Response of pulps of different origins to the upgrading effect of bulk added green denatured soy protein, in correlation to morphological structure & chemical composition of cellulose fibers

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Abstract: Soy-protein is used, for the first time, as bulk binder in papermaking from wood pulps (hardwood and softwood pulps). Wood pulps represent the major pulps used for paper production. A green denaturing method, involving only biodegradable compounds, was found sufficient to expose the functional groups of proteins. Addition of denatured soy-protein caused a considerable increase in all strength properties of paper, at all beating degrees. The effect was highest in non-wood (for comparison) followed by hardwood and softwood pulps respectively. This could be correlated to ratio of fiber length/width, fines, and hemicellulose content of pulps. The less the ratio, and the higher the fines and hemicellulose content, the more was the increase in strength properties; due to more exposed surfaces. The outstanding effect of soy-protein was magnifying the desired opacifying effect and retention of inorganic fillers e.g. kaolin, while eliminating the loss in strength, which occurs normally due to fillers.

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1. Introduction:

Pulp fibers differ in morphological properties e.g. length and width; fiber porosity, fiber surface area, and chemical composition. This difference depends on the plant origin of pulps. These factors together affect the properties of paper obtained from the pulp (Annergren, 1999).

In many cases, different substances are added to the pulp to increase paper strength and/or fillers retention. This is because the fiber-additive-fiber bond is stronger than the fiber-to-fiber bond.

The present work aims at studying the effect of pulp type on the capacity of soy protein as strength promoter for paper. The work will, also, asses the effect of pulp type on soy protein capacity as retention aid for inorganic fillers. Fillers, namely kaolin are added mainly to increase opacity in writing and printing paper. Furthermore, the work aims at *correlating* the morphological structure and chemical composition of fibers to the capacity of soy protein as strength promoter and retention aid.

In this work, soy protein is used, for the first time, in the paper furnish of wood pulps (hardwood pulp and softwood pulp) as a bulk binder. Wood pulps represent the major pulps used for paper production. For sake of comparison, the wood pulps will be compared to an important non-wood pulp, namely bagasse, in which soy protein was used in previous work (Fahmy *et al.*, 2010). Soy protein, being natural and biodegradable, is preferred to synthetic adhesives, which pollute the environment and cause troubles in paper recycling.

Soy protein, like other proteins, has the majority of its functional groups inaccessible; due to internal bonding. Because of this bonding, a natural untreated paste of protein is a poor adhesive. Thus, *denaturing* i.e. treatment is required to break the internal bonds, uncoil, unfold, and disperse the protein molecules. Thus, the functional groups become exposed and available at the surface (Tanford, 1968; Almarza *et al.*, 2009; Prashar *et al.*, 2011; Coutouly *et al.*, 2013).

From several preliminary experiments, we found that denaturing by treatment with (urea + NaOH) is quite sufficient, more economic, and greener than other complicated denaturing processes. Therefore, it was adopted as a green denaturing method in the present work.

2. Material and Methods:

2.1. Raw Materials:

- Bleached hardwood and softwood pulps were used. Table 1 shows the chemical composition of the pulps.

- Study of the morphological structure of pulp fibers:

The morphology of the fibers of softwood and hardwood was studied for beaten and unbeaten pulps. The main fibre parameters were measured by image analysis of a diluted suspension in order to obtain the average length, the average width, the coarseness, and the proportion of fine elements. Table 2 shows the morphological properties of these pulp fibers.

- Defatted soy flour was prepared from soybean as described elsewhere (Carrao & Gontijo, 1994).

- Egyptian upgraded kaolin (Farch El-Gozlan) which was prepared on pilot scale at CMRDI, El-Tebeen, Egypt through STC Project, was the paper filler used in this work.

- Urea and Sodium Hydroxide (Aldrich) were laboratory grade chemicals.

