

Surface sizing of paper with polyvinyl alcohol

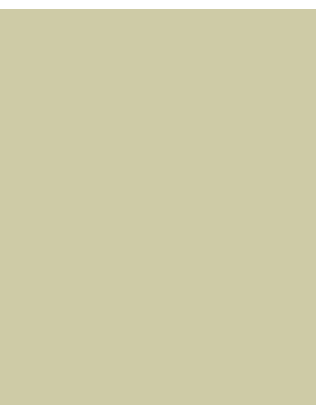
Abstract: *During surface sizing, some amount of the applied surface sizing agent penetrates into the uneven structure of paper and the rest forms a layer on the surface of paper. Use of enzymatically modified or oxidized starch for surface sizing is a common practice in paper mills. Polyvinyl alcohol (PVA) is a water soluble polymer having high film forming ability that makes it a good surface sizing agent. In present study, PVA was cooked in different concentrations (1 to 8% W/V) and applied on paper in different amounts using different rods of automatic laboratory bar coater. After surface sizing with PVA at different sizing weights followed by calendering, the strength and optical properties of paper were increased in comparison to control (Base paper/ starch surface sized paper). After surface sizing with 2% PVA using rod 4, the time for air leak before/ after calendering was found to be 850/ 3500 Gurley seconds whereas with 4% PVA using rod 2 the time for air leak before/ after calendering was found to be 2000/ 5000 Gurley seconds. The modifications after surface sizing with PVA on the paper surface were investigated using FTIR and SEM.*

Key Words: *Polyvinyl alcohol; Air permeance; Surface sizing; Paper formation; Optical properties*



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Introduction

Paper industry is among those well established industries that have a large scope of improvement in the manufacturing process as well as the quality of end product. For this, research interest around the world is growing on a rapid pace. The areas of research include: i) Reducing effluent load due to pulping and bleaching ii) Identifying new raw materials and blending them with different existing raw materials of papermaking iii) Use of different available bio based additives to replace synthetic additives during papermaking iv) To reduce the energy of refining the pulp by use of enzymes or other bio based chemicals v) To increase the mechanical and surface properties of paper by use of certain biopolymer in papermaking vi) To modify the paper surface by paper coating.

In papermaking process, surface sizing has become a common practice to fulfill an increasing demand concerning the quality of writing and printing paper (W&P) grades (1). Scarce research has been done on surface sizing of paper. The process of manufacturing different paper grades depends on the end product requirement like for W&P grades bleaching is required

whereas for liner board (back bone of paperboard packaging) no bleaching is required. But to improve the surface properties of both W&P and liner board, surface sizing is required. Surface sizing is a process aimed to control the penetration of liquids into paper for improvement in printability and absorption properties of paper (2-4). Surface sizing of W&P and liner board will give better printing quality to W&P and in paperboard it will help in providing better barrier properties. The surface sizing will further benefit in many other properties of both W&P and paperboard. Different chemicals have been used to modify the paper surface to alter its hydrophilic character to prevent excessive absorption of liquids and inks (1,5). The primary purpose of these surface modifications by polymeric additives is to bridge the inter-fiber distances by filling the gaps and establishing bonds between fibers and fibrils that would not have otherwise formed (6). The combination of several factors such as sizing agents (chemical composition, viscosity, temperature, pH, charge, other additives, etc.) and initial paper properties (basis weight, bulk, internal sizing, moisture content, porosity, surface energy, surface roughness, etc.) are known to influence the ultimate impact of surface sizing process (4). Surface sizing is carried out to provide base paper with the right hydrophobicity which should prevent the larger portion of ink from penetrating and absorbing more in to paper with simultaneous stay or adsorption onto the surface of the paper without spreading (7).

Paper properties are mostly dependent on the pulp refining level. Paper tensile strength will increase to some extent with refining whereas the other like tear, stiffness, etc. will decrease. So, the end paper properties requirement and the raw material quality need to be considered and optimized to fulfill end properties requirement perfectly. For a good packaging grade paper, good tear strength and good barrier properties are desired. The paper made from more refined pulp will give better air resistance but the tear will be less. The only solution is to maintain tear by controlled refining of pulp and increase the air resistance with surface sizing. Not only in paperboard but in W&P also, air permeance is important. There are other benefits of surface sizing like with the sizing chemical other required chemicals can be added (synthetic or biomaterials) for specific purpose. For example in W&P paper the optical whitening agent can be used with sizing chemical to increase the optical properties of paper whereas in paperboard of packaging grade paper the anti microbial agents or humectants or any other chemical can be added and applied to attain the desired properties. The addition of such chemical in wet-end of papermaking is less efficient whereas the addition with surface sizing agent on dried paper is more effective and easy.

Polyvinyl alcohol (PVA) is used for surface sizing for its specific properties including good adhesion to fillers and fibers, good film forming property, good barrier

properties, etc. It is a colorless, flammable, odorless, tasteless, translucent and granular water soluble synthetic polymer. It is derived from polymerization of vinyl acetate using radical initiator and methanol as solvent and chain transfer agent and its subsequent hydrolysis with methanol and sodium hydroxide (8). The benefits of using PVA are improved surface strength and dimensional stability of the sized paper, decreased picking and dusting in printing, reduced water absorption etc. (8). PVA is a semi crystalline polymer which comprises of the hydrocarbon chain bearing hydroxyl group on every second carbon. It shows strong interactions between its monomers due to hydrogen bonding between hydroxyl groups (9). The studies revealed that fully hydrolyzed PVA makes strong hydrogen bonding with neighboring chains, which further arrange themselves in a tightly packed structure (10-12). Besides, PVA is non-immunogenic, non-mutagenic and non-carcinogenic, so its application in different areas is promising as far as the health issues are concerned (13). Despite many advantages, the use and availability of the literature regarding PVA in paper industry is very limited. PVA is used for sizing while in paper coating it is used as adhesive with latex or starch or can be used alone (14). The film forming capacity of PVA is high because it contains large numbers of hydroxyl ions which form hydrogen bonds with fibers (15). Starch blended with PVA forms films that are biodegradable and with strength properties better than LDPE-films (16). PVA films

possess good barrier properties for gases; this barrier property provides potential application of PVA in food packaging (14).

