7. Strengthening of Security Paper

Review Article

Tanmay Jain
Third Year Bachelor of Technology
Surface Coating Technology

Karan Bhangaonkar
Third Year Bachelor of Technology
Surface Coating Technology

Abstract

Security papers generally have a very short life span and hence cost a country billions of dollars for making new papers and in disposing of the old ones. It is therefore desirable that novel methods be explored for increasing the life span of such papers. Though numerous additives have been used till date, none of them have been able to increase the life span substantially. We applied inductive reasoning to establish various hypotheses for increasing the durability of paper, and did an exploratory research to determine the results of those hypotheses.

1. Introduction

The history of paper used in currency dates back to as far the 7th century. Generally, banknotes are made from cotton rag paper with a weight of 80 to 90 grams per square meter. Linen, abaca, or other textile fibers are often added to cotton. This type of paper is different from ordinary paper; it is much more resilient, resists wear and tear, and is devoid of whitening agents. Banknote paper is infused with polyvinyl alcohol or gelatin to give it extra strength unlike most printing and writing paper. Polymer banknotes like the ones made from biaxially-oriented polypropylene have also been developed recently to improve durability.

A review of the life of cellulose-based bank notes in various countries providing an interesting cross-section of countries by size, socioeconomic and environmental conditions etc tells us whatever the handling, environmental or quality standards used in these countries, there is nothing unusual about having notes with lives of two years or less. Following generalizations may be made keeping in mind the data conclusively provided by conferences such as the Pacific Rim Banknote Printers Conference.

- Countries have between two and six denominations with life of two years or less;
- Countries have at least two denominations with a life of 18 months or less;
- 75 per cent of all of the countries have at least one denominations with a life of around 12 months or less;
- 63 per cent of all of the countries have at least two denominations with a life of around 12 months or less.

Therefore it can be recognized that there is an immediate need to improve the durability of currency notes. In the recent past a few countries have suggested that we switch to polymeric substrates instead of rag paper. Even though both have their own advantages and disadvantages, we decided to pursue rag paper since it has several properties which are highly desirable in such applications, including dead foldability, tear resistance, printability and embossability. As may be appreciated, these properties combine to give bank notes their familiar feel and functionality. A few of the problems associated with plastic substrates have been listed below.

Problem with the Australian plastic substrate notes:

- They are found to be rather complex in construction and relatively expensive to produce. Moreover, when transmission security devices are laminated between layers in the substrate, an area of weakness and high stress is created which reduced both durability and security.
- First, the oriented polypropylene substrate(OPP) substrate does not dead fold, causing problems in that the film retains either a flat or curved form, jamming cash registers and automatic handling equipment.
- Second, the OPP substrate has poor initiated tear resistance in the processing of currency, which quite frequently creates nicks on the edges of bills, resulting in catastrophic tears.
- The OPP product also does not exhibit the tactility of paper currency, due to the fact that OPP does not emboss well during the intaglio process.

2. Objective

The objective of the paper is to explore different methods to improve the durability of currency notes, and security paper in general. The following properties need an immediate redressal;

- Tear Resistance:
  1. Tear initiation
  2. Tear propagation
- Water Resistance
- Stain Resistance

3. Literature Review

It is necessary that we first understand what gives paper 'strength'. Paper is essentially is composed of cellulose.

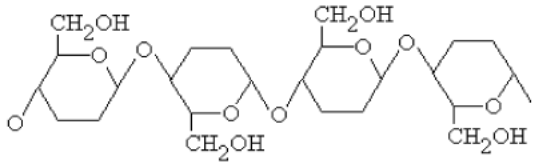


Figure 1: Cellulose

The packing of cellulose can be explained as in figure 2. The important point to note is that these cellulose, and eventually the fibers, are held together by H-bonds. The integrity of a paper sheet is dependent on the hydrogen bonds which form between the fine structures of cellulose fibers during the pressing and drying operations. The bonds between hydroxyls of neighboring fibers are very strong when the paper is dry, but are severely weakened as soon as the paper becomes wet. Bonding between the hydroxyls of cellulose and water is as energetic as bonding between two cellulose hydroxyls. As a consequence, ordinary paper loses most of its strength when it is wet or exposed to very high humidity. The sheet loses its stiffness and bursting, tensile and tearing strength.