2. 2. Methods:

2.2.1. Preparation of Soy protein Isolate (SPI):

A total of 100g of defatted soy flour was suspended in 700ml distilled water and stirred for 30min. The pH of the mixture was then adjusted to 9.0 with 0.2N NaOH and stirred for 2hrs. The slurry was centrifuged to separate the insoluble portion. The pH of the remaining solution was adjusted to 4.5 by addition of hydrochloric acid to precipitate soy protein which was washed with distilled water to remove undesirable carbohydrates such as raffinose. The isolated soy protein was then air-dried.

2.2.2. Preparation of SPI binders:

Fifteen grams of soy protein isolate was suspended in 35ml distilled water with stirring, 12g urea, dissolved in 18 ml distilled water, was added to the mixture with stirring for 20 min (the mixture was still suspension). 0.42g NaOH, dissolved in 10 ml distilled water, was added to the mixture with stirring for 20min to have a viscous solution. The obtained product was homogenous and stable at pH 9. Protein concentration of 2.5% was used in papermaking experiments.

2.3.1. Paper testing:

The conventional hand sheets with a basis weight of 60g/m^2 were prepared on a Rapid Khöten sheet former following the standard method IS0 5269-2. The pulp drainability was evaluated by measuring the Shopper Riegler degree (SR – ISO 5267-1). Before testing, the hand sheets were conditioned (23°C, 50% relative humidity – ISO 187).

2.3.2. Paper properties:

The physical and mechanical properties of paper sheets prepared from the pulp were determined by measuring basis weight, thickness, the tensile, burst and tear strength according to standards ISO 536, ISO 534, ISO 1924-3, ISO 2758 and ISO 1974. As well, the brightness and opacity were determined by using Hunter Lab Colour/Difference Meter D25-2. As recommended by the various standards used, all the measurements were made 5 times.

2.3.3. Determination of retention of fillers:

The retention of fillers in the present investigation was calculated according to the following:

Filler retention % = (Retained filler/Added amount of filler) x 100

3. Results and Discussion:

In order to get an integrated picture, the pulps were beaten for successively longer times to obtain pulp samples with Schopper Riegler (°SR) degrees of 30, 40, 50, and 60°SR. Paper sheets were prepared from these samples and tested for strength properties, brightness, and opacity.

3.1. Experiments on Hardwood Pulp: -

Table 3 shows the properties of paper sheets made from hardwood pulp without any addition. It is clear from Table 3 that all the properties improved with increasing the Schopper Riegler, reaching an optimum at 40 and 50°SR.

Table 4 shows the properties of paper sheets made from hardwood pulp with addition of soy protein. All strength properties increased due to addition of soy protein. The increase in breaking length reached 13.72% relative to the soy protein free sample at 50°SR. The increase in burst index reached 39.19% relative to the soy protein free sample at 50°SR. The increase in tear index reached 5.4% relative to the soy protein free sample at 50°SR.

Table 5 shows the properties of paper sheets made from hardwood pulp and *10% kaolin without* soy protein. Addition of kaolin led to decrease in all strength properties of paper relative to the paper sheets made from hardwood pulp without any addition. This is due to the well known effect of fillers in disrupting the interfiber-bonding. Expectedly, the opacity improved considerably due to kaolin addition in all samples.

Table 6 shows the properties of paper prepared from Hardwood pulp with addition of both soy protein and 10% kaolin. It is clear from Table 6 that soy protein succeeded to eliminate and counteract the decrease in strength properties which occurred due to addition of kaolin in absence of soy protein. The kaolin-soy protein paper sheets enjoyed the opacifying benefits of kaolin, while their strength properties remained intact and nearly identical to those of sheets without kaolin addition (compare Table 6 and Table 3).

Addition of soy protein, also, led to magnification of the desired opacifying effect of kaolin at 30 and 40ºSR. This magnifying effect will be shown later, in case of softwood, to be more significant and to prevail at all the applied ºSR degrees.

