

**A
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ON**

“Wet strengthening of paper by application of photo reactive, functional polymers”

Submitted for partial fulfillment of the requirement for award of the degree of

**MASTER OF TECHNOLOGY
IN
PULP AND PAPER ENGINEERING**

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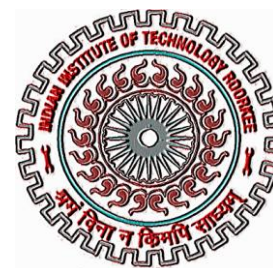
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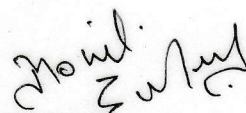
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CANDIDATE'S DECLARATION

I hereby declared that the work which is being presented in this Dissertation Report entitled "*Wet strengthening of paper by application of photo reactive, functional polymers*" in partial fulfillment of the requirement for the award of the degree of Master of Technology in Pulp and Paper, IIT Roorkee, is a record of my own work carried out, under the supervision of **Prof. Dr. Markus Biesalski**, Department Of Macromolecular And Paper Chemistry Technical University-Darmstadt, Germany, **Prof. Dr. A. k. Ray**, Department Of Paper Technology, IIT Roorkee, India and **Dr. U. K. Ghosh**, Department of Polymer and Process Engineering, IIT Roorkee, India.

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

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



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GLOSSARY:

AIBN	Azo-bis-(isobutyronitril)
DMAA	N,N-dimethylacrylamide
MABP	4-Benzolphenyl-2-methacrylate
PDMAA	Poly(dimethylacrylamide)
PVAm-BP	Poly vinyl amide-modified benzophenone
P(DMAA-co-MABP)	Poly(dimethylacrylamide-co-4-Benzolphenyl-2-methacrylate)
PCC	Precipitated Calcium carbonate
GCC	Grounded calcium carbonate
TiO ₂	Titanium dioxide
UF	Urea formaldehyde
MF	Melamine-formaldehyde
PAE	Polyamide-epichlorohydrin
G-PAM	Glyoxalated- polyacrylamide
DAS	Dialdehyde starch
SR	Schopper-Reiglar
UV	Ultraviolet
SZP	System zeta potential
GSM	Gram per square meter

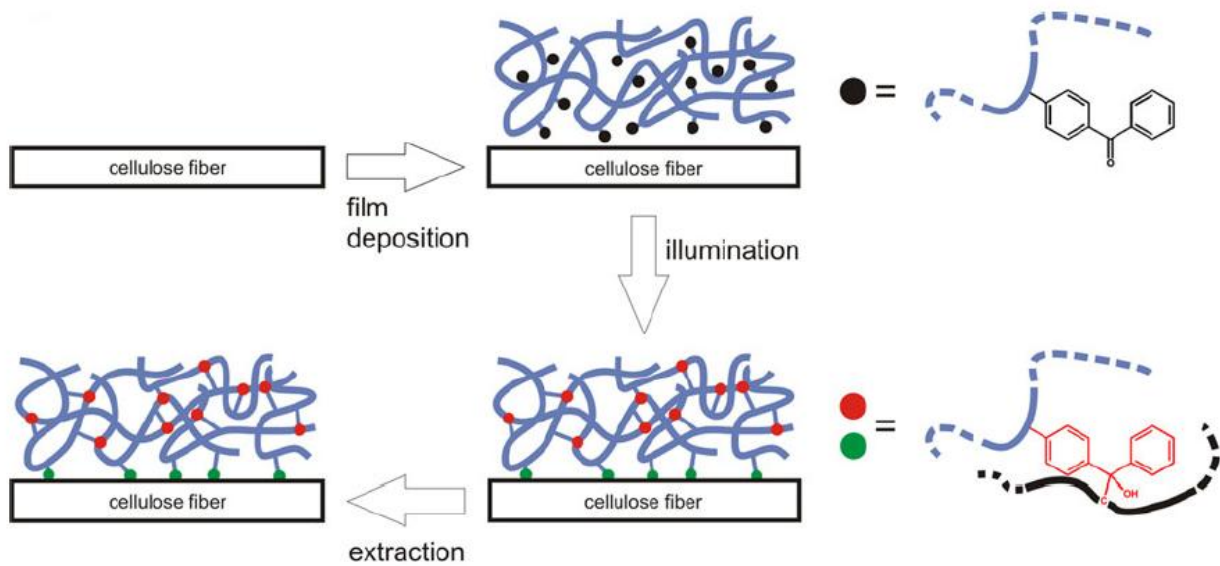
1. Introduction

Paper consists of cellulosic fibrous network and these fibre-fibre contacts are held together by intermolecular forces like hydrogen bonding or van der Waals forces (Rance, 1980). Without any water absorption these cellulosic fibres hardly come that close to each other to make hydrogen bonds between them, but fibres swell, once fibres absorb some water during paper making and these swelled fibres with increased fibre flexibility, mechanically entangled with each other during drying operation. Mechanically entangled swelled fibres have the ability to form hydrogen bridges in between them, and these hydrogen bridges are hydrogen bonds within fibres and fibre fibrils which are responsible for the dry strength of paper material.

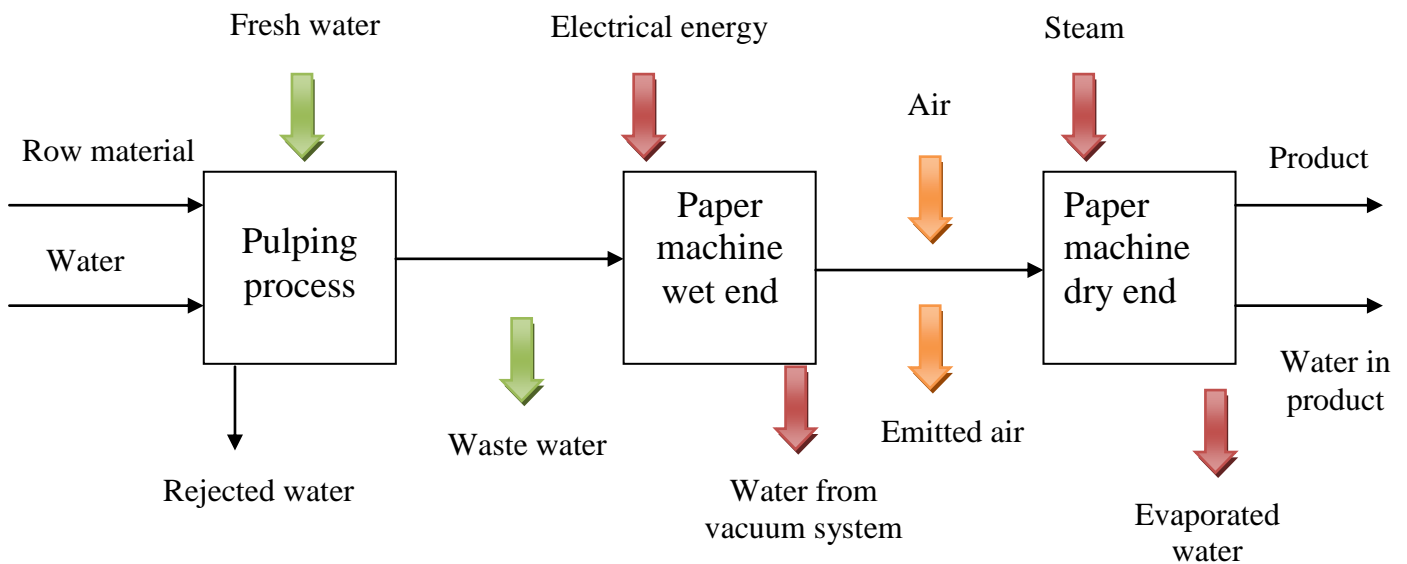
When paper material comes in contact with moisture or is soaked in water, it loses most of its dry strength properties. When paper is introduced to high moisture or water, paper fibres absorb water and become more flexible and swell (Stannett, 1967), hydrogen bonds break (Britt K., 1948), and the paper substrate loses its original dry strength. Paper substrate with a wet strength of more than 15% of its dry tensile strength should be considered as wet strength paper (Britt K. W., 1944).

Wet strength properties of paper substrate become more and more important when it comes under consideration to make products like tea bags, paper board, packaging paper, currency paper, wall and poster paper, maps, linerboard, corrugated board, carrier board, etc. (Britt K. A., 1965).

Photo-reactive polymers attach covalently to the cellulosic fibre surface with the help of a benzophenone group which can be excited by UV-light to form long-living triplet states at the carbonyl group, with the latter resembling a reactive biradical because the surface of cellulose microfibrils carries an abundant number of aliphatic CH-groups (Bohm, 2012) and these photo-reactive functional polymers, carrying a photo-reactive benzophenone group, were introduced to paper substrate by wet and surface application. These modified paper substrates were illuminated with UV-light to increase the wet strength of the paper substrate.



Scheme 1 Attachment of Photo-reactive polymer, carrying photo-reactive benzophenone group to cellulose fibres. By the irradiation with UV light, photochemical reaction of the benzophenone groups with aliphatic C–H–groups of the cellulose fibre occurs and a surface-attached polymer network is formed.(black, green and red dots schematically indicate non-reacted benzophenone groups, benzophenone groups which have reacted to other polymer segments and those that did react with cellulose fibres, respectively. (Bohm, 2012)



Scheme 2 Industrial paper making process.

2. Review of literature:

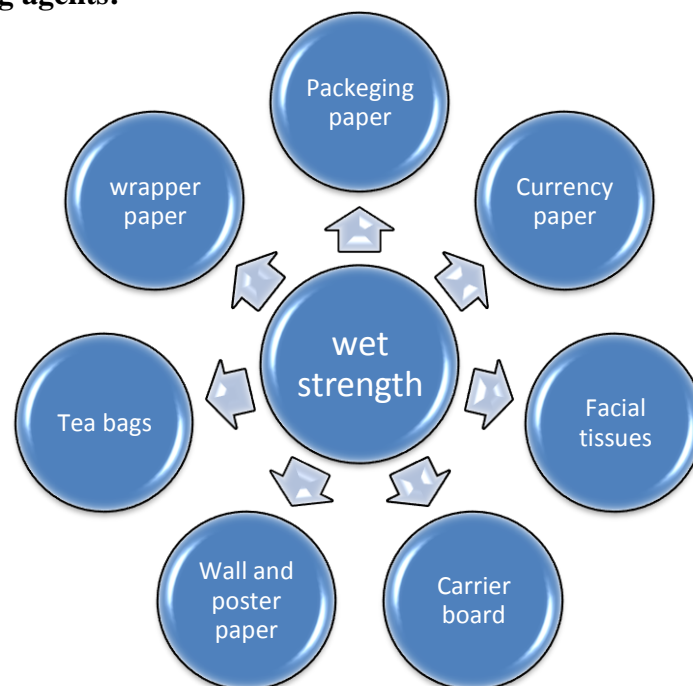
1.1. Charge of cellulosic fibre:

During paper making process, fibre charge influences paper properties. Cellulose fibres contain carboxyl-, hydroxyl-, phenolic-, and sulfonic acid groups and because of these groups fibres contain negative charge at all pH values. Generally, in normal paper making condition, carboxyl and sulfonic groups give negative fibre charge and these groups are located either on the surface or inside the cell wall. These surface charges are important for paper or fibre strength. (Fors, 2000)

1.2. Polymer adsorption:

As cellulosic fibre contains negative charge on surface, because of this most cationic additives has ability to adsorb on fibre surface. That is why polymer used in paper making process often cationic in nature. When a solvent is poor, then polymer adsorption is becomes more favourable than the polymer-solvent interaction. Factors affecting polymer adsorption are density and distribution of charges, molecular weight of polymer and presence of fines. Polymer adsorption is generally a reversible process, in that polymer can detach from fibre surface. However, changes in pH, ionic strength etc might cause desorption of polymer from the fibre surface. (Bengtsson, 2005)

1.3. Wet strengthening agents:



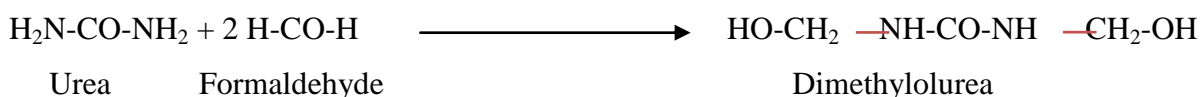
Scheme 3 Wet strengthen in paper material.