If water can be prevented from reaching the sites of the bonding by sizing or coating the sheet, then a measure of wet strength may be attained. High molecular weight species are strongly absorbed on the fibers and are large enough to bridge two fibers.

Low molecular weight species are not retained as well because of fewer charge sites. At this point, it is necessary that we understand some of the relevant properties of paper, and the factors which affect them.

4. Tensile Strength

Some of the factors that affect the tensile strength of paper are listed below,

4.1. Fiber Length

1. A long fiber can have more bonds with other fibers and therefore will be held more strongly than a short fiber.
2. The tensile strength of the wet web increases rapidly with fiber length.
3. Likewise, tensile strength, breaking strain and fracture toughness also increase with fiber length.
4. The probability of two fibers crossing is proportional to the mean value of fiber length squared.

4.2. Fiber-fiber bond strength

- Cellulose molecules are held together by

  1. Covalent bonds;

2. H-bonds;

3. Van der Waal's forces;

4. Any covalent or ionic bond that may be formed between the cellulose and some polymeric mediators.

4.3. Other factors

- Beating: more the beating less will be the TS.
- Bleaching: it may decrease the TS.
- Drying under stress: Drying under an axial tension increases tensile strength but decreases breaking strain.
- Recycled pulp: it swells less and therefore less TS.
- Internal Stresses developed during packing of fiber networks: these are local stresses.