To prepare the paper with high air permeance, papermakers have to do extra refining that eventually decreases the tear, bulk

and stiffness of the paper. With application of oxidized starch (OS) as surface sizing agent the optical properties are reduced. Here, the application of PVA may provide higher air permeance and better optical properties than OS when used for surface sizing of paper.

The aim of the present study was to investigate and compare the performance of different concentrations (1 to 8% W/V) of PVA as sizing agent to oxidized starch and determine their specific impact on the physical, structural and surface properties of the paper.

Materials and Methods

Materials

The base paper used for surface sizing in the present study was procured from an integrated pulp and paper mill of north India and PVA was also obtained from a paper mill. The oxidized starch was obtained from Bharat Starch Industries Limited, Yamuna Nagar. All other chemicals used for present work were of high purity and analytical grade.

Analytical techniques

Characterization of oxidized starch and PVA

Gelatinization temperature of oxidized starch was 70°C as given by the provider. Method IS: 4706 (part II) was used to determine the moisture and total ash content of starch. The viscosity of the starch was measured by using Brookfield viscometer using spindle number 1 at speed of 100 rpm. The cold water solubility of starch was determined by the method adopted by Eastman & Moore 1984 (17).

The characteristics of PVA e.g. degree of hydrolysis, ash content, purity and volatile matter were already given by the provider as 98.7%, 0.31%, 95.8% and 3.43%, respectively. The IS method (IS: 12715) was used for the measurement of moisture content of PVA. The viscosity of PVA was analyzed using same method as for the oxidized starch. The charge demand for both OS and PVA was measured on Mutek PCD 03 pH Particle Charge Detector; here both OS and PVA were titrated with cationic/ anionic polymer to neutralize the charge.

FTIR-ATR (Attenuated total reflectance) analysis

The FTIR-ATR spectra were obtained by means of Frontier MIR LiTa/KBr/Al spectrometer (PerkinElmer, UK). Base and surface sized paper were analyzed by using ATR cell operating with a resolution of 1 cm⁻¹, 50 scans, in the range of 4000 to 400 cm⁻¹. The crystal used in the ATR cell (from PIKE Technologies) was diamond with a refractive index of 2.4. Incident radiation at an angle of 45° was applied.

Scanning Electron Microscopy (SEM)

Scanning electron microscope (JEOL JSM- 6510 LV) was used for analyzing the surface morphology of the base paper with and without surface sizing with PVA. The sample of the base paper with or without surface sizing was cut into pieces of 1 by 1 cm² and coated with 5 nm thick gold film before analysis. The scanning electron micrographs were taken at various magnifications and the micrograph at 300 and 1500X magnification were used for presenting the difference in surface characteristics after surface sizing.

Preparation of oxidized starch and PVA

A slurry of 6%, 10% and 14% (w/v) oxidized starch was prepared using distilled water. The dispersed slurry was taken to a beaker that was further placed into another beaker containing boiling water to maintain the temperature of slurry at 90°C. The cooking of OS was done on a boiling water bath with continuous mild stirring for about 30 minutes. PVA was dispersed to 15% (w/v) slurry by mixing it with distilled water

and cooked by similar process as that of oxidized starch but only for 20 minutes. The cooked PVA was then diluted to different concentrations (1 to 10%) by mixing it with distilled water.

Surface sizing

The oxidized starch of 6%, 10% and 16% was used for surface sizing. The PVA solutions of 1 to 10% were used for surface sizing. After cooking the sizing agents (oxidized starch and PVA) in water bath for surface sizing of base paper, the sizing agents were applied using an automatic laboratory bar coater (RK print coater). The sizing agent pick up (sizing weight or g/m²) could be controlled by using rods of different numbers and by adjusting speed of the bar coater. In the present study, the speed was taken constant (at maximum). The surface sizing with oxidized starch (of different concentrations) was done with rod 4 only. PVA (of different concentration) was surface sized with different rods (1 to 4) for minimum and maximum application of PVA on the base paper surface. The rods of different number are used because each rod allows only a specific space between the base paper and the rod surface. The rod 1 provides the minimum space while the rod 4 provides the maximum. At same concentration of PVA the viscosity is same therefore; when different rods are used for application the amount

applied is directly proportional to the space available between the rod and the base paper. After surface sizing the sheets were supercalendered in plant scale supercalender by applying a linear nip pressure of 76 bar at 50°C. All the sheets were passed through double nip.

All sheets after sizing agent application (uncalendered or supercalendered) were conditioned at 27±2°C and 65±5% relative humidity for 24 hours as per ISO: 187.

Paper properties

The strength and surface properties of hand sheets like burst index (L & W Bursting Strength Tester, Code:181), breaking length (L & W Tensile Strength Tester, Code:060) were determined as per standards IS:1060 (Part I). Air permeance (L & W, Air Permeance Tester Code:SE 166) and wax pick number were determined by following T 460 om-11 and IS:1060 Part III, respectively. Paper gloss was measured as per ISO 8254-3 using L & W gloss tester code 224. Optical properties were measured by instrument Elrepho of L & W, code 070/071. Formation index was measured by Micro-Scanner code LAD07. All the experiments were performed in triplicate and the average value was reported.