Soy protein led to increase in the retention of kaolin relative to the soy protein free case. The retention of kaolin increased from 15% in absence of soy protein to 20% in presence of soy protein, at 40ºSR.

3.2. Experiments on Softwood Pulp: -

Table 7 shows the properties of paper sheets made from softwood pulp without any addition. It is clear from Table 7 that all the properties improved with increasing the beating i.e Schopper Riegler, reaching an optimum at 40 and 50ºSR.

Table 8 shows the properties of paper sheets made from softwood pulp with addition of soy protein. All strength properties increased due to addition of soy protein. The increase in breaking length reached 6.47% relative to the soy protein free sample at 50°SR. The increase in burst index reached 9.98% relative to the soy protein free sample at 50°SR. The increase in tear index reached 7.5% relative to the soy protein free sample at 50°SR.

Table 9 shows the properties of paper sheets made from softwood pulp and *10% kaolin without* soy protein. Addition of kaolin led to decrease in all strength properties of paper, relative to the paper sheets made from hardwood pulp without any addition. This is due to the well known effect of fillers in disrupting the interfiber-bonding. Expectedly, the opacity improved considerably due to kaolin addition in all samples.

Table 10 shows the properties of paper prepared from softwood pulp with addition of both soy protein and 10% kaolin. It is clear from Table 10 that soy protein succeeded to eliminate and counteract the decrease in strength properties which occurred due to addition of kaolin in absence of soy protein. The kaolin-soy protein paper sheets enjoyed the opacifying benefits of kaolin, while their strength properties remained intact and nearly identical to those of sheets without kaolin addition (compare Table 10 and Table 7).

Addition of soy protein, also, led to magnification of the desired opacifying effect of kaolin, at all the applied Schopper Riegler degrees.

Soy protein led to increase in the retention of kaolin relative to the soy protein free case. The retention of kaolin increased from 10% in absence of soy protein to 18% in presence of soy protein, at 40ºSR.

3.3. Correlating the effect of pulp type (morphological structure and chemical composition of fibers) to the *capacity* of soy protein as strength promoter and retention aid:

In this work, soy protein is used, for the first time, as bulk binder in papermaking from wood pulps (hardwood and softwood pulps). For sake of comparison, the wood pulps are compared to an important non-wood pulp, namely bagasse, which was used in previous work with soy protein (Fahmy *et al.,* 2010).

Addition of denatured soy protein causes a considerable increase in all strength properties of paper made from all three pulp types. The capacity is highest in bagasse (taken for comparison) followed by hardwood and softwood pulps respectively.

This can be correlated to the ratio of fiber length/width, fines, and hemicellulose content of pulps. The less the ratio, and the higher the fines and hemicellulose content, the more is the increase in strength properties. This is because more fiber surfaces are exposed due to the decrease in the ratio of length to width, and due to the increase in fines. Apparently, hemicellulsoe-binder-hemicellulose bond is stronger than the cellulose-binder-cellulose bond.

Soy protein addition eliminates the loss in strength, which normally occurs due to inorganic fillers used in papermaking e.g. kaolin. Simultaneously, the addition causes magnification of the desired opacifying effect and retention of kaolin. This magnification of the opacifiyng effect of kaolin was more obvious in softwood than hardwood.

Table 1: Composition of bleached hardwood and softwood pulps

	Hardwood bleached pulp	Softwood bleached pulp
Cellulose %	82	86.2
Hemicellulose %	15.9	10.8
Lignin %	1.5	2.6
Extraneous compounds %	1. 0.6	0.4

Table 2: (A) Morphological properties of *Hardwood* pulp

Schopper Riegler (°SR)	Unbeaten pulp (14)	30	40	50	60
Fiber length (mm)	0.661	0.623	0.593	0.572	0.565
Fiber width (µm)	20.25	20.25	20.55	20.7	21
Coarseness (mg/m)	0.0561	0.0721	0.0722	0.0751	0.0776
Fine elements (% in length)	16.6	27	27.1	28.4	30.3