Most of the untreated paper substrate loses more than 92% of its original dry strength within few seconds of being saturated with water. Some temporary wet strength chemical treated paper substrate loses their wet strength slowly when they are soaked in water. Some chemical treated paper substrate shows more wet strength properties when they are soaked in water for a long time, these chemical called permanent wet strength agents (Britt K. W., 1979). Animal glues or regenerated cellulose were used before World War II for making wet strength paper, and this process was called parchmentizing process (Maxwell, 1950). Then a process in which heat treatment at rising temperature 210°C to 450°C were used (Anderson, 1975) (Back, 1989), was not widely accepted because of limited effectiveness. Later on formaldehyde was used as wet strength additive because it has capability to crosslink to cellulose at low pH and high temperature (Stamm, 1959) (Caulfield, 1976). However this process of wet strengthening of paper was also rejected because of brittleness in paper substrate and the bad odor of formaldehyde.

After 1935, the use of thermosetting aminoplast (MF and UF) came into commercial use (Britt K. W., 1979). In these years (1935 to 1941), significantly improvement in wet strength properties because of addition of certain water soluble synthetic polymer to paper and curing *in situ* could be achieved.

-During period of 1942 to 1950, a greater increase in use of wet strength resins was observed. In 1960s, a thermosetting resin was developed to avoid the acidity requirements for the cure of UF and MF resin.

UF resins are classified in protection mechanism, because it shows homo-cross-linking in low p^H condition. As urea reacts with formaldehyde under slightly alkaline condition to form methylolurea.

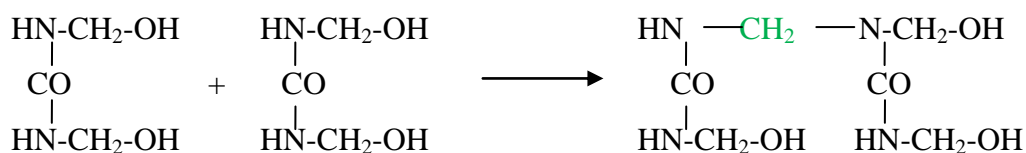


Equation 1 Methylolation reaction

When this methylol groups come under contact with low p^H condition, a polymer is formed by the self-condensation. And further low p^H and high temperature gives methylene or ether linkage with the elimination of water.

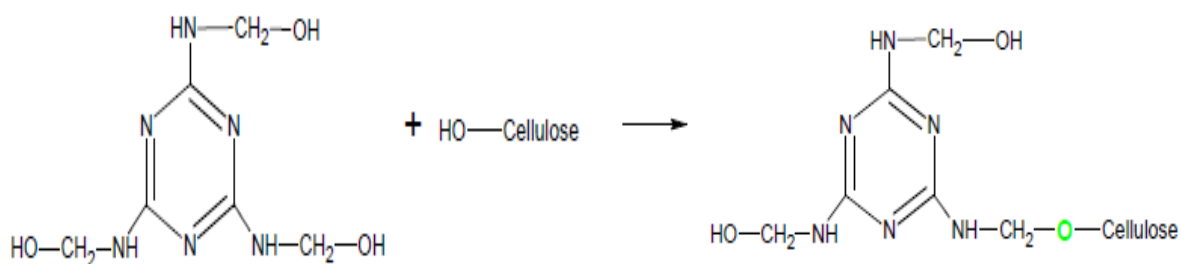


Equation 2 Creation of ether linkage



Equation 3 Creation of methylene linkage

MF resins are classified in protection and reinforcement mechanism, because MF resins can crosslink intra or intermolecular within resins or it can cross link with cellulose, but it is generally assumed that homo-cross-linking (protection mechanism) is major mechanism to give wet strength by applying MF resins. This conclusion is mainly supported by the fact that the activation energy of hydrolytic cleavage is the same (23 kcal/mole) for both UF and MF resins. (chan, 1994), but some model experiments also reveal that MF resins can react with cellulose molecules. (Bates, 1966)



Equation 4 Hexamethylol melamine reacts with cellulose to form an ether linkage between them. (Jocher, 2011)

Melamine reacts with formaldehyde under slightly alkaline condition to form methylol melamines. Depending on the number of modes of formaldehyde presents, a range of products from monomethylol to hexamethylol melamine can be formed. Polycondensation occurs at low P^H and high temperature.

MF resins are strong wet strengthening agents, but limited to acidic use under alkaline paper making conditions. Indeed, MF resins are better than UF resins at imparting moist stiffness to paper sheets. (Fahey, 1962)

Now these synthetic resins such as urea formaldehyde (UF), melamine-formaldehyde (MF), polyamide-epichlorohydrin (PAE), polyethyleneimine (PEI), glyoxalated- polyacrylamide (G-PAM), and dialdehyde starch (DAS). UF, MF, and PAE are regarded as permanent wet strength agents, as these chemicals are class of chemicals that adhere to pulp fibres and form linkages between fibres through covalent bonding. These linkages supplement and reinforce the natural hydrogen bonding in

the dry sheet and, because they're covalent, cannot be broken by soaking in water and are resistant to cleaning chemicals. Papers treated with these resins, such as kitchen towels and wipers, typically have a wet tensile strength of 15 percent or greater of their dry tensile strength.

PAE resins are widely used and commercially available chemical which share 90% of market share in terms of wet strength agents. (Health Effect Assessment Summary Table EER 920.6-303(90-3), NTIS No. P890-921100, 1990)

Polyamide-epichlorohydrin (PAE) resin can be used at neutral-to-alkaline pHs. PAE resins have a high level of wet strength permanence, help improve machine efficiency, and do not adversely affect paper absorbency. Recent development work has focused on improving the wet strength efficiency of PAE products while increasing product solids and decreasing organic chlorine content.

All PAE resins, the polymer contains quaternary ammonium groups that adsorb onto negatively charged paper fibres and that continue to cross-link even as the paper dries and cures. That means the wet strength of paper treated with PAE wet-strength resin continues to increase after it's been put into storage. (Dulany, 1989)

PEI was of wet-strength resins developed by Germany in 1930s, but PEI has the problem repulping because of this wet strength agent has limited in use today. Two other resin G-PAM and DAS, are regarded as temporary wet strength agents, which share around 10% market portion (Health Effect Assessment Summary Table EER 920.6-303(90-3), NTIS No. P890-921100, 1990).

All of the above resins can be applied by wet end or surface application at level of 0.5 to 3% based on the pulp fibre mass. By this, wet tensile strength can be improved from less than 10% to up to 40-50% of original dry tensile strength.

1.4. Problems in current wet-strength agents:

Wet strength agents such as UF, MF, PAE are considered under subject of scrutiny now because UF and MF resins contains about 2 to 5 % of free formaldehyde in the resin when supplied (Stange, 1994) (Dulany, 1989). An effort has been made to reduce this free formaldehyde (Chan, 1989). It is witnessed that last few years there is tremendously decline in uses of UF and MF resin. PAE has also been condemned for emission of absorbable organic halogen compounds (AOX) from paper mills and treated paper. (Devore, 1991).

Over the years, researchers have modified the basic chemistry to make stronger performing resins with reduced by-products, 1, 3-dichloropropanol (1, 3-DCP) and 3-monochloropropan-1, 2-diol (3-MCPD), as well as aminochlorohydrin (ACH) and polymer bound CPD (PB-CPD).

Industries are using Membrane Separation Technology, which can help paper mills decrease levels of both 1, 3-DCP and 3-MCPD and overall AOX. (Richard J Riehle, 2008)

Meanwhile, the development of new effective wet strength resin without formaldehyde and organic chloride is still in its infancy. Most of the current efforts have suffered from some difficulties (Stange, 1994), such as insufficient resin effectiveness, detrimental effects on dry properties, incompatible curing conditions, or high cost.