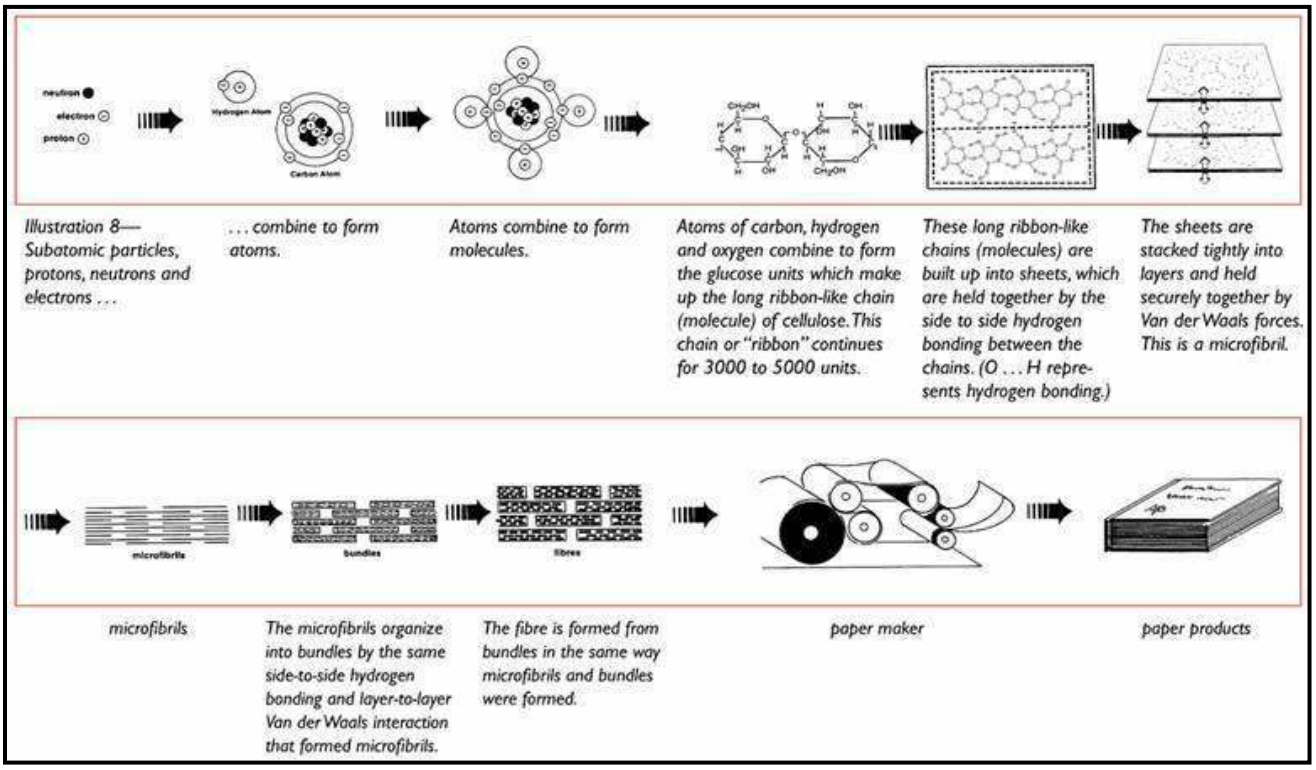


Figure 2: The process of Paper Manufacture

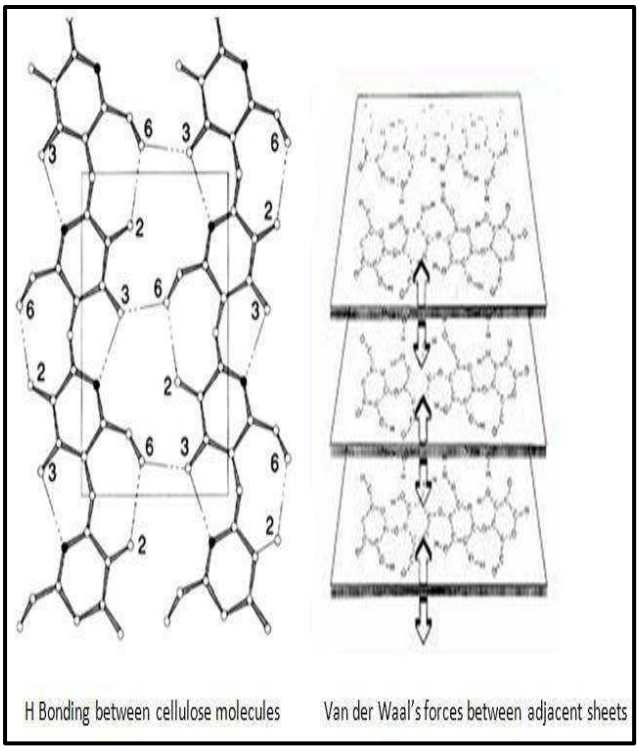


Figure 3: Secondary forces between cellulose.

The above points can be reinforced by closely studying the Page Equation, which gives the relation between various factors like the length and the diameter of a fiber and the eventual tensile breaking length, T, of the paper;

$$\left[\frac{1}{T}\right]=\left[\frac{9}{8Z}\right]+\left[\frac{(12g\cdot C)}{(P\cdot l\cdot b\cdot RBA)}\right]$$

The Page Equation

$$RBA=\frac{(S_0-S)}{S_0}$$

l	= fiber length (length)
b	= fiber-fiber bond strength (N/m²)
RBA	= relative bonded area (unit less)
g	= gravitational constant -(length/second² = 9.8 m/s²)
T	= tensile breaking length (length)
Z	= zero span tensile (length)
C	= fiber coarseness (weight/length)
P	= fiber perimeter (length)

The relative bonded area (RBA) in Page's equation is a measure of the contact area between fil

This implies that,

- T α fiber length
- T α fiber-fiber bond strength
- T α contact area b/w fibers in the sheet
- T α 1/(fiber coarseness)

5. Tear Strength

- In a well bonded, refined fiber's paper, stress is localized at the point of propagation, whereas a moderately bonded paper will delocalize the stress.(Ref. US patent no. 4,609,432)
- Synthetic fibers have more tensile strength than cellulose fibers, and hence when the sheet is torn they do not rupture but come out of the sheet structure. (Ref. US patent no. 5,223,095)

The amount of synthetic fiber to be added has to be optimized; since more of it will decrease the tensile strength. Even the length should be optimized, as well as its diameter.

