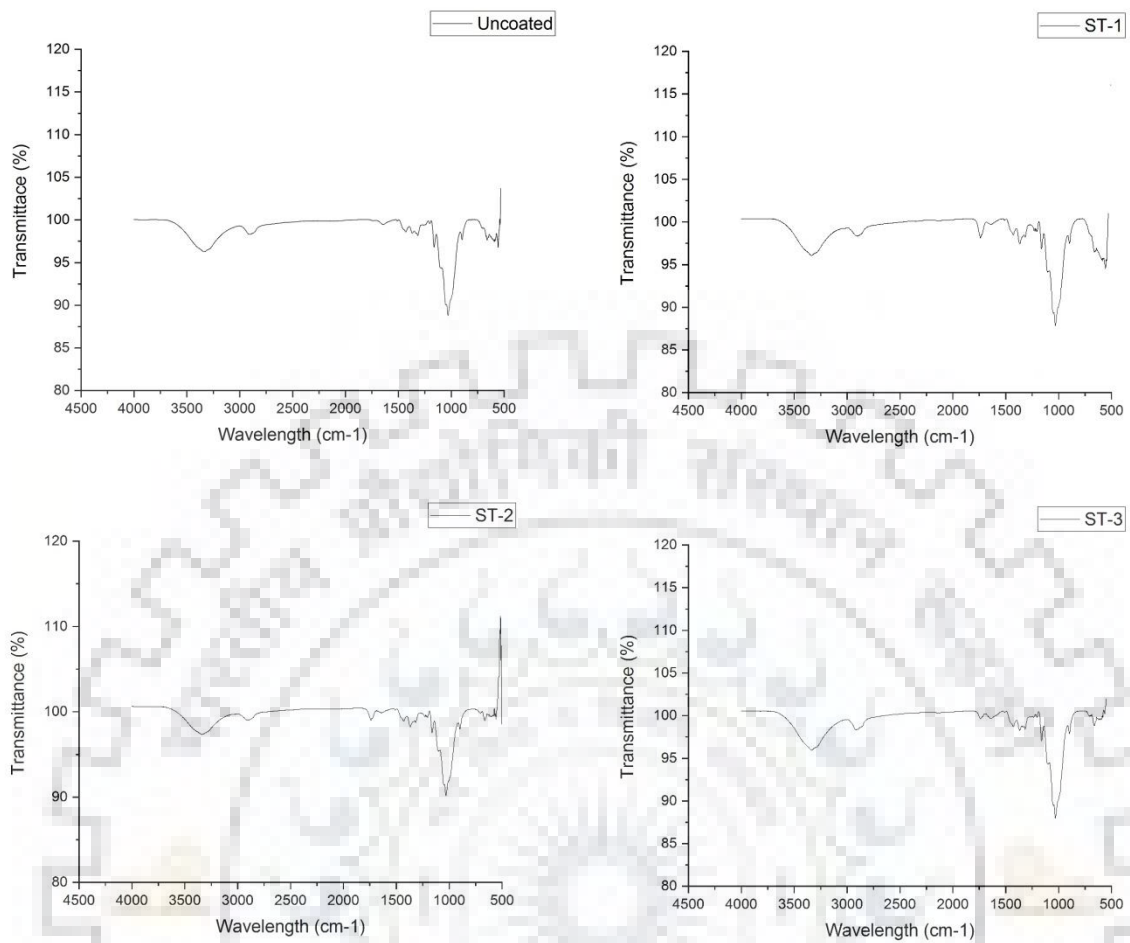


Figure 25: FI-IR peaks showing for uncoated paper and three different coating formulation from modified starch based coating paper.



5. Conclusions:

From the above all the results we can see that Acrylic based coating materials i.e. formula-00, formula-05 and formula-08 are good in all barrier performance and at the same time bio-based coating materials also have good results in some cases. The modified starch cross-linked with citric acid having excellent performance in case heat sealing because bio-polymers are generally not suitable for seal application due to their weak peeling tendency. From the above investigation we can see that modified starch based coating formulations are suitable for the required application for the packaging grade paper.