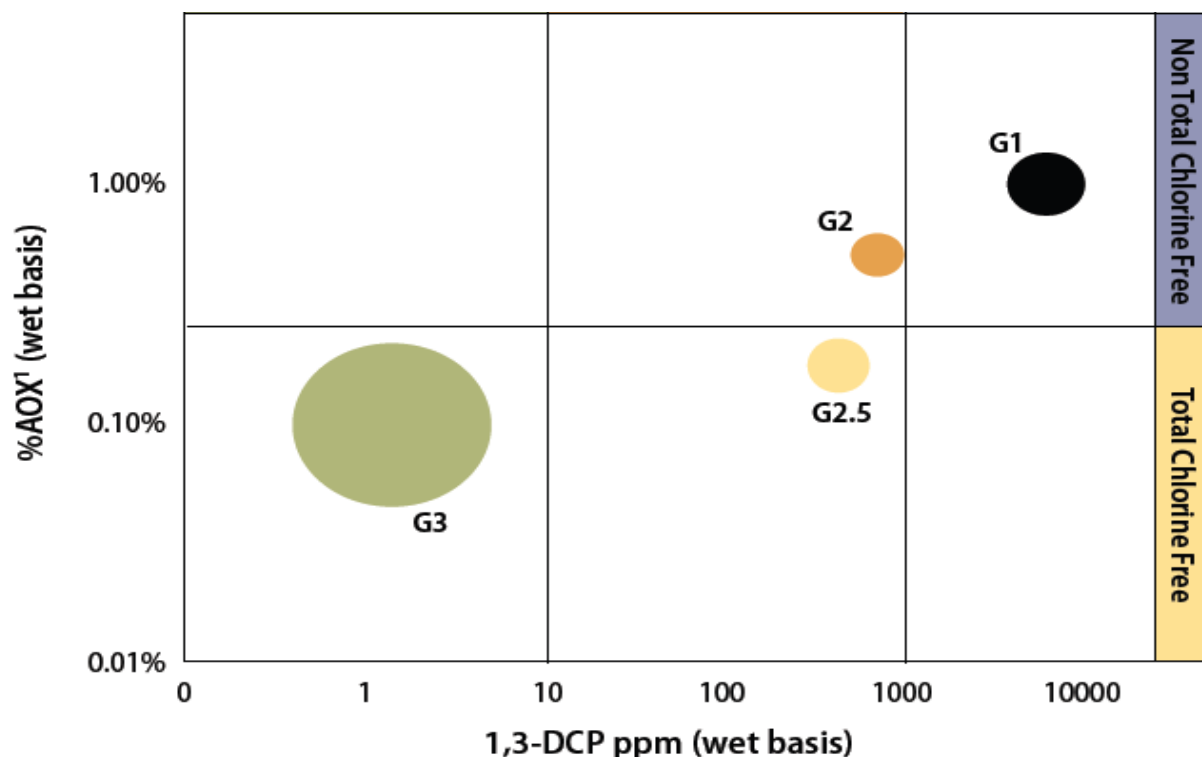


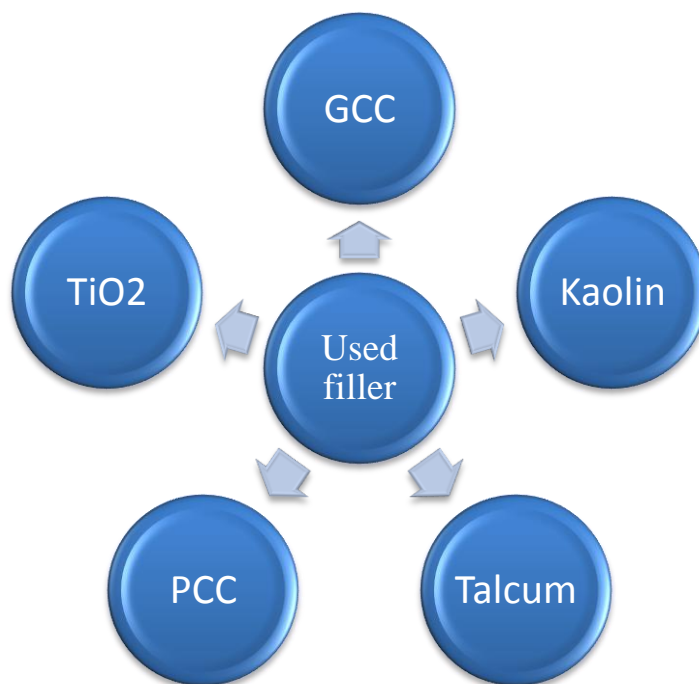
Figure 1 Widely used industry descriptors of G1, G2, G2.5 and G3 PAE resins, environmental labelling established by Nordic Ecolabel and recommendations issued by the German Federal Institute of Risk Assessment (Bundesinstitut für Risikobewertung, or BfR).

1.5. Fillers in paper:

Mineral fillers are used in paper material, they fill the spaces between fibres and they improve certain properties such as: optical (brightness, light scattering, opacity, and gloss), structural (smoothness, bulk, and air permeability) and printing. Mainly mineral fillers (PCC, GCC, Talcum, kaolin and TiO₂) are commonly used in manufacturing of printing papers, because these filler improve optical properties like brightness and whiteness of paper material. (Xujun Hua, 2011)

These mineral based fillers affect paper properties which are essentially based on particle shape (scalenohedral, rhombohedral and lamellar) and also on particle aggregation (structured and non-structured). Structured filler like scalenohedral and rhombohedral (calcium carbonate and calcinated kaolin) are useful to achieve opacifying agents imparting to paper high light scattering but these paper properties can be achieved with bulky and porous paper which influence negative strength properties.

Lamellar fillers, like kaolin and talc are responsible for denser and thinner sheets with less influenced strength properties. So these lamellar fillers give low air permeability and higher smoothness and do not act as an ocacifying agent. Structured fillers give higher sizing demand and drainage rate. In these structured fillers, talc is best in terms of sizing agent consumption because it has hydrophobicity characteristic and a narrow particle size distribution. (Velho, 2002)



Scheme 4 Used fillers in experiments.

Including fillers contents into paper could be an alternative strategy to reduce fibre consumption, improve paper printing qualities. Fillers mainly reduce fibre-fibre bonding in paper material because of this tensile strength of paper material get reduced. (Xujun Hua, 2011)

Fillers are having lower cost than fibres, and paper machine can be operated at high speed with filler paper material because paper with filler is easier to dry than paper without fillers, it gives more energy saving during drying operation of paper and it shows paper with fillers is more cost effective.

In wet condition of paper with fillers can be break easily at the draws of paper machine, whereas in dry state fillers containing papers are having more tendencies towards breaking in printing, conversion and end uses. (Sutman, 2011)

Fillers addition is a wet end operation in paper mill, before paper making filler should be added into stock solution; during this operation retention aids can be added to increase the retention of fillers in paper. Retention aid gives more binding to filler towards cellulose fibre, and by this drainage problem of fillers can be overcome. (Sutman, 2011)

2. Goals and Strategy

2.1. Goals:

The first purpose of project was to use a photo-reactive polymer as a wet strengthen agent without the disadvantage of free formaldehyde and AOX release.

Another aspect of the research was to observe the impact of ‘fillers’ and ‘intensity of UV irradiation’ on wet strength properties of paper substrate containing photo-reactive polymer.

And testing of

1. Zeta Potential(Z.P.) measurement
2. Dry tensile strength
3. Wet tensile strength
4. Relative wet strength
5. Elongation at break

2.2. Strategy:

2.2.1. Polymer (PDMAA-co-MABP) Preparation:

As Martina Ewald prepared polymer, DMAA (16.4ml) and MABP (0.426gm) were separately dissolved in ethyl ether (100ml) then these solutions were mixed in 250ml schlenk flask with small amount of AIBN (52.4mg) initiator in it. This flask was kept under nitrogen atmosphere and then freeze-pump-thaw process was applied three times to remove any air from the flask. Then this flask kept 10 hrs under contact with hot oil bath (60°C) to complete the reaction inside the flask. Then this precipitated solution was dried under high vacuum and filtered. 15.9gm yield of dry polymer was obtained. NMR was performed to check the purity of the polymer and we found no monomer inside it, small amount of ethyl ether and ethyl acetate also present with the polymer and ratio of MABP to DMAA is 1% in polymer.

2.2.2. Polymer solution preparation:

To prepare 1% stock solution of PDMAA-co-MABP polymer, polymer was added in defined amount of distilled water and kept for stirring for 2 hr on magnetic stirrer.

2.2.3. Filler solutions preparation:

Different types of fillers were used, which were GCC, PCC, Talcum, Kaolin and TiO₂. 5% of stock solution for each type of fillers in distilled water was made. Stirred for 1 hr on magnetic stirrer and after kept in Ultrasonic bar for 10 minutes.

2.2.4. Retention aid solution preparation:

To prepare 0.03% stock solution of PAM, 0.72mg PAM added to 200ml of distilled water and magnetic stirred for 15 min.

2.2.5. Paper sheets making:

Rapid-Köthen (RK) hand sheet former was used to prepare paper sheets. Before making hand sheets pulp was prepared with disintegration of 35gm of pulp in each run of Hylec Pulp Disintegrator.

And then this pulp has been transfer to the pulp distributor for proper mixing and to avoid settlement of pulp during paper sheet making.

First sheet was made for calculate pulp consistency in pulp distributor. And after measuring a required volume has been calculated for making specific grammage of paper sheets.

Then paper sheets were prepared with hand sheet former, and dried into dryer with specific pressure and same time (10min).

For filler containing paper sheets, which were prepared with 2.4 gm of pulp fibre by adding fillers according to their concentration and retention aid.

Filler concentration (wt% of dry fibre)	Filler in gm	Vol. of 5% stock solution(ml)	Retention aid (0.003 wt% of dry fibre) (in mg)
5%	0.12	2.4	0.72
10%	0.24	4.8	0.72
20%	0.48	9.6	0.72

2.2.6. Operating conditions of size press:

Polymer was applied by surface application by using size press. Rolls rotation speed of 13 m/min with 4.5 bar pressure between the rolls was used. We performed with 1% PDMAA-co-MABP polymer solution on eucalyptus paper sheets and paper sheets were weighted in the wet condition after applying polymer on it. Applied polymer weight was calculated by measuring weight before and after of size press application, and found that we actually applied $1.05\% \pm 0.014$ of Polymer relative to dry fibre (wt %). Paper sheets were dried by drum drier under condition 100 °C temperature and 20 rotations per

minutes then covered with aluminium foil to store in climate room contains 23°C temperature and 49 % humidity.

2.2.7. UV-irradiation:

An UV chamber (254 nm wavelength) was used to irradiate paper sample. To see the effect of different types of filler and their different concentration, $2 \times 0.2 \text{ J/cm}^2$ intensity of exposure (both side of paper sample) was used and for observation of effect of UV exposure on strength properties of paper, paper sheets were irradiated with different intensity of UV exposure like 0.005, 0.010, 0.015, 0.020, and 0.025 J/cm^2 .

2.2.8. Strength measurement:

For strength measurement, Zwick Roell tensile tester was used and tensile strength, tensile index, elongation at break (Muchorski, Tensile properties of paper and paperboard [TAPPI T 494], 2006) were measured, paper sheets with dry-wet condition, UV exposed-unexposed condition were used to see effect of these on strength properties of paper. For wet strength measurement, some distilled water was taken in plastic trays and kept these water trays in 23°C temperature and 49 % humidity climate room for some time so it reaches the same temperature as climate room. Paper sample strips then introduced to water for 10 min to get saturate with water. Then these strips were withdrawn straight to blotting paper and pressed gently to remove excess water. After blotting, paper sample strips were placed to the tensile tester [T 456om-10]. To calculate relative wet strength

$$\text{Relative wet strength (\%)} = \frac{\text{wet tensile strength}}{\text{dry tensile strength}} \times 100 \%$$

2.2.9. Filler content measurement:

Paper sample with specific area (15 cm length and 2 cm in width for each sample) were ignited into muffle furnace at 525°C for 3 hr. and before and after ignition weight were calculated for each sample (Ash in wood, pulp, paper and paperboard, T 211 om-02, 2002) (one sample for each used filler concentration from both UV exposed and unexposed paper material). And weights were calculated for 20cm diameter paper sheet.

In second stage, paper without filler ignited with same temperature and same duration and weights were calculated before and after ignition.

In third stage, only fillers were ignited with same temperature and duration and weights were calculated before and after ignition.

Filler content measured by

Filler content (in gm) = Ash content in 20 cm dia. Paper sheet + Ash content in filler
- Ash content in filler without paper

$$\text{Filler content (in \%)} = \frac{\text{filler content in gm} * 100}{(\text{paper sheet weight (20 dia.)})}$$

3. Experimental design:

3.1. Variation in types of pulp and concentration of polymer:

Different type of pulps like eucalyptus bleached and beech sulphite bleached were used with variable polymer concentration (0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5%). Photo-reactive polymer was applied by the wet end application according to mass of dry pulp fibre in paper sheet (2.45 gm. 7 sheets were prepared for each polymer concentration and paper sheets were weighed under condition of 23°C temperature and 49 % humidity.