Hypothesis employed

a. Binding the fibers at the point of intersection/ overlap.
b. Providing reinforcement in the form of cotton gauze.
c. Increasing the H-bonding.

d. Using wet/ dry strength additives and binders in a blend.

6. Experimental Method

To test the above hypothesis the following experiments were performed. The detailed SOP of each experiment is followed by the relevant result. All the samples made were handmade and their data is compared to an untreated handmade paper; in both the cases all other conditions and procedures were same.

6.1. Experiment

The following is the SOP followed and standardized for making the handmade cotton rag paper.

1. Chop the cotton fibers and waste paper by scissors.
2. Weigh 9gm of fibers and 1gm of waste paper.
3. Take 1400ml of water in a beaker, add 14gm of NaOH and 14ml of Hydrogen Peroxide to it.
4. Heat till 75’C and keep adding the fibers and the waste paper while maintaining rigorous stirring.
5. Continue the heating for an hour.
6. Wash the fibers collected with water.
7. To refine this fibers further, ball mill them (we used Retsch Planetary Ball Mill, at 450 rpm, for 15mins).
8. Disperse half of the above fibers in water.
9. Pour this mix into a tub which has a stainless steel sieve kept in it; the same quality and size is used in every sample.
10. Let the fibers settle on the sieve for 3 hrs.
11. Remove the sieve from the tub and leave it to dry.
12. Peel the paper off the sieve.
13. To give the paper a smooth finish, hot press it for 10mins at R.T.

6.2. Experiment

Using aqueous polyurethane dispersion (PU) as a binder to test hypothesis no. 1 by coating the fibers and curing them before dispersing them in water. The PU aqueous dispersion used throughout is Drokyl 77106, supplied by DRC resins and coats.

After step 7, the fibers weredipped in the PU dispersion and left to cure in the oven for around 2 hours at 100”C.

The experiment was done for various concentrations of PU.

Sample No. 1: PU 20% w/w of pulp.

Sample No. 2: PU 40% w/w of pulp.

Sample No. 3: PU 80% w/w of pulp.

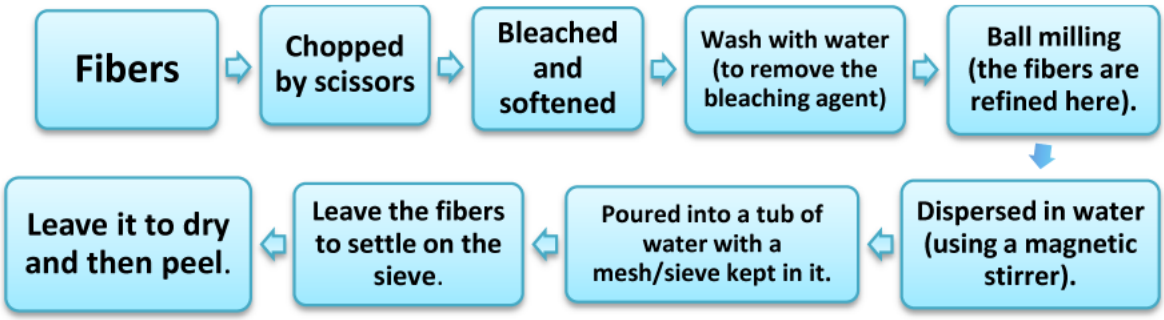
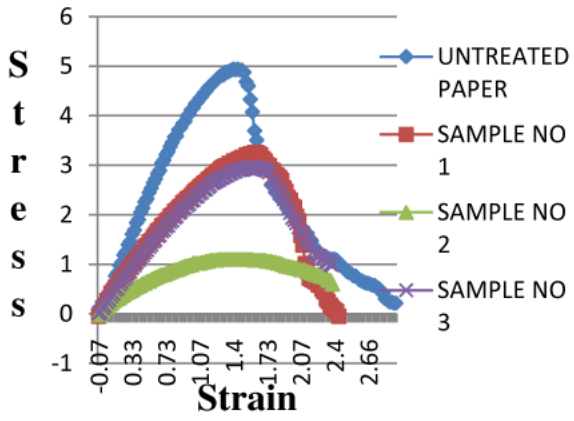


Figure 4: The process

As can be observed above, dipping the fibers in PU reduced the tensile strength of the paper. It is quite interesting to note that the tensile strength of 20% w/w PU and 80% w/w PU is almost the same whereas the 40% w/w PU has shown a considerable dip in the tensile strength.