Results and Discussion

The study was carried out to encounter the effect of surface sizing with different concentrations of PVA solution and its application with different rods. Surface properties as well as physical properties of paper surface sized with different concentration of PVA solution with same rod and with different rods showed significant differences in comparison with paper surface sized only with oxidized starch. Hence, optimum combination of concentration of PVA solution and the applicator i.e. rod was screened for comparable or better quality of paper surface sized with oxidized starch solution.

Characterization of PVA and oxidized starch solution

The PVA solution of different concentrations was made diluting the original cooked solution of 15% (W/V). The solids level of PVA at different concentration levels along with viscosity at same temperature is shown in table 1. The viscosity data shows that the viscosity of 4% PVA solution was 60 cP. The viscosity 60 cP is appropriate for surface sizing because mostly paper mills carry out surface sizing using starch (10-20% solid content) with viscosity ranging 25-90 cP. General properties of 1% solution namely streaming potential, colloidal charge,

Table 1: Characterization of PVA

PVA solution, %	1	2	4	6	7	8	9	10
Viscosity, cP	16	25	60	160	259	436	760	1356
Temperature, °C	20							
Solids, %	1.14	2.22	4.21	6.28	7.23	8.16	9.22	10.3

viscosity at 30°C and pH for oxidized starch were found to be -160 mV, 215 µeq/g (cationic charge demand), 10 cP and 6.00, respectively whereas for PVA the values were -105 mV, 50 µeq/g (cationic charge demand), 14 cP and 6.00, respectively. Moisture content and total ash content of oxidized starch were 11.6% and 3.3%, respectively. Viscosity of oxidized starch was 16 cP at 6%, 33 cP at 10% and 75 cP at 16% solids level at 60°C. Cold water solubility was found to be 5.22%. Moisture content of PVA was 1.33%.

Effect of surface sizing of PVA on breaking length and burst of uncalendered paper

Breaking length in machine direction (MD)/ cross direction (CD) was increased after surface sizing with 4% PVA solution with different rods 1 to 4. Breaking length (meter) of base paper used for surface sizing was 4051/ 2112 in MD/ CD. Surface sizing with 4% PVA solution with different rod 4 increased the breaking length to 4954/ 2612 (MD/ CD) in comparison to the base paper. Impact on breaking length after surface sizing with different rods is shown in table 2.

Table 2: Effect of surface sizing with PVA on strength properties of uncalendered paper

Particulars	Base	Rod 1	Rod 2	Rod 3	Rod 4	
PVA solution, %	-	4				
Breaking length, m	MD	4051	4423	4613	4812	4954
	CD	2112	2293	2413	2545	2612
Burst index, kN/g	5.91	6.12	6.27	6.33	6.51	

The increase in breaking length may be attributed to the fact that after surface sizing the PVA filled the pores of the paper and at the same time forms a layer on the surface. Due to the pores filling and film formation on the surface the breaking length increased.

Increase in burst strength with surface sizing with PVA was observed and calculated in terms of burst index. Burst index of base paper was found to be 5.91 kN/g which increased after surface sizing with 4% PVA solution with all rods 1, 2, 3 and 4. The results are similar to earlier study where breaking length and burst index of paper increased after surface sizing with PVA (18). The increased values of burst index after surface sizing are given in table 2. The maximum value of burst index attained was 6.51 after surface sizing with rod 4.

Effect of surface sizing with PVA on air permeance of paper with and without supercalendering

The time required for 100 ml air to flow through the sample is reported as the value of air permeance. The air permeance of base paper was found to be 14 Gurley seconds. The surface sizing of base paper was done using oxidized starch and PVA. The concentration of oxidized starch used for surface sizing was 6%, 10% and 16% whereas PVA concentration was taken from 1% to 10%. The rod 4 was fixed for performing surface sizing with oxidized starch (all concentrations) so that maximum amount of starch pick up can be maintained at the fixed concentration. As the viscosity of PVA above 4% concentration is high therefore above 4% PVA concentration

the surface sizing was done with rod 0 only so that minimum amount can be coated on the base paper. Till 4% PVA concentration, as the viscosity was not so high, the rods used for surface sizing were 1 to 4 so that at fixed concentration the different amount of PVA could be coated (from low to high i.e. rod 1 will coat the least amount of PVA while rod 4 will coat the highest) and comparison could be done with maximum amount of starch coated base paper at that starch concentration.

Starch of 6% concentration when coated on base paper with rod 4 provided 30 Gurley seconds whereas after supercalendering the value increased to 81 Gurley seconds. The results are similar to earlier study where improvement in air leak time of paper after surface sizing with PVA was observed (6,15,18).

1% PVA when coated with rod 1 on base paper provided 29 Gurley seconds whereas after supercalendering the value increased to 87. The figure 1 shows the comparison of 6% starch coated with rod 4 with 1% PVA solution coated with rod 1 to 4. As observed in figure 1, 1% PVA solution when coated with rod 1 is almost comparable to 6% starch coated with rod 4 and on further increasing the rod number for PVA sizing provides better Gurley seconds than that of starch at 6%. The air leak time increases after supercalendering. In supercalendering the paper is pressed under nip load. This pressure allows the paper fibers to fill the hills and valley of the paper surface and if sized with PVA, the PVA application also becomes more uniformly distributed. As the pores of paper are now closed after supercalendering therefore the time for air leak or Gurley second increases multifold after supercalendering. The results are similar to earlier study where air permeance of paper surface sizing with PVA increased after supercalendering (19).