Pulp	Eucalyptus bleached, Beech sulphite bleached
Polymer	Photo-reactive polymer (PVAm-BP)
Polymer relative to dry fibre (wt %)	0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5%.
Polymer applied	By wet end application
GSM of paper sheet	80 ± 1.5
U.V. exposure	2x 0.2 J/cm ²

Table 1 Variation in types of pulp and concentration of polymer

An average GSM value of paper sheets was calculated (80 ± 1.5). 40 paper strips were produced for each concentration with 1.5 cm wide and 16 cm length of each strip. 20 paper strips were used for dry strength measurement and another 20 strips were used for wet strength measurement. Within these 20 paper strips, 10 paper strips were used for UV irradiation and another 10 paper strips for no UV irradiation. Each paper strip was irradiated by 0.2 J/cm² intensity of UV light for both side of strip. In conclusion, 10 paper strips were used for each type of strength measurement.

3.2. Variation in type of GSMs and concentration of polymer:

Eucalyptus bleached pulp was used with variable polymer concentration (0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5%). Variable GSM (25.0, 76.8, and 128.9) paper sheets were produced and polymer was applied by the wet end application according to mass of dry pulp fibre in paper sheet. For each concentration, 7 sheets were prepared. Paper sheets were weighed under condition of 23°C temperature and 49 % humidity and by these weights, average GSM values of paper sheets were calculated (25.0, 76.8, and 128.9). 40 paper strips were created for each concentration with 1.5 cm wide and 16 cm long of each strip. Each paper strip was irradiated by 0.2 J/cm² intensity of UV light for both side of strip. At last 10 paper strips were used for each type of strength measurement.

Pulp	Eucalyptus bleached
Polymer	Photo-reactive polymer (PVAm-BP)
Polymer relative to dry fibre (wt %)	0.25%, 0.5%, 0.75%, 1%, 1.25% and 1.5%.
Polymer applied	By wet end application
GSM of paper sheet	25.0, 76.8, 128.9
U.V. exposure	2x 0.2 J/cm ²

Table 2 Variation in types of GSM and concentration of polymer

3.3. Variation in type of fillers and its concentration:

Eucalyptus bleached pulp was used with PDMAA-co-MABP photo-reactive polymer in it. Variable filler concentrations (5%, 10% and 20 wt% of dry pulp fibre) were used. Paper sheets (76.8 GSM) were prepared and polymer was applied by the wet end application according to mass of dry pulp fibre in paper sheet. For each concentration, 7 sheets were prepared. Paper sheets were weighed under condition of 23°C temperature and 49 % humidity and by these weights, average GSM values of paper sheets were calculated (76.8). 40 paper strips were produced for each concentration with 1.5 cm wide and 16 cm length of each strip. Each paper strip was irradiated by 0.2 J/cm² intensity of UV light for both side of strip. At last 10 paper strips were used for each type of strength measurement.

Pulp	Eucalyptus bleached
Fillers	GCC, PCC, Talcum, Kaolin and TiO₂
Fillers related to dry fibres (wt %)	5%, 10% and 20%
Polymer	Photo-reactive polymer (PDMAA-co-MABP)
Polymer relative to dry fibre (wt %)	1.05% ± 0.014
Polymer applied	By surface application
GSM of paper sheet	Depends upon type and content of fillers
U.V. exposure	2x 0.2 J/cm ²

Table 3 Variation in types of filler and content of filler

3.4. Variation in type of fillers and intensity of UV exposure:

Eucalyptus bleached pulp was used with PDMAA-co-MABP photo-reactive polymer in it. Paper sheets with different type of fillers (GCC, PCC, Talcum, Kaolin and TiO₂) were made and polymer was applied by the wet end application according to mass of dry pulp fibre in paper sheet. Variable UV

light intensities (0.005, 0.01, 0.015, 0.02, 0.025 (J/cm²)) were used with single 254nm wavelength to expose the paper sheets. For each concentration, 7 sheets were formed. Paper sheets were weighted under condition of 23°C temperature and 49 % humidity and by these weights, average GSM values of paper sheets were calculated (76.8g/m²). 40 paper strips were produced for each concentration with 1.5 cm wide and 16 cm long of each strip. At last 10 paper strips are used for each type of strength measurement.

Pulp	Eucalyptus bleached
Fillers	GCC, PCC, Talcum, Kaolin and TiO₂
Fillers related to dry fibres (wt %)	20%
Polymer	Photo-reactive polymer (PDMAA-co-MABP)
Polymer relative to dry fibre (wt %)	1.05% ± 0.014
Polymer applied	By surface application
GSM of paper sheet	Depends upon type and content of fillers
U.V. exposure	0.005, 0.01, 0.015, 0.02, 0.025 (J/cm²)

Table 4 Variation in types of filler and intensity of exposure

4. Result and Discussion

Zeta potential values were calculated with the changes in polymer concentration relative to dry fibre (wt %).

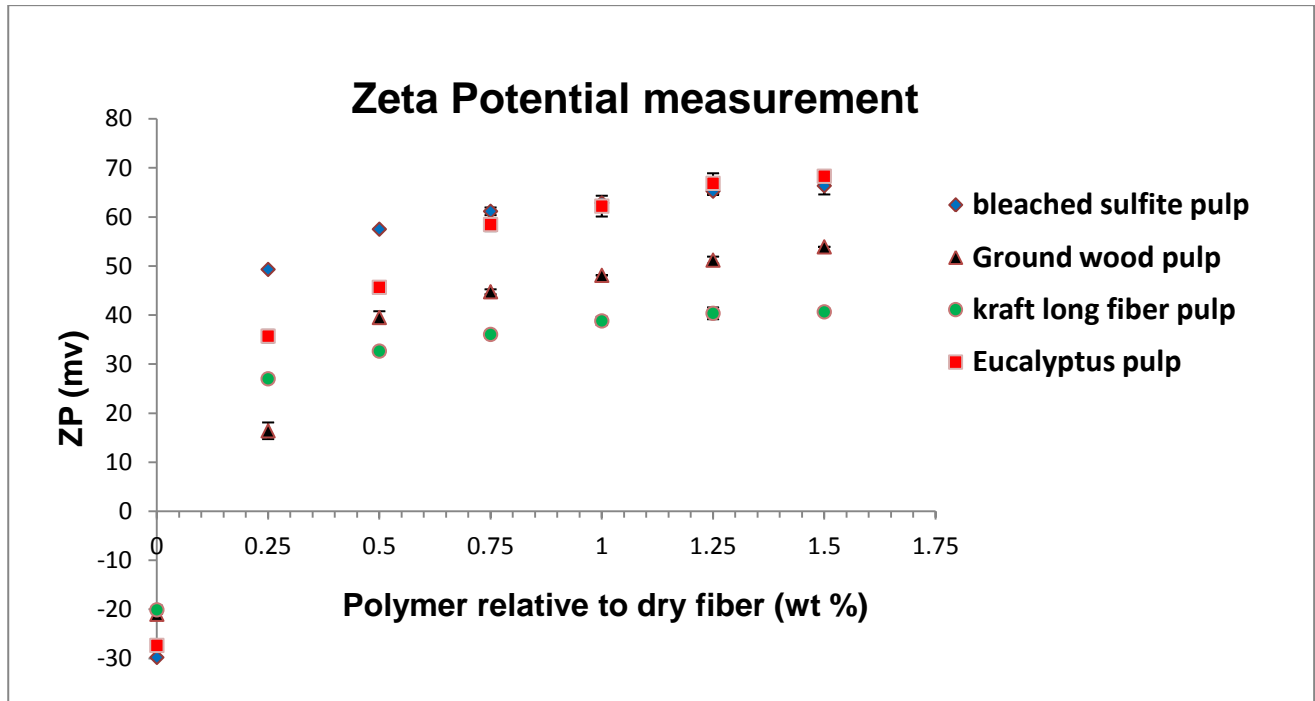


Figure 2 Zeta Potential (mv), as a function of the polymer relative to dry fibre (wt %) for Eucalyptus bleached (red), Beech sulphite bleached (blue), Long fibre Kraft unbleached (Mondi Monopole) (green), Ground wood (black).

From the graph, zeta potential values increases with the increase in polymer concentration. In the range of 0% to 0.25 % polymer concentration, zeta potential values become negative to positive and further increment in polymer concentration (between 0.25% to 1.5%), slightly increment in zeta potential values for all types of pulp. Ground wood pulp shows a slightly less increment in ZP within range of 0% to 0.25% of polymer concentration and little higher increment in ZP in range of 0.25% to 0.5%. Beech sulphite pulp shows maximum increase in zeta potential values within range of 0% to 0.25% of polymer concentration.

It can be concluded that ground wood pulp has low tendency to adsorb photo-reactive polymer at low concentration of polymer because mechanical pulp has more impurities which means this GW pulp contains other anionic impurities to adsorb cationic polymer. Bleached eucalyptus pulp and beech sulphite pulp show good adsorbability of polymer within range of 0 to 0.25%, because these pulps come under chemical treatment and contain less impurity.

Chemically treated pulp has higher adsorbability for PVAm-BP polymer. Therefore Beech sulphite and bleached eucalyptus pulp were used for experiments.