The reason for this behavior may be attributed to the decrease in H-bonding between the fibers because of presence of inert PU. It may also be because of very less density of fibers in one layer (paper has multiple layers of cellulose fibers).

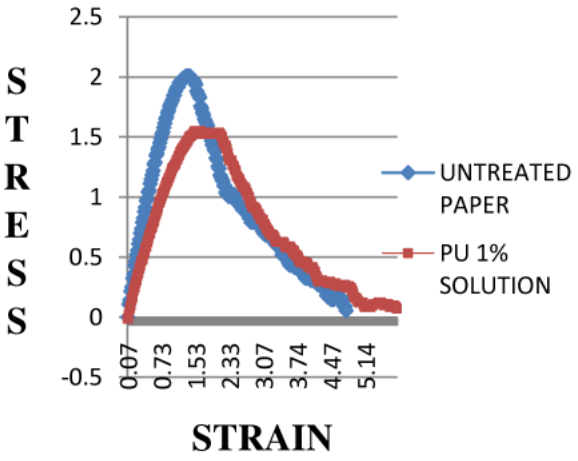


Graph 1: Stress v/s Strain plot for Paper strengthened with PU binder

6.3. Experiment

Using aqueous polyurethane dispersion (PU) as a binder to test hypothesis no. 1 by dispersing the fibers in PU solution.

In step 8, instead of water, a 1% PU solution (1% w/w of water) is used.



Graph 2: Stress v/s Strain plot for Paper strengthened with PU binder (1 % wt)

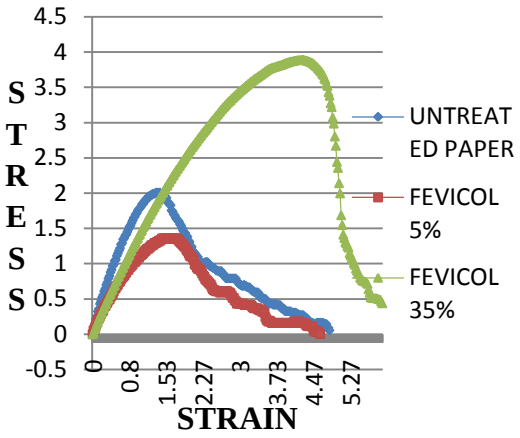
It is observed that there is no considerable change. The possible reason could be that since there are very few fibers in one plane (structure of the paper is multi-layered), the point of intersections/ overlap maybe very

few to affect the strength of paper considerably. It may also be possible that the resin did not bind with the fibers at all, and cross-linked with its own molecules. Possible diagnostic could be; if we wet press the paper, it may bring the fibers close enough to bind as desired; or other more interactive binders can be tested.

6.4. Experiment

Fevicol in various proportions was dispersed in water and then the fibers were dispersed in the solution.

Fevicol was dispersed in water in step 8 in various concentrations by weight of pulp.



Graph 3: Stress v/s Strain plot for Paper strengthened with fevicol (35%)

Low concentration of fevicol did not show any considerable change, though the 35% paper showed good improvement in the break stress of the paper.

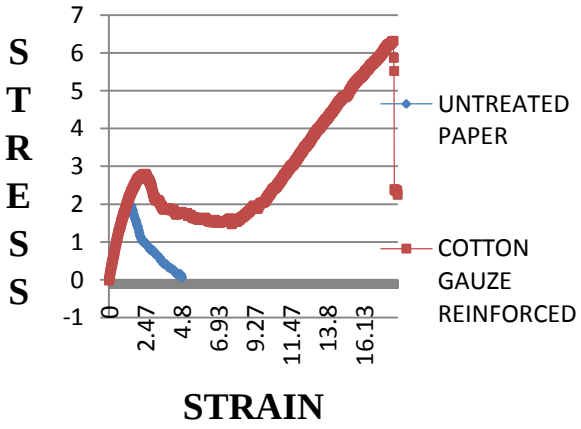
6.5. Experiment

Hypothesis No 2 was tested by reinforcing the paper with cotton gauze.