Consumer demands for more natural foods, and also for environmental protection have excited the development of new packaging materials. Edible films and coatings have been receiving considerable attention over the last years due to their possibility to be used as edible packaging materials over synthetic ones and to reduce environmental pollution. Besides, development of edible films and coatings can reduce post-harvest losses and also can provide less expensive packaging materials for industry and lower the prices of food products.



5. Rererences:

1. Park, H.J. and Chinnan, M.S. (1995). Effect of Plasticizer Level and Temperature on Water Vapor Transmission of Cellulose-Based Edible Films, *J. Food Process Engg*, 18(4): 417–429.
2. Ke, Z. and Yongping, B. (2005). Improve the Gas Barrier Property of PET Film with Montmorillonite by in situ Interlayer Polymerization, *Mater. Lett.*, 59(27): 3348–3351.
3. Lagarón, J.M., Cabedo, L., Cava, D., Feijoo, J.L., Gavara, R. and Giménez, E. (2005). Improving Packaged Food Quality and Safety. Part 2: Nanocomposites, *Food Addit. Contam*, 22(10): 994–998.
4. Yang, H.S., Yoon, J.S. and Kim, M.N. (2005). Dependence of Biodegradability of Plastics in Compost on the Shape of Specimens, *Polym. Degrad. Stab.*, 87(1): 131–135.
5. Dogan, N., & McHugh, T. H. (2007). Effects of microcrystalline cellulose on functional properties of hydroxy propyl methyl cellulose microcomposite films. *Journal of Food Science*, 72(1), E016eE022. <http://dx.doi.org/10.1111/j.1750-3841.2006.00237.x>.
6. Leceta, I., Guerrero, P., de la Caba, K., 2013. Functional properties of chitosan-based films. *Carbohydrate Polymers* 93, 339-346.
7. Abdelhedi, O., Nasri, R., Mora, L., Toldrá, F., Nasri, M., Jridi, M., 2017 Collagenous proteins from black-barred half beak skin as a source of gelatin and bioactive peptides. *Food Hydrocolloids* 70, 123-133.
8. Andres C. 1984. Natural edible coating has excellent moisture and grease barrier properties. *Food Processing* 45(13):48–9.
9. Anker M. 1996. Edible and biodegradable films and coatings for food packaging: a literature review. Goteborg, Sweden: SIC
10. Alves, V. D., Castelló, R., Ferreira, A. R., Costa, N., Fonseca, I. M., & Coelho, I. M. (2011). Barrier properties of carrageenan/pectin biodegradable composite films. *Procedia Food Science*, 1, 240–245



11. Bonilla, J., Atarés, L., Vargas, M., & Chiralt, A. (2012). Edible films and coatings to prevent the detrimental effect of oxygen on food quality: Possibilities and limitations. *Journal of Food Engineering*, 110(2), 208–213.
12. Dettmar, P. W., Stugala, V., & Richardson, J. C. (2011). The key role alginates play in health. *Food Hydrocolloids*, 25, 263–266.
13. Wang, L., Auty, M. A. E., & Kerry, J. P. (2010). Physical assessment of composite biodegradable films manufactured using whey protein isolate, gelatin and sodium alginate. *Journal of Food Engineering*, 96(2), 199–207.
14. Han, J. H., & Aristippos, G. (2005). Edible films and coatings: A review. In J. H. Han (Ed.), *Innovations in food packaging* (pp. 239–262). San Diego, CA: Academic Press.
15. Lee, K. Y., Shim, J., & Lee, H. G. (2004). Mechanical properties of gellan and gelatin composite films. *Carbohydrate Polymers*, 56(2), 251–254.
16. Tharanathan, R. N. (2003). Biodegradable films and composite coatings: Past, present and future. *Trends in Food Science and Technology*, 14(3), 71–78.