4.1. Effect of grammage on paper strength (Paper containing PVAm-BP):

4.1.1. Effect on dry tensile strength:

Dry tensile strength values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

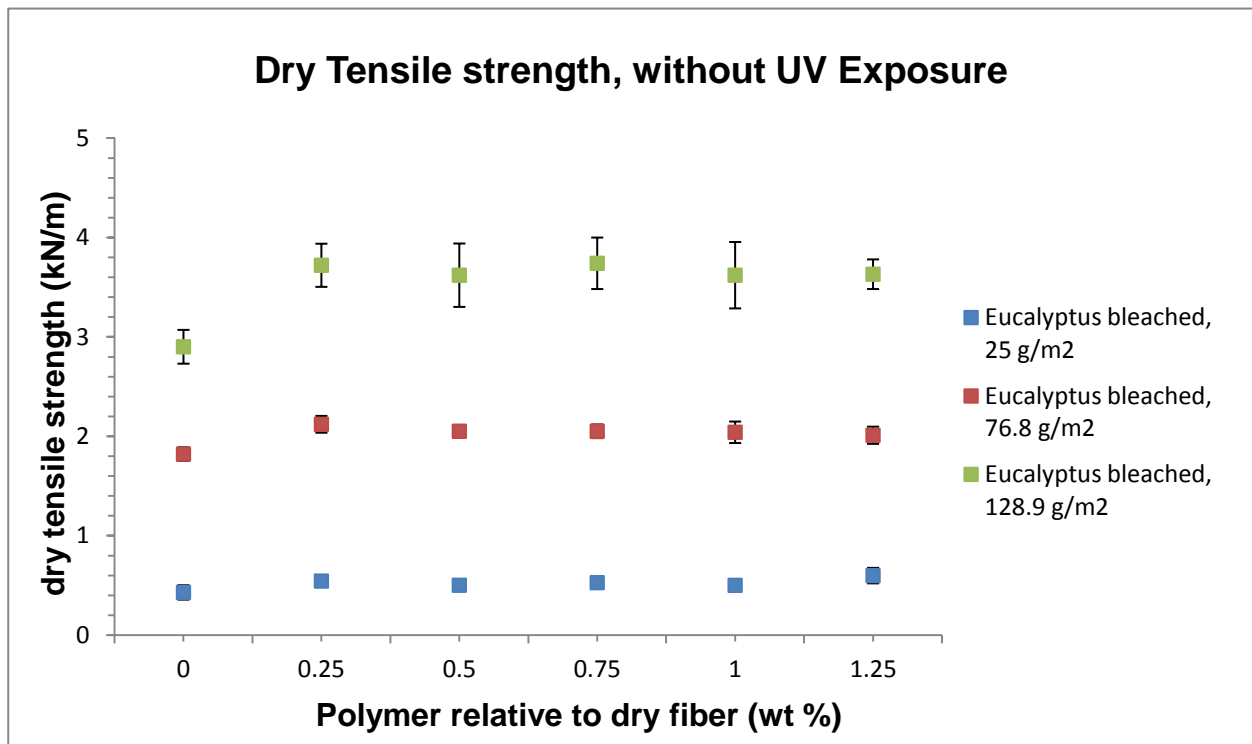


Figure 3 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

From the graphs, there is no significant difference in dry tensile strength by increasing concentration of photo-reactive polymer at any grammage of paper sheet. But in comparison between different grammage of eucalyptus pulp (25, 76.8 and 128.9 g/m²), 128.9g/m² shows higher dry tensile strength values and 25g/m² grammage shows lowest dry strength values.

It can be concluded that paper sheet with higher grammage and same type of pulp, has high dry tensile strength, because increase fibre mass have more number of fibre-fibre bonds and to break those bonds higher force is required, and this higher force gives higher dry tensile strength values.

If a higher dry tensile strength is required for some final paper product then a higher grammage of paper material can be a good idea.

Dry tensile strength values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

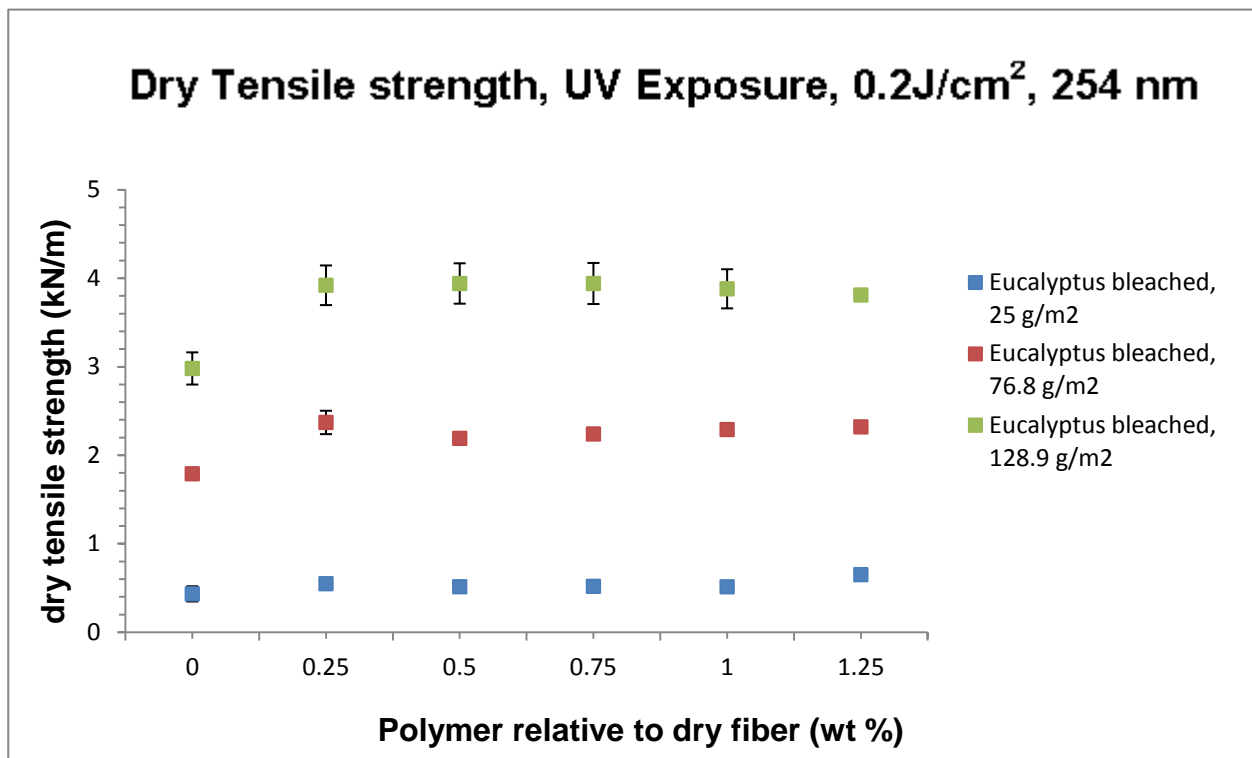


Figure 4 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

From the graph, it was observed that there is no significance difference in dry tensile strength values even when paper sheets were UV irradiated at 0.2J/cm² inside 254nm UV chamber. It can be concluded that there is no effect of PVAm-BP on dry tensile strength of paper. PVAm-BP should not use for increase only dry tensile strength of paper substrate.

4.1.2. Effect on dry tensile index:

Dry tensile index values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

From the graphs, there is no significant difference in dry tensile index by increasing concentration of PVAm-BP at any grammage of paper sheet. But in comparison between different grammage of eucalyptus pulp (25, 76.8 and 128.9 g/m²), 25g/m² grammage shows lowest dry tensile index values and further increasing in grammage, there is no significant increment in dry tensile index values. Generally grammage of paper sheet doesn't affect the tensile index value, but 25g/m² grammage sheet

shows little lesser dry tensile index values because at this grammage, paper sheet is very thin and very less dense in nature, and a little force can break this sheet, that is why it has less tensile index values.