The cotton gauze was placed and stuck on the sieve, before placing it in water, and then the dispersed pulp was poured on it.

The reinforcement increased the stress as well as the strain to over 3 times.

To further improve upon this result, a gauge of very fine pores can be used, which will give us control over the opacity of paper, and may also increase the strength further. A binder can also be used in this system.



Graph 4: Stress v/s Strain plot for Paper reinforced with cotton gauge.

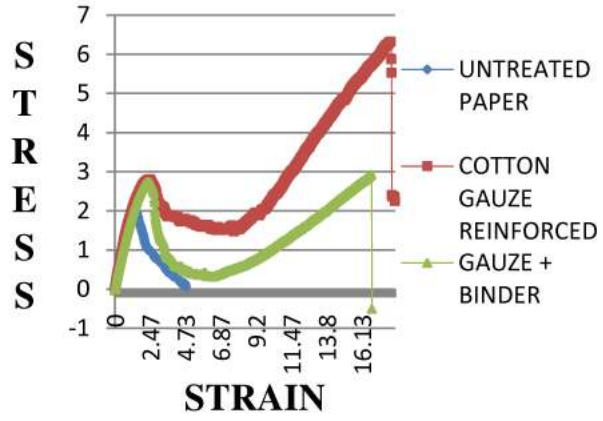
Though, using such reinforcement may cause a hindrance to security features such as those embedded in the paper, like the security thread or the watermark.

6.6. Experiment

6.7. Hypothesis No 2 was tested by reinforcing the paper with cotton gauze and adding a binder to it.

In step 8, PU dispersion was used instead of water, and a cotton gauge was also used.

Interestingly the polyurethane has not affected the 1st peak, i.e the peak which shows the tensile strength of the paper, whereas it has decreased the 2nd peak, i.e the peak which shows the tensile strength of the cotton gauze present inside the paper.

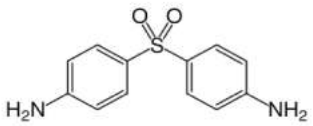


Graph 5: Stress v/s Strain plot for Paper strengthened with cotton gauge and PU binder.

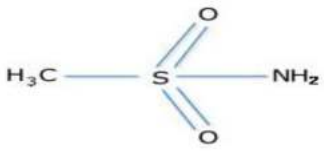
6.8. Experiment

4-Aminophenyl sulfone (Dapson) and methanesulfonamideare used to test hypothesis 3. They were dispersed in water in step 8.

4-Aminophenyl sulfone, provides for strong H-bonds since the lone pairs of N go into resonance and therefore making the N more electron deficient.

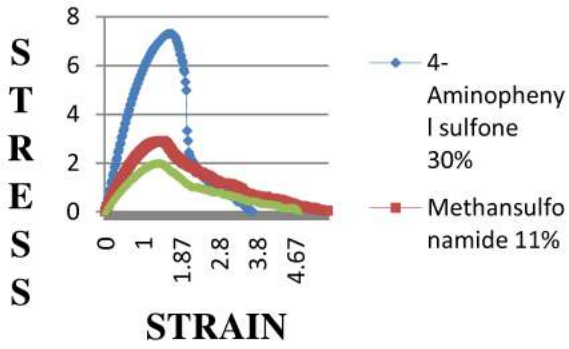


Methanesulfonamide also acts in the above manner, but since the SO_2 group is closer to the amino group, it makes the amino group more electron deficient, and should strengthen the H-bonding even more.



When 4-aminophenyl sulfone was used, stress increased to more than double its original value and for methanesulfonamide there was almost no effect in the properties of paper, which was unexpected.