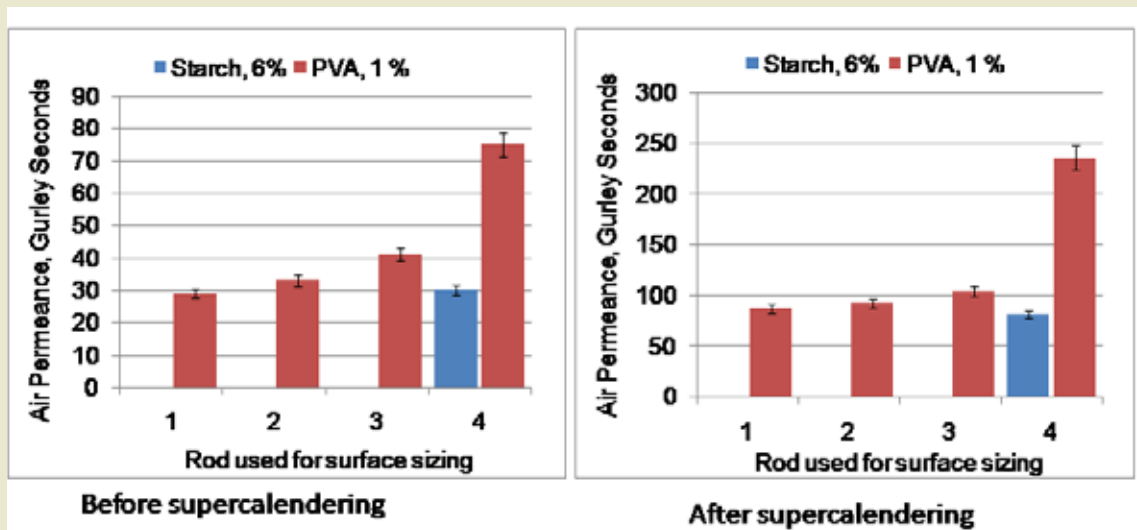


Figure 1: Effect of surface sizing with PVA and starch solution on air permeance of paper

Starch of 10% concentration when coated on base paper with rod 4 provides 115 Gurley second whereas after supercalendering the value increases to 738 Gurley seconds. The PVA of 2% when coated with rod 4 on base paper provides 850 Gurley seconds whereas after supercalendering the value increases to 3500. The base paper coated with PVA of 2% with rod 2 and 3 showed Gurley less than that obtained by 10% starch coating with rod 4 in both cases of with and without supercalendering. The figure 2 shows the comparison of 10% starch coated with rod 4 with PVA 2% solution coated with rod 1 to 4. PVA of 2% solution when coated with rod 4 is better than starch of 10% coated with rod 4.

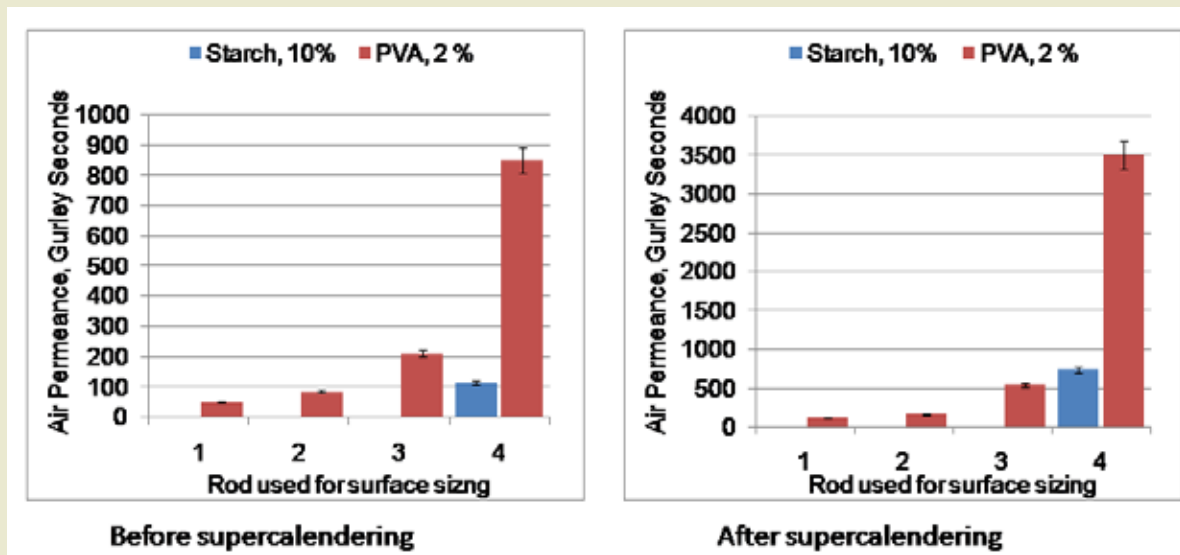


Figure 2: Effect of surface sizing with PVA and starch solution on air permeance of paper

The base paper coated with PVA of 4% with rod 1 and 2 showed Gurley less than that obtained by 16% starch coating with rod 4 in both cases of with and without supercalendering. Starch of 16% concentration when coated on base paper with rod provides 569 Gurley second whereas after supercalendering the value increases to 6190 Gurley seconds. The PVA of 4% when coated with rod 2 on base paper provides 5000 Gurley seconds after supercalendering. The table 3 showed the comparison of 16% starch coated with rod 4 with PVA 4% solution coated with rod 1 to 4. The viscosity of PVA more than 4% is higher therefore the surface sizing was only done with rod 0. The maximum value that the instrument provides as Gurley second is 42500. The value of supercalendered base paper after surface sizing with 4 % PVA by rod 4 provides the same value. The surface sizing with 9% PVA solution by rod 0 before and after surface sizing provided maximum value of air permeance. The conclusion of the table 3 is that PVA of (7 to 10) % solution when coated with rod 0 is better than starch of (6, 10 and 16)% when coated with rod 4 in both cases of with and without supercalendering.