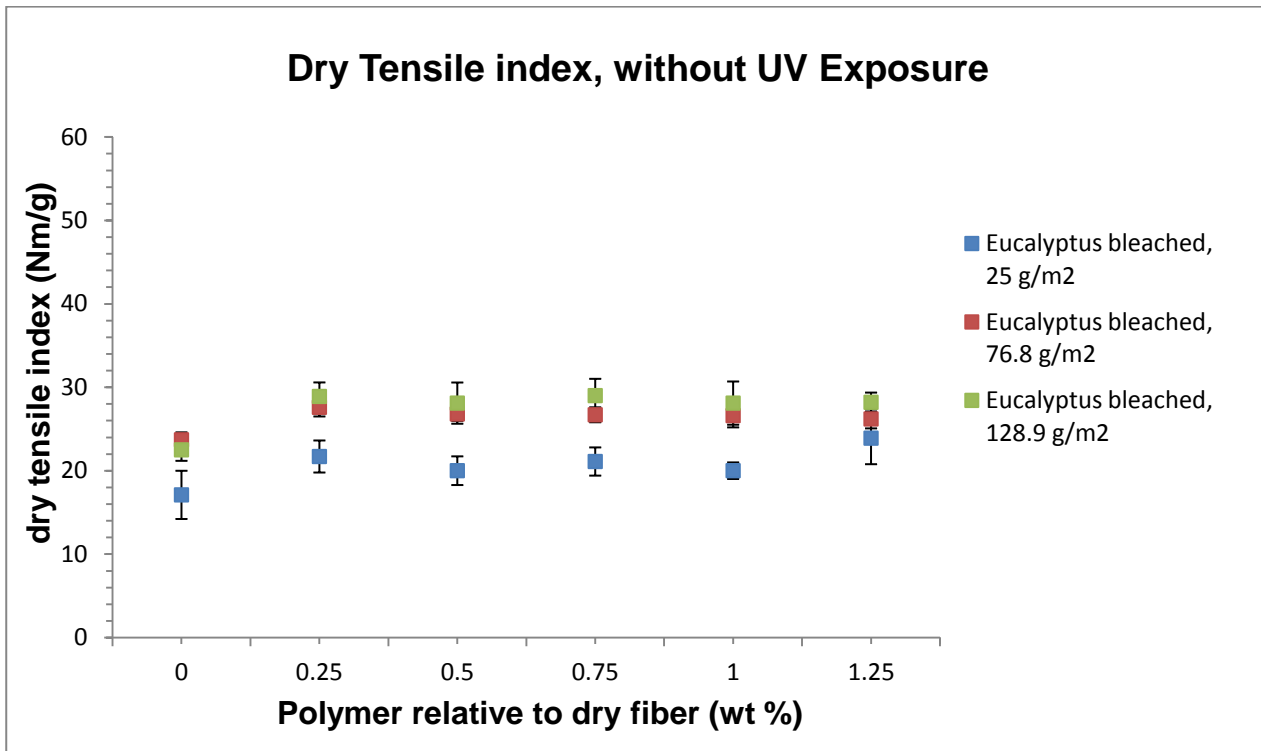


Figure 5 Dry tensile index, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

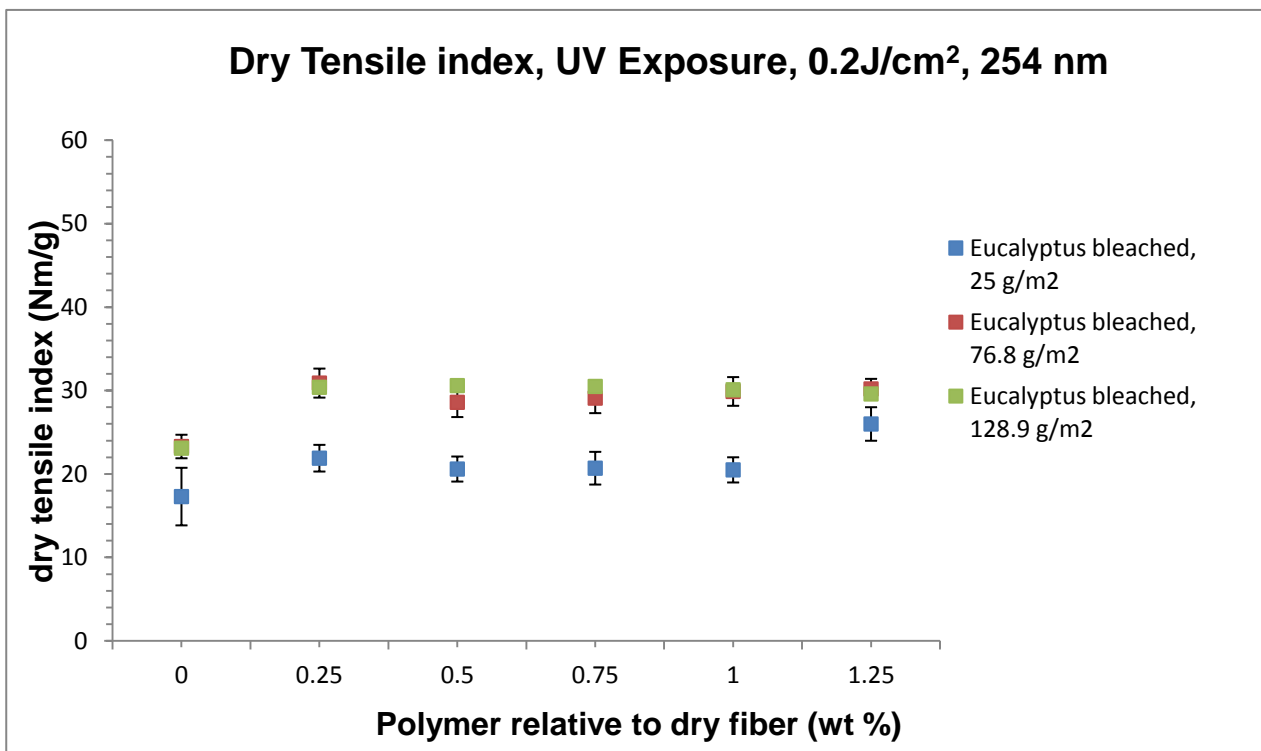


Figure 6 Dry tensile index, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

Dry tensile index values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

From the graph, it was observed that there is no significance difference in dry tensile index values even when paper sheets were UV irradiated at $0.2\text{J}/\text{cm}^2$ inside 254nm UV chamber. It can be concluded that there is no effect of PVAm-BP on dry tensile index of paper. PVAm-BP should not use for increase only dry tensile index of paper substrate.

4.1.3. Effect on dry elongation at break:

Dry elongation at break values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

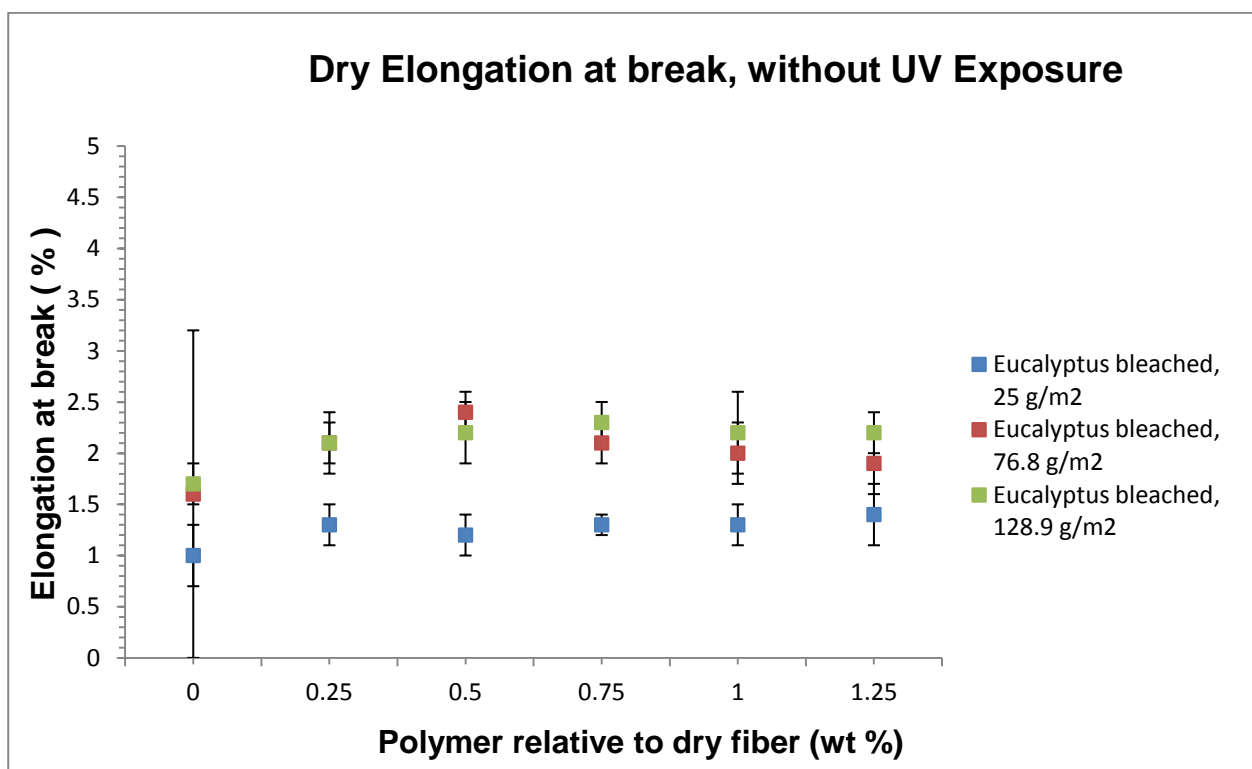


Figure 7 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached $25\text{g}/\text{m}^2$ (blue), Eucalyptus bleached $76.8\text{g}/\text{m}^2$ (red), Eucalyptus bleached $128.9\text{g}/\text{m}^2$ (green).

From the graphs, there is no significant difference in dry elongation at break by increasing concentration of photo-reactive polymer at any grammage of paper sheet. But in comparison between different grammage of eucalyptus pulp (25 , 76.8 and $128.9\text{g}/\text{m}^2$), $25\text{g}/\text{m}^2$ grammage shows lowest dry

elongation at break values and it was also observed that another two grammage (76.8 and 128.9g/m²) have same elongation at break values.

It can be concluded that paper sheet with grammage of 25g/m² has lower flexibility and it breaks by little force. And higher grammage values do not affect the flexibility so they show same elongation at break values.

Dry elongation at break values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

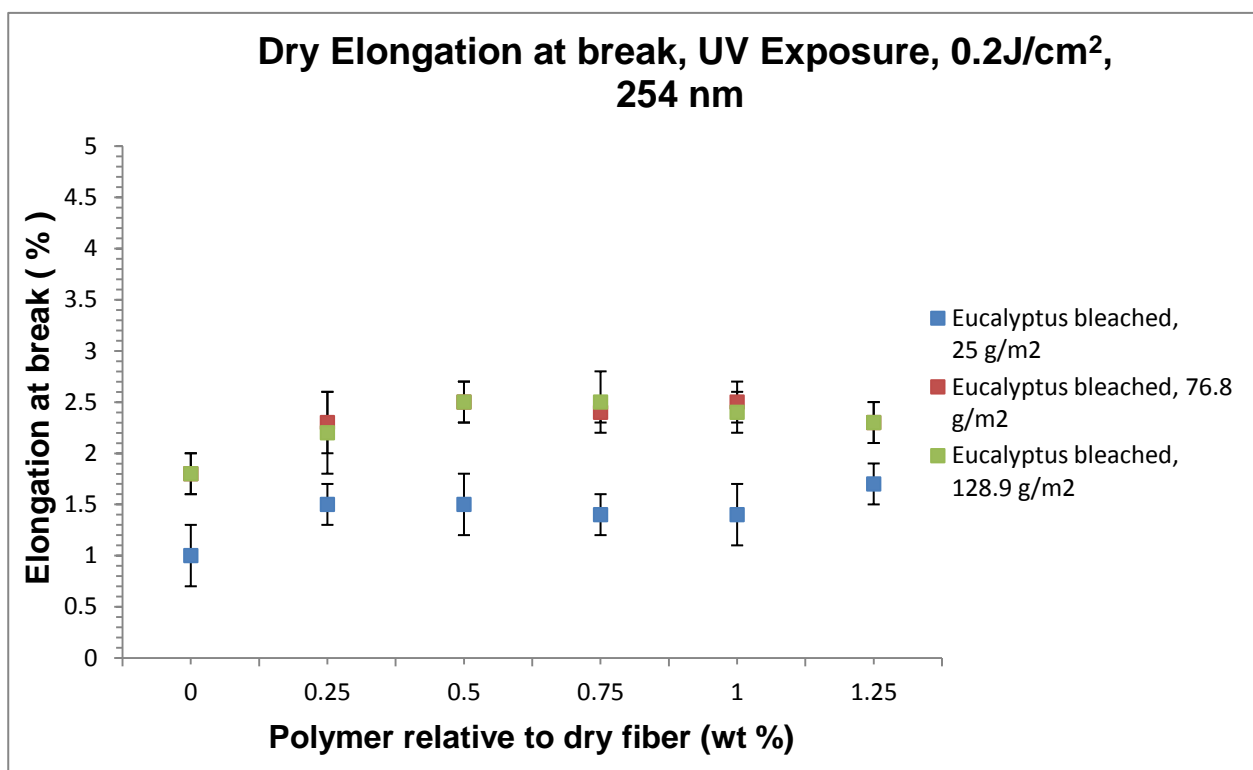


Figure 8 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

From the graph, it was observed that there is no significance difference in dry tensile index values even when paper sheets were UV irradiated at 0.2J/cm² inside 254nm UV chamber. It can be concluded that there is no effect of PVAm-BP on dry elongation at break of paper. PVAm-BP should not use for increase dry elongation at break of paper substrate.