The difference between them is that MS is



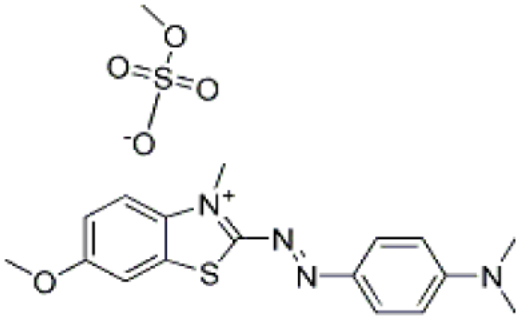
Graph 6: Stress v/s Strain plot for Paper strengthened with Dapson and Methanesulfonamide

water soluble whereas Dapson is only slighlty soluble; therefore it maybe deduced

that water soluble compounds remain dissolved in the water, and don't interact with the fibers.

6.9. Experiment

Using the dry strength additive cationic Polyacrylamide in various proportions.



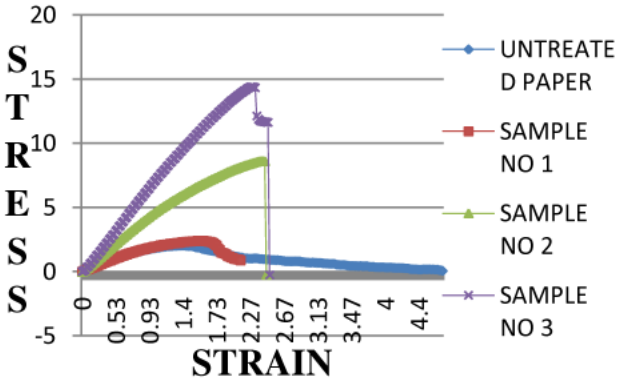
Cationic Polyacrylamide was added very slowly to the water while stirring vigorously taking care that lumps were not formed, and then the pulp was dispersed in this solution.

Cat. PAM was added in various proportions;

SAMPLE NO. 1 = 20% CPAM (w/w % of pulp)

SAMPLE NO. 2 = 33% CPAM (w/w % of pulp)

SAMPLE NO. 3 = 50% CPAM (w/w % of pulp)



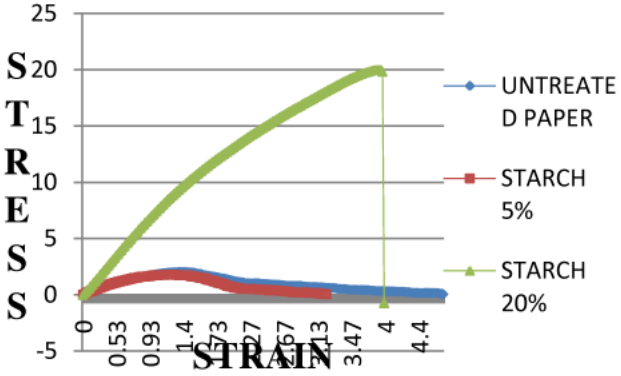
Graph 7 : Stress v/s Strain plot for Paper strengthened with Cationic Polyacrylamide

With increasing percent of CPAM, the break stress considerably increased, though the break strain remained constant.

6.10.Experiment

Using the binder starch in various proportions to test hypothesis 3.

Corn Starch was added very slowly to the water while stirring vigorously taking care that lumps were not formed, and then the pulp was dispersed in this solution.



Graph 8: Stress v/s Strain plot for Paper strengthened with Starch

High % of CPAM and Starch both give a significant rise in the break stress of paper, whereas the low % compositions showed almost no effect at all.

Starch dissolves in water at higher temperatures, and even CPAM needs considerable stirring time to dissolve in water.It may be deduced from the above

results that when taken in high % composition, some of it is settles onto the pulp.

The low % composition gets dissolved completely and therefore does not settle onto the pulp and hence no change in properties.

7. Conclusion

Of all the compounds and materials tried above, 4-aminophenyl sulfone, cationic polyacrylamide, starch and reinforcing using gauze showed promising results, which can be further explored.

An interesting observation from the above experiments was that water soluble compounds/ polymers in low concentration did not show any considerable effect, whereas when used in a higher concentration they all showed promising results.

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