Table 3: Effect on air permeance values after surface sizing with and without supercalendering

Rod	4		1		2		3		4	
PVA solution, %	4									
Starch solution, %	16									
	B	A	B	A	B	A	B	A	B	A
Air permeance, Gurley seconds	569 ±25	6190 ±80	498 ±55	2120 ±65	2500 ±90	5000 ±98	22400 ±350	44900 ±250	45200	45200
Rod	0									
PVA solution, %	6		7		8		9		10	
	B	A	B	A	B	A	B	A	B	A
Air permeance, Gurley seconds	1370 ±65	2890 ±80	6720 ±160	14800 ±450	10800 ±350	33600 ±999	45200	45200	45200	45200

B* -Before supercalendering and A*-After supercalendering

Effect of surface sizing with PVA on Wax Pick and Z-directional strength of uncalendered paper

The Z-directional strength (kPa) of paper refers to the ability of a paper or board to tensile loading is a direction perpendicular to the plane of paper. The Z-directional strength of base paper was 370 which increased to 425 by surface sizing with PVA solution of 4% by rod 4. Value of Z-directional strength in all other cases of surface sizing was found to be less than 425 but higher than that of base paper as shown in table 4.

Table 4: Effect of surface sizing on surface properties of paper before supercalendering

Particulars	Base	Rod 1	Rod 2	Rod 3	Rod 4
PVA solution, %	-	4	4	4	4
Wax pick, Number	14	15	16	17	18
Z-D Strength, kPa	370	385	404	412	425

Wax Pick number of base paper was found to be 14 which after surface sizing with PVA increased to 17 after surface sizing with PVA of 4% with rod 3. The increased value of wax pick after surface sizing with PVA is shown in table 4. The increase in Z-directional strength and wax pick was mainly because of the film forming nature of PVA. After surface sizing with PVA on paper it forms a film due to which both these properties increased. The results are similar to earlier study where wax pick (6,15,18) and Z-directional strength (18) increased after surface sizing with PVA.

Effect of surface sizing with PVA on formation index and gloss of paper with and without supercalendering

Formation analysis is an important paper property which is done using transmitted light having intensity of 128 GL. There is no general method to measure "formation" quality. Formation is generally defined as the small scale variation of the fiber distribution within the sheet. It is possible to have two very different specimens and very different in appearance with the same formation index (20). After surface sizing but before supercalendering the formation index was impacted less. The value of formation index increased more after the application with rod 3 and rod 4 as shown in table 5. After supercalendering the formation index was increased to very high values even when PVA of 1% solution was used for surface sizing. The values of formation index after surface sizing are shown in table 5 and 6. Initially when surface sized sheets were not calendered, the sizing agent (PVA) applied to the paper did not enter into the paper surface and the film formed by PVA is not uniform because the paper was not pressed. But, after supercalendering the sizing agent was equally distributed inside the pores of the paper and film become more uniform because of the applied pressure of the nips.

Table 5: Effect of surface sizing on surface properties before supercalendering

Particulars	Base	Rod 1			Rod 2			Rod 3			Rod 4		
		1	2	4	1	2	4	1	2	4	1	2	4
PVA solution, %													
Formation index	121±12	115±08	121±09	122±10	123±11	131±08	134±11	132±07	139±09	143±11	135±13	141±11	146±10
Gloss, %	6.2	6.2	6.2	6.3	6.4	6.6	6.7	6.4	6.7	6.9	7.1	7.2	7.4

When light hits the paper surface same incident light immediately reflects back from the surface. Angle of reflection is same as that of angle of incident that is light reflects specularly. Gloss of base paper and after surface sizing with PVA was found to be in the range of 6.2 to 7.4. The paper sheets after surface sizing with PVA solution of 1%, 2% and 4% by rod 4 and supercalendering showed gloss in the range of 16-21. The increase in gloss is because after supercalendering the PVA is well distributed inside the paper and the fill formed on the paper is absolutely unified.

The values of gloss after supercalendering are shown table 6. The results are similar to earlier study where gloss of paper increased after surface sizing with PVA (19).

Table 6: Effect of surface sizing on surface properties after supercalendering

Particulars	Base	Rod 1			Rod 2			Rod 3			Rod 4		
PVA solution, %	-	1	2	4	1	2	4	1	2	4	1	2	4
Formation index	170±10	180±10	184±13	187±08	182±13	189±07	194±13	195±06	199±08	204±12	211±14	223±14	239±11
Gloss, %	9-10	15-16	16-17	16-17	16-17	17-18	17-18	16-17	17-18	18-19	17-18	18-19	20-21

Effect of surface sizing with PVA on optical properties of paper with and without supercalendering

The surface sizing with PVA (1, 2 and 4)% solution by rod 1 to 4 showed positive impact on the optical properties of paper as shown in figure 3, 4 and table 7. The surface sizing by rod 4 of 1%, 2% and 4% solution of PVA without supercalendering increased the brightness to 87.3, 87.9 and 88.2, respectively in comparison to base paper brightness of 85.9. The supercalendering decreased the brightness of the PVA sized paper but in comparison to supercalendered base paper the brightness was found to be better. The surface sizing by rod 3 of 1%, 2% and 4% solution of PVA without supercalendering increased the brightness to 85.3, 85.8 and 86.0, respectively in comparison to base paper brightness of 84.6. The brightness after surface sizing with and without supercalendering is shown in figure 3. Increase in brightness after addition of PVA on base paper rod 4 was earlier reported by Ashori et al. 2005 (6).