4.1.4. Effect on wet tensile strength:

Wet tensile strength values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

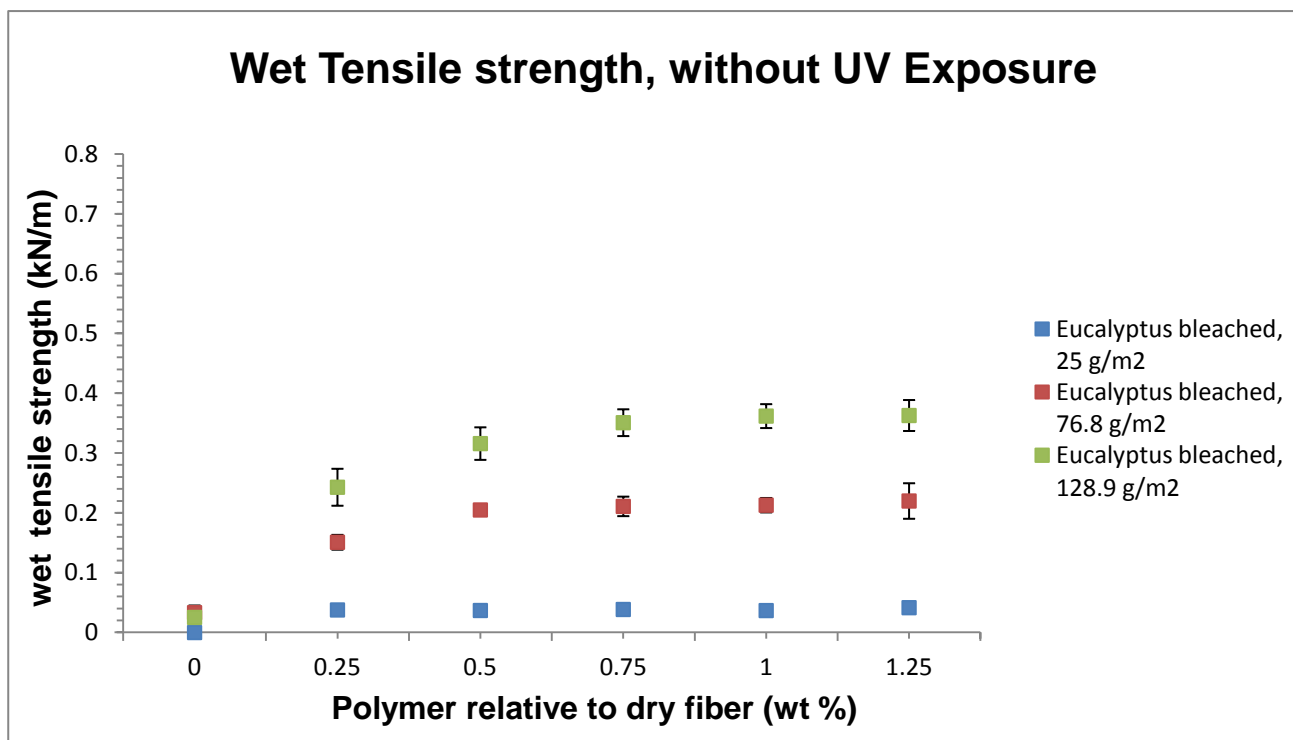


Figure 9 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

From the graphs, there is significant increase in wet tensile strength within range of 0% to 0.25% of photo-reactive polymer concentration. But further more increase in polymer concentration, it shows slightly increase in wet tensile strength. But in comparison between different grammage of eucalyptus pulp (25, 76.8 and 128.9 g/m²), 128.9g/m² shows higher wet tensile strength values and 25g/m² grammage shows lowest wet strength values.

It can be concluded that paper sheet with PVAm-BP polymer in it, shows increase in wet tensile strength with increase in grammage of paper sheet. Because with increase in fibre mass, there is an increase in adsorb PVAm-BP polymer content to the fibre mass and high adsorb polymer gives higher wet tensile strength values to paper sheet.

Wet tensile strength values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

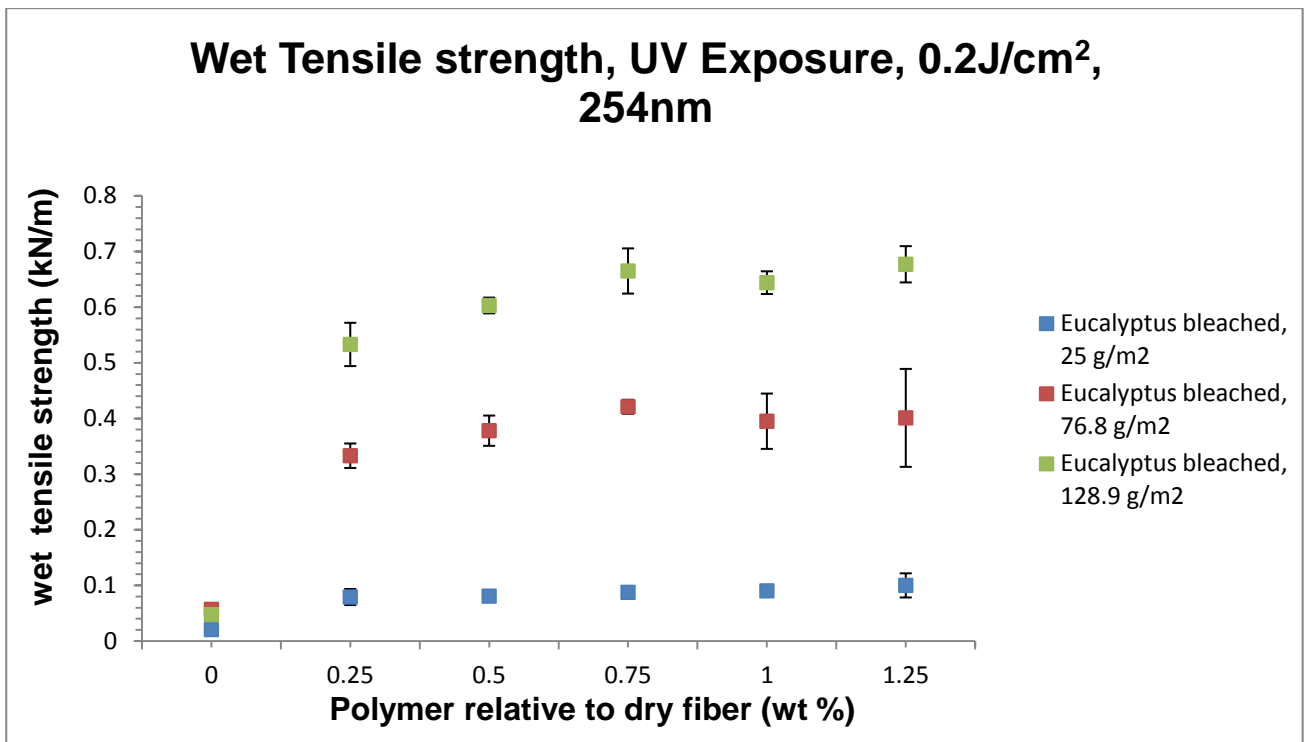


Figure 10 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

From the graph, when paper sheets were UV irradiated at 0.2J/cm² inside 254nm UV chamber, it was observed that wet tensile strength values increase more compared to unexposed paper. And higher grammage paper sheets show higher wet tensile strength.

It can be concluded that PVAm-BP with UV exposure gives paper sheet a high wet tensile strength in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets.

PVAm-BP can be used for increase wet tensile strength of paper substrate. And UV irradiation to paper substrate containing photo-reactive polymer, gives high wet tensile strength.

4.1.5. Effect on wet tensile index:

Wet tensile index values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

From the graphs, there is significant increase in wet tensile strength within range of 0% to 0.25% of photo-reactive polymer concentration. But further more increase in polymer concentration, it shows slightly increase in wet tensile strength. In comparison between different grammage of

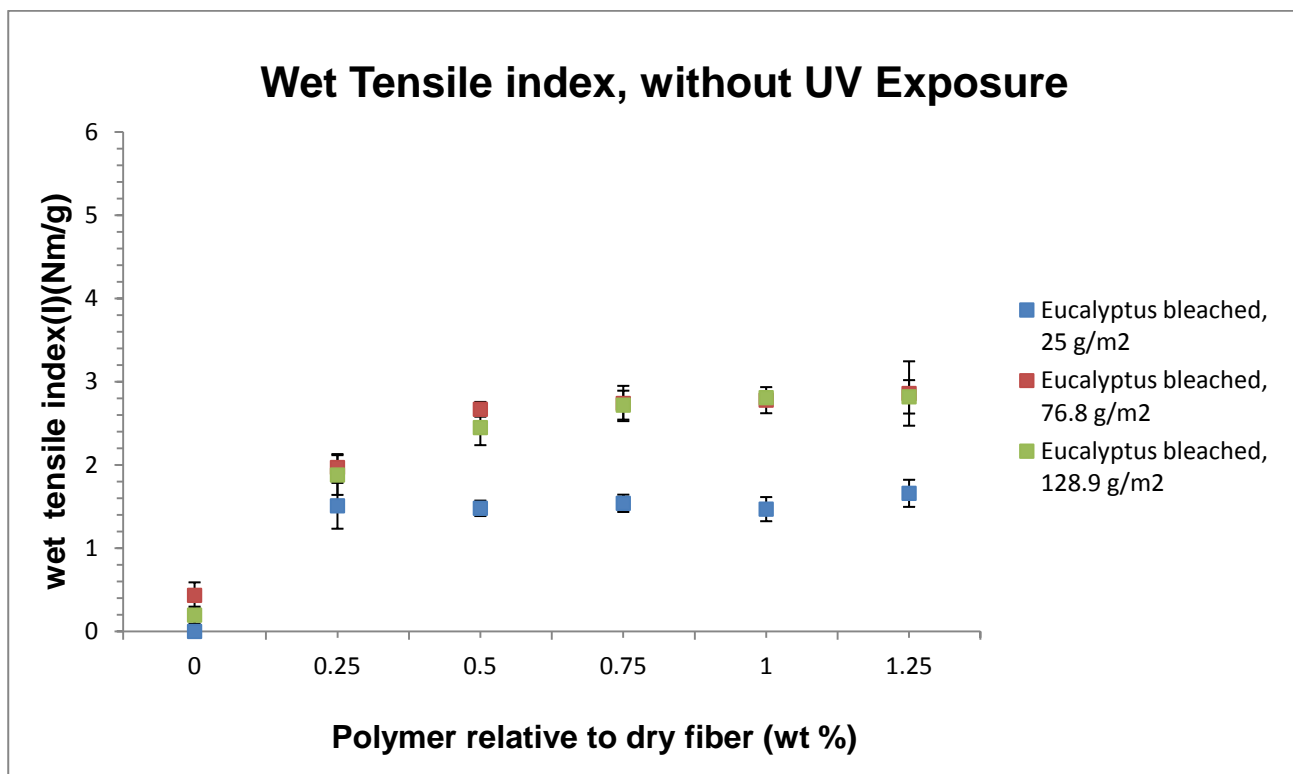


Figure 11 Wet tensile index, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

eucalyptus pulp (25, 76.8 and 128.9 g/m²), 25g/m² grammage shows lowest wet tensile index values and further increasing in grammage, there is no significant increment in wet tensile index values.

Generally grammage of paper sheet doesn't affect the tensile index value, but 25g/m² grammage sheet shows little lesser wet tensile index values because at this grammage, paper sheet is very thin and very less dense in nature, and a little force can break this sheet, that is why it has less wet tensile index values.

Wet tensile index values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

It can be concluded that PVAm-BP with UV exposure gives paper sheet a high wet tensile index in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets.

PVAm-BP can be used for increase wet tensile index of paper substrate. And UV irradiation to paper substrate containing photo-reactive polymer, gives high wet tensile index values.