(B) Morphological properties of *Softwood* pulp

Schopper Riegler (°SR)	Unbeaten pulp (14)	30	40	50	60
Fibre length (mm)	1.99	1.869	1.836	1.752	1.674
Fibre width (µm)	27.2	27.8	27.4	27.4	27.4
Coarseness (mg/m)	0.1461	0.108	0.123	0.123	0.125
Fine elements (% in length)	13	18.7	20.3	22.1	23.9

Table 3: Properties of paper prepared from *Hardwood* pulp without any addition

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	4.2	4.8	5.1	5.0
Burst Index (Kpa, m^2/g)	2.28	2.58	2.73	2.76
Tear Index ($mN.m^2/g$)	3.8	3.78	3.7	3.6
Brightness %	82.64	81.34	80.96	79.56
Opacity%	84.66	84.76	83.2	82.2

Table 4: Properties of paper prepared from *Hardwood* pulp with addition of soy protein

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	4.4	5.3	5.8	5.6
Burst Index (Kpa, m^2/g)	2.52	3.3	3.8	3.9
Tear Index ($mN.m^2/g$)	4.2	4.1	3. 9	3.8
Brightness %	83.06	82.26	81.18	79.13
Opacity%	85.8	85.5	82.8	82.2

Table 5: Properties of paper prepared from *Hardwood* pulp and 10% kaolin *without* soy protein

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	3.5	3.7	3.8	3.6
Burst Index (Kpa, m^2/g)	1.96	2.10	2.23	2.30
Tear Index ($mN.m^2/g$)	3.02	3.25	3.3	3.2
Brightness %	81.6	80.95	79.2	79.1
Opacity%	87.2	89.2	90.1	91.2

Table 6: Properties of paper prepared from *Hardwood* pulp with addition of both soy protein and 10% kaolin

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	4.1	4.7	4.9	4.8
Burst Index (Kpa, m^2/g)	2.25	2.45	2.81	2.92
Tear Index ($mN.m^2/g$)	3.91	3.90	3.71	3.64
Brightness %	80.95	79.35	79.13	78.13
Opacity%	90.84	89.84	87.85	87.32

Table 7: Properties of paper prepared from *Softwood* pulp without any addition

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	8.13	8.53	8.65	8.6
Burst Index (Kpa, m^2/g)	6.41	6.87	7.21	7.25
Tear Index ($mN.m^2/g$)	12.13	12.1	12	11.93
Brightness %	81.6	79.6	78.89	78.6
Opacity%	74.28	73.28	73.2	72.2

Table 8: Properties of paper prepared from *Softwood* pulp with addition of soy protein

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	8.45	8.95	9.21	9.2
Burst Index (Kpa, m^2/g)	6.28	7.58	7.93	7.98
Tear Index (mN.m^2/g)	13.04	13	12.9	12.8
Brightness %	81	79.26	78.58	78.13
Opacity%	75.8	75.5	74.8	73.21

Table 9: Properties of paper prepared from *Softwood* pulp and 10% kaolin *without* soy protein

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	7.5	7.75	7.89	7.81
Burst Index (Kpa, m^2/g)	5.2	5.6	5.8	5.9
Tear Index (mN.m^2/g)	10.8	11.23	11.5	11.56
Brightness %	78.2	77.1	76.2	76.1
Opacity%	81.5	81.2	81	80.5

Table 10: Properties of paper prepared from *Softwood* pulp with addition of both soy protein and 10% kaolin

Schopper Riegler (°SR)	30	40	50	60
Breaking length Km	8.1	8.45	8.67	8.78
Burst Index (Kpa, m^2/g)	6.04	7.24	7.52	7.34
Tear Index (mN.m^2/g)	12.61	12.52	12.47	11.61
Brightness %	80.95	79	79.13	78.13
Opacity%	83.84	82.81	82.5	82.32

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