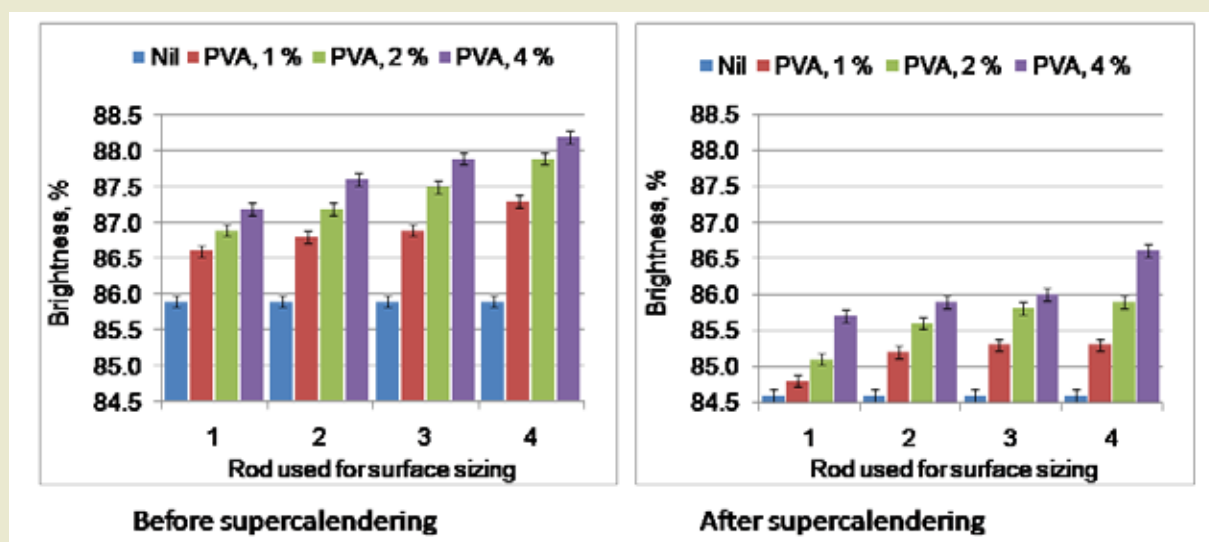


Figure 3: Effect of surface sizing on brightness of paper

CIE whiteness of uncalendered base paper was 131.5 and that of supercalendered base paper was 129.3. The whiteness values after surface sizing done with PVA solution of 4% by rod 1, 2, 3 and 4 was found to be 135.8, 137.1, 136.5 and 137.9, respectively in comparison to that of uncalendered base paper. Similarly, after supercalendering the value of whiteness was reduced to 133.9, 134.2, 135.2 and 135.7, respectively. The overall impact of PVA surface sizing with different rods on whiteness is shown in figure 4.

Opacity is a measure of the degree to which a material is able to obstruct the passage of light. There was reduction in opacity values after surface sizing with PVA. The reduction was less in uncalendered sheets whereas

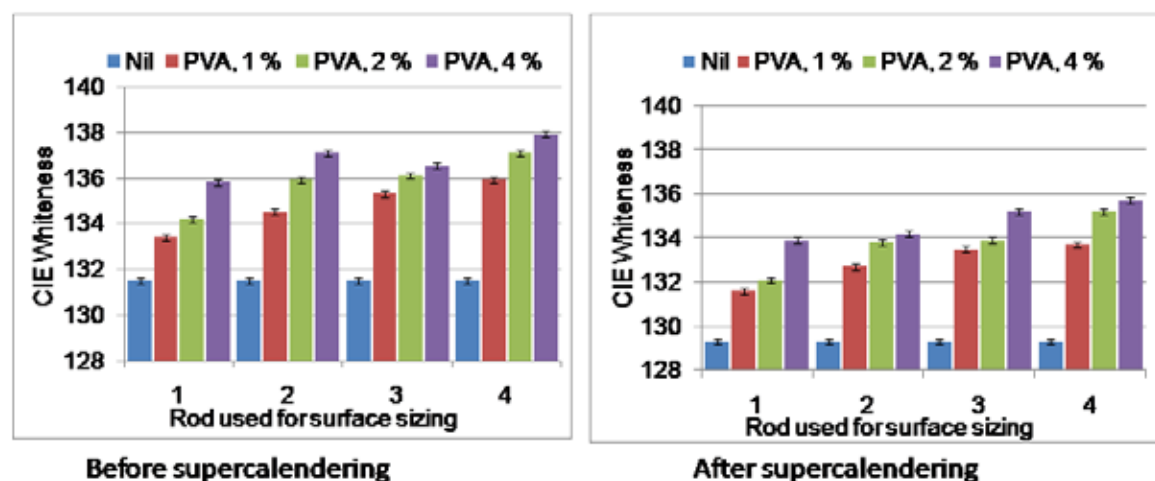


Figure 4: Effect of surface sizing on CIE whiteness of paper

in supercalendered paper the opacity further reduced as shown in table 7 and 8. Initially when surface sized sheets were not calendered, the sizing agent (PVA) applied to the paper did not enter into the paper because the paper was not pressed. But, after supercalendering the sizing agent was equally distributed inside the pores of the paper because of the applied pressure. This caused air to remove out of the paper which provided less scattering to the light and the opacity decreased.

Scattering coefficients (m^2/kg) of paper after surface sizing with PVA of different concentration was decreased in both cases (uncalendered and supercalendered) as shown in table 7 and 8. Initial scattering coefficient was 65.5 after surface sizing the coefficient reduced to the range 63-58. The scattering coefficient reduction in case of supercalendering was higher. The reason of more reduction in scattering coefficient after surface sizing was similar to that of opacity. L^* , a^* and b^* are different coordinates which provide the idea of shade of paper. L^* indicates lightness whereas negative value of a^* represent green shade and positive value red shade. The negative value of b^* implies blue shade and positive value yellow shade. The value of base paper in terms of L^* , a^* and b^* were impacted with supercalendering and surface sizing with PVA. The values of L^* , a^* and b^* with and without supercalendering were shown in table 7 and 8. Yellowness and tint of uncalendered paper (with and without surface sizing) was found to be in the range of -20 to -22 and -1.80 to -2.90, respectively.

Table 7: Effect of surface sizing on optical properties before supercalendering

Particulars	Base	Rod 1			Rod 2			Rod 3			Rod 4		
		1	2	4	1	2	4	1	2	4	1	2	4
PVA solution, %	-												
Opacity, %ISO	93.0	92-93											
Scattering coefficient, m^2/kg	65.5	62.8	62.3	61.8	62.4	62.0	61.1	61.9	60.6	59.9	60.8	59.2	58.3
L^*	92.9	92.8	92.9	93.1	93.0	93.2	93.1	93.3	93.4	93.7	93.8	93.8	94.3
a^*	3.51	3.82	3.94	4.10	3.95	4.02	4.14	3.99	4.09	4.10	4.33	4.45	4.56
b^*	-9.34	-10.7	-10.9	-11.2	-11.3	-11.3	-11.6	-11.3	-11.3	-11.6	-11.5	-11.8	-11.9
R 457 Fluorescence C	9.24	9.83	9.88	9.76	9.74	9.78	9.77	9.63	9.76	9.99	10.2	11.5	11.5

Table 8: Effect of surface sizing on optical properties after supercalendering

Particulars	Base	Rod 1			Rod 2			Rod 3			Rod 4		
PVA solution, %	-	1	2	4	1	2	4	1	2	4	1	2	4
Opacity, %ISO	93.0	82.7	83.7	84.1	82.8	83.8	84.1	83.0	86.0	87.6	84.2	86.8	88.2
Scattering coefficient, m ² /kg	57.5	33.8	35.7	36.3	33.8	35.9	36.4	34.7	39.6	39.6	35.4	39.8	39.8
L*	91.3	91.3	91.3	91.4	91.4	91.4	91.5	91.4	91.6	92.1	92.2	92.2	92.5
a*	3.25	3.61	3.70	3.81	3.67	3.75	3.86	3.70	3.83	3.87	4.14	4.19	4.26
b*	-9.96	-11.3	-11.5	-11.8	-11.8	-11.9	-12.2	-11.9	-11.9	-12.2	-12.0	-12.4	-12.5
R 457 Fluorescence C	9.19	9.63	9.68	9.70	9.64	9.71	9.73	9.66	9.80	9.92	9.96	11.0	11.1

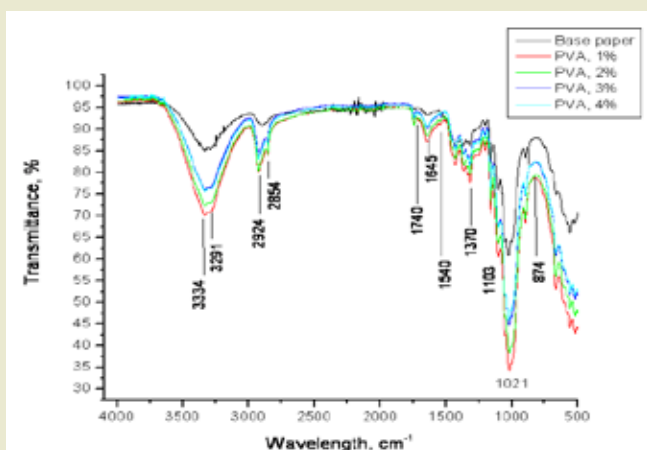


Figure 5: FTIR spectra of paper surface sized with different concentrations of PVA with same rod (Rod 1)

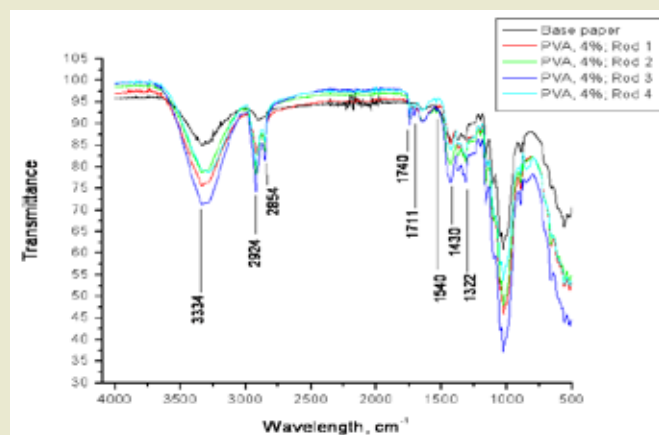


Figure 6: FTIR spectra of paper surface sized with same concentrations of PVA with different rods

FTIR analysis of PVA surface sized paper using different concentrations versus same rod and vice versa

FTIR spectra of PVA surface sized papers using different concentrations of PVA solution with same rod showed distinguishable differences in the intensities of absorption bands (Figure 5). Using rod 1 for 1%, 2%, 3%, and 4% PVA solutions, the intensity of absorption band corresponding to the -OH stretching vibration at 3334 cm⁻¹ was the maximum for 1% PVA solution. The CH₂ stretching was observed in PVA surface sized papers with increased intensities as compared to base paper at

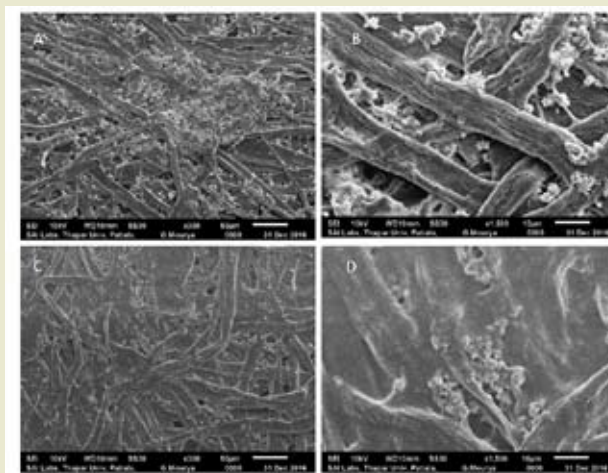


Figure 7: SEM images (A) base paper at 300X magnification (B) base paper at 1500X magnification (C) 4% PVA using Rod 1 at 300X magnification (D) 4% PVA using Rod 1 at 1500X magnification

2924 cm^{-1} and a new peak was observed at 2854 cm^{-1} . Another new absorption peak at 1740 cm^{-1} was observed in all PVA surface sized papers due to the presence of carboxyl or carbonyl groups in polyvinyl acetate as PVA is a product synthesized from hydrolysis of polyvinyl acetate. FTIR spectra of PVA surface sized papers using same concentration (4%) of PVA solution with different rods (1, 2, 3, 4) also showed an absorption band at 1711 cm^{-1} due to ester functional group of unhydrolyzed polyvinyl acetate (21). Absorption bands at 1430 cm^{-1} and 1322 cm^{-1} which indicate the bending modes of the methylene groups (21) also increased significantly in their intensities in 4% PVA surface sized papers. The more retention of PVA was found in 1% PVA concentration with rod 1 among different concentrations applied (Figure 5) whereas for 4% PVA the maximum retention as apparent from peak intensities was found with rod 3 (Figure 6).

Scanning electron microscopy (SEM) of base paper and surface sized papers

As shown in Figure 7, scanning electron micrographs of base paper surface had uneven morphology consisting of gaps due to the fiber network. After surface sizing, these gaps were filled by the sizing agent (PVA) that resulted in more uniform and high smoothness of paper surface. In turn, optical properties were improved along with surface

properties of paper. A comparison of the image B (base paper at 1500X) and image D (base paper surface sized with 4% PVA using Rod 1 at 1500X) shows that the surface smoothness increased after surface sizing. A clear film of PVA can be seen on the surface (images C & D).

Conclusion

Paper properties such as strength, surface and optical were found to be increased after surface sizing with PVA while scattering coefficient and opacity decreased. The impact of supercalendering on gloss, formation index and air permeance of paper was found to be positive while on optical properties it was found to be negative. In short, PVA was found to be an efficient surface sizing agent with and without supercalendering.

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References

1. Moutinho, I.M.T., Ferreira, P.J.T., Figueiredo, M.L., - Industrial and engineering chemistry research, 46(19): 6183-6188 (2007).
2. Shirazi, M., Esmail, N., Garnier, G., Van de ven, T.G.M., - Journal of dispersion science and technology, 25(4): 457-468 (2004).
3. Ferreira, P.J., Gamelas, J.A., Moutinho, I.M., Ferreira, A.G., Gómez, N., Molleda, C., Figueiredo, M.M., - Industrial and engineering chemistry research, 48(8): 3867-3872 (2009).
4. Stankovska, M., Gigac, J., Letko, M., Opalena, E., - Wood research, 59(1): 67-76 (2014).
5. Moutinho, I.M.T., Ferreira, P.J.T., Figueiredo, M.L., - Bioresources, 6(4): 4259-4270 (2011).
6. Ashori, A., Raverty, W.D., Harun, J., - Fibers and polymers, 6(2): 174-179 (2005).

7. Kilpainen, T., Manner, H.J., -In conference, International printing and graphics arts TAPPI press, 245-250 (2000).
8. Sievanen, H., Suitability of foam coating on application of thin liquid films. Masters thesis, Lappeenranta university of technology, (2010).
9. Han, X., Sensen, C., Xianguo, H., - Desalination, 240(1-3): 21-26 (2009).
10. Seoudia, R., Mongy A.E., Shabaka A.A., - Physica B: Condensed matter, 403: 1781– 1786 (2008).
11. Zhang C.H., Yang F.I., Wang, W.J., Chen B., - Separation and purification technology, 61: 276–286 (2008).
12. DeMerlis C.C., Schoneker, D.R., - Food and chemical Toxicology, 41: 319–326 (2003).
13. Nair, B., - International journal of toxicology, 17(5_suppl): 67-92 (1988).
14. Pourciel, M.L., Launay, J., Sant, W., Conédéra, V., Martinez, A., Temple-Boyer, P., - Sensors and actuators B: Chemical. 94(3): 330-33645 (2003).
15. Lertsutthiwong, P., Nazhad, M.M., Chandkrachang, S., Stevens, W.F., - Appita journal, 57(4): 274-280 (2004).
16. Jonhed, A., Andersson, C., Järnström, L., - Packaging technology and sciences, 21(3): 123-135 (2008).
17. Eastman, J.E., Moore, C.O., Cold water soluble granular starch for gelled food compositions. U. S. Pat. Appl. 4465,702 (1984).
18. Bhardwaj S., Bhardwaj, N.K., - Appita Journal, 71(4): 321-329 (2018).
19. Schuman, T., Wikstrom, M., Rigdahl, M., - Surface and coating technology, 183: 96-105 (2004).
20. Bhardwaj S., Bhardwaj, N.K., Negi, Y.S., -Appita Journal, 70(2): 139- 148 (2017).
21. Zuber, M., Zia, K.M., Bhatti, I.A., Jamil, T., Rizwan, A., - Carbohydrate polymers, 87(4): 2439-2446 (2012).
22. Hebeish, A., El-Rafie, M.H., Rabie, A.M., El-Sheikh, M.A., El-Naggar, M.E., - Journal of applied polymer science, 131(8): 40(2014).