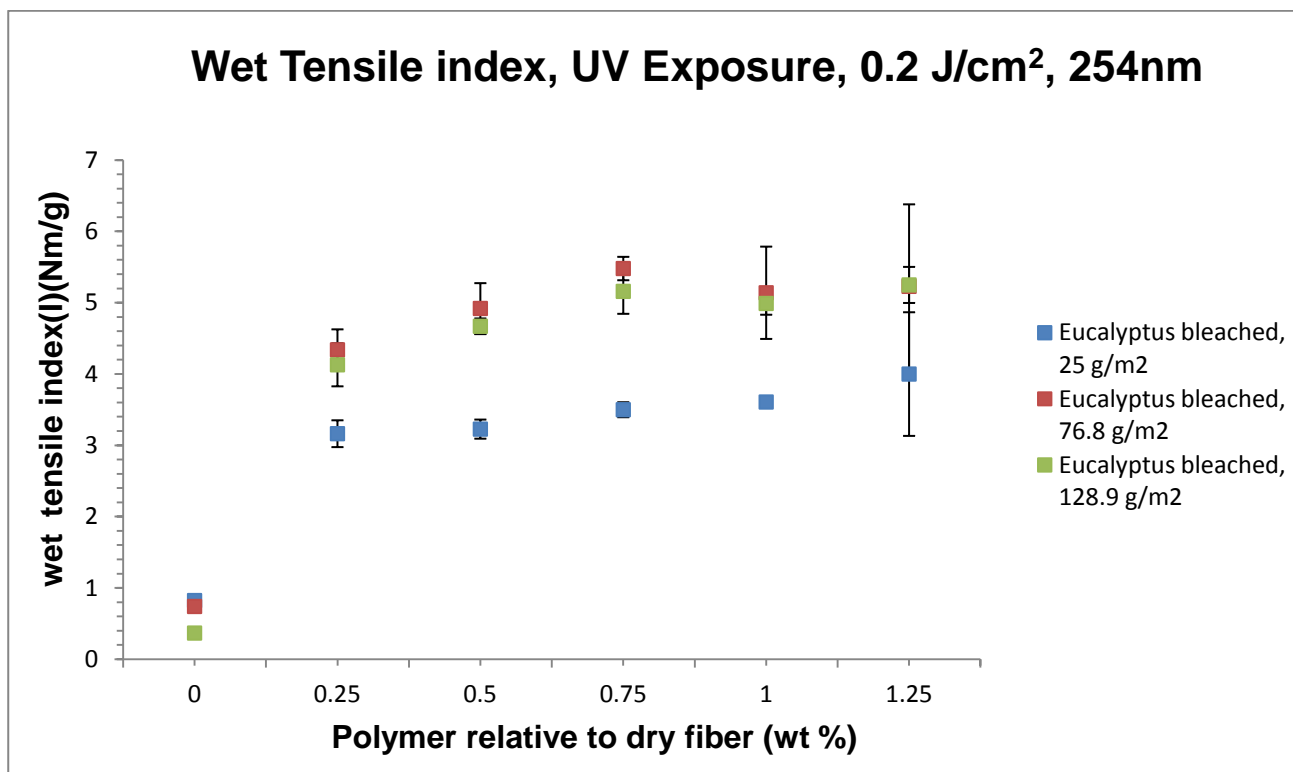


Figure 12 Wet tensile index, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

4.1.6. Effect on wet elongation at break:

Wet elongation at break values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence of UV irradiation.

From the graphs, there is significant increase in wet elongation at break within range of 0% to 0.25% of photo-reactive polymer concentration. But further more increase in polymer concentration, it shows slightly increase in wet elongation at break but grammage of 25 g/m² show no significant difference in elongation at break after 0.25% of polymer concentration. In comparison between different grammage of eucalyptus pulp (25, 76.8 and 128.9 g/m²), 25g/m² grammage shows lowest wet elongation at break values and it was also observed that another two grammage (76.8 and 128.9g/m²) have same elongation at break values.

It can be concluded that paper sheet with grammage of 25g/m² has lower flexibility and it breaks by little force. And higher grammage values do not affect the flexibility so they show same elongation at break values.

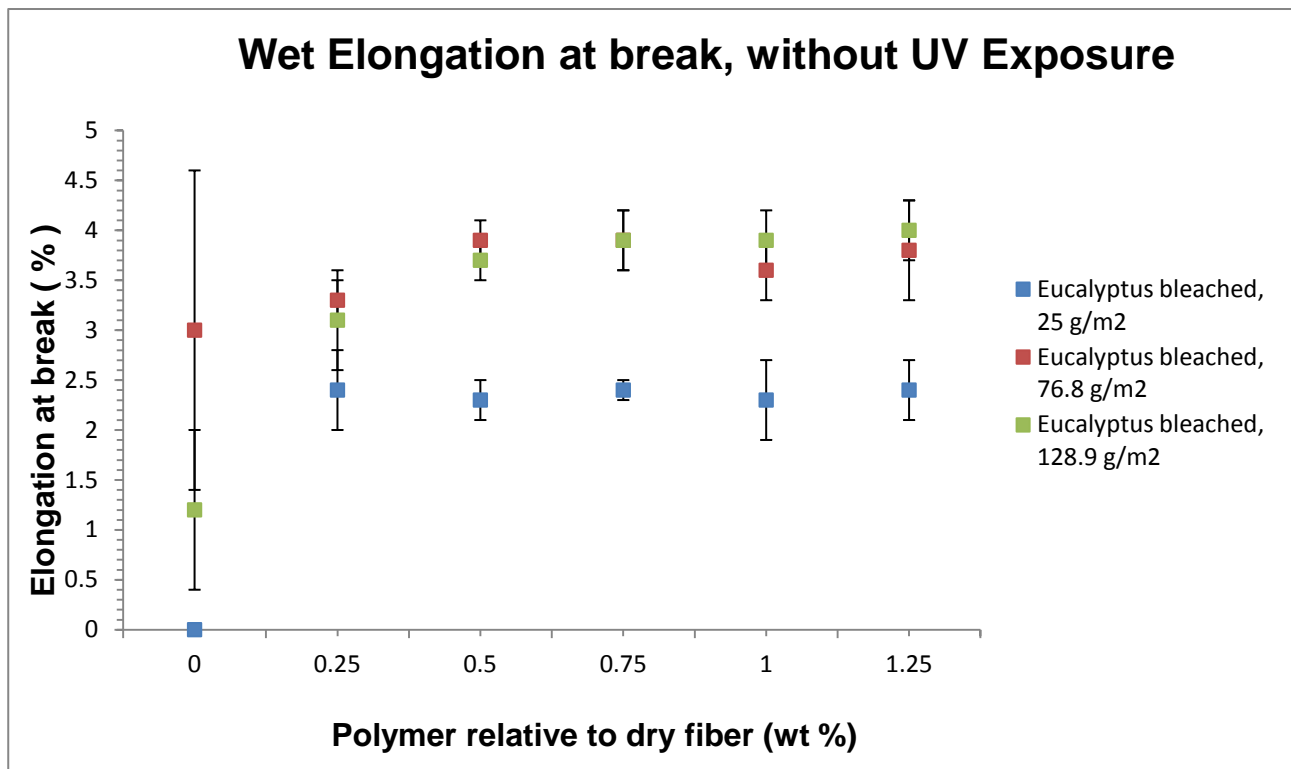


Figure 13 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m² (green).

Wet elongation at break values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in presence of UV irradiation.

In presence of photo-reactive polymer in paper substrate, it has been observed that significant increase in wet elongation at break within range of 0% to 0.25% of polymer. But further more increase in polymer concentration, it shows slightly increase in wet elongation at break values.

It can be concluded that PVAm-BP with UV exposure gives paper sheet a high wet elongation break values in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets. PVAm-BP can be used for increase wet elongation break of paper substrate. And UV irradiation to paper substrate containing photo-reactive polymer, gives high wet elongation break values.

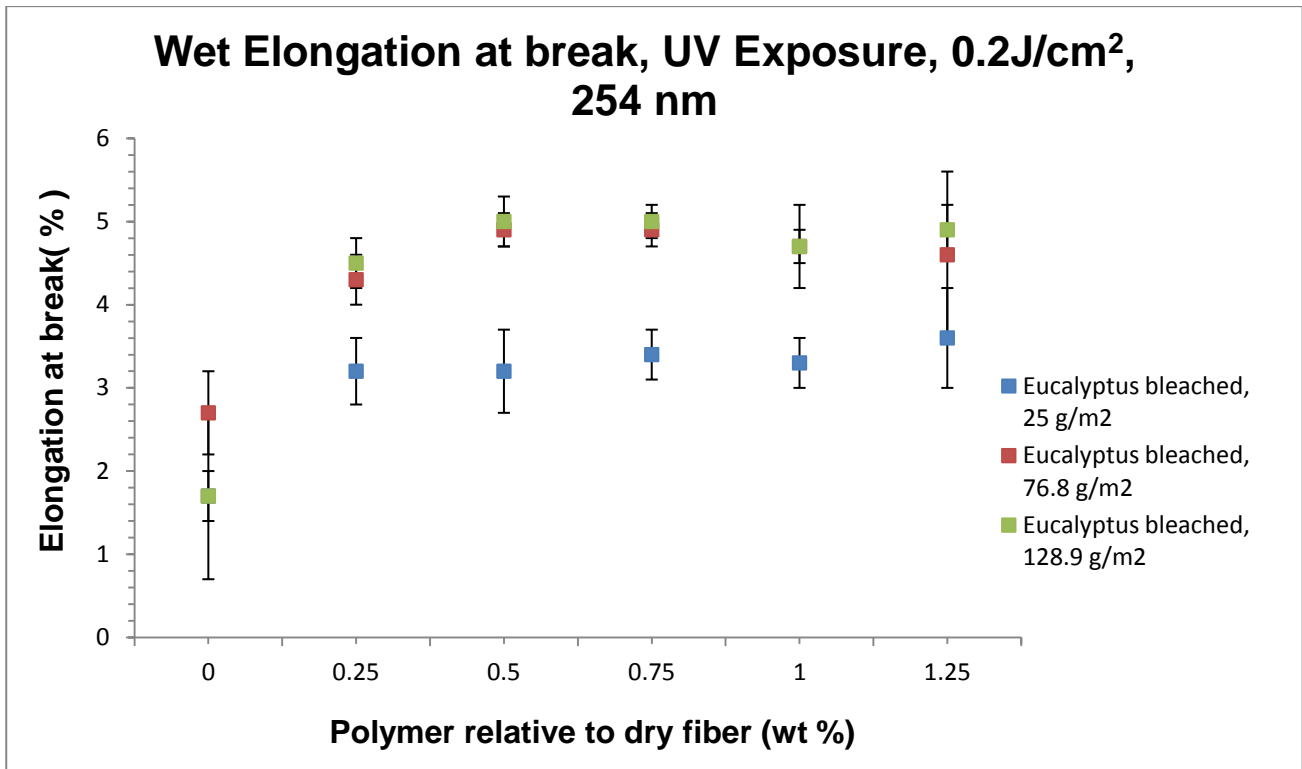


Figure 14 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

4.1.7. Effect on relative wet strength:

Relative wet strength values were calculated for different grammage of eucalyptus bleached pulp with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

In presence of photo-reactive polymer in paper substrate, it has been observed that significant increase in relative wet strength within range of 0% to 0.25% of polymer. But further more increase in polymer concentration, it shows slightly increase in relative wet strength values.

It has been observed that photo-reactive paper substrate with UV exposure shows wet tensile strength of around 17% of its dry tensile strength, and without UV exposure it was around 10% (At 1.25% polymer concentration).

In presence of UV exposure, all three grammage values which were observed (25, 76.8 and 128.9g/m²) shows almost same relative wet strength at individual concentration of photo-reactive polymer.

It can be concluded that PVAm-BP with UV exposure gives paper sheet a high relative wet strength values in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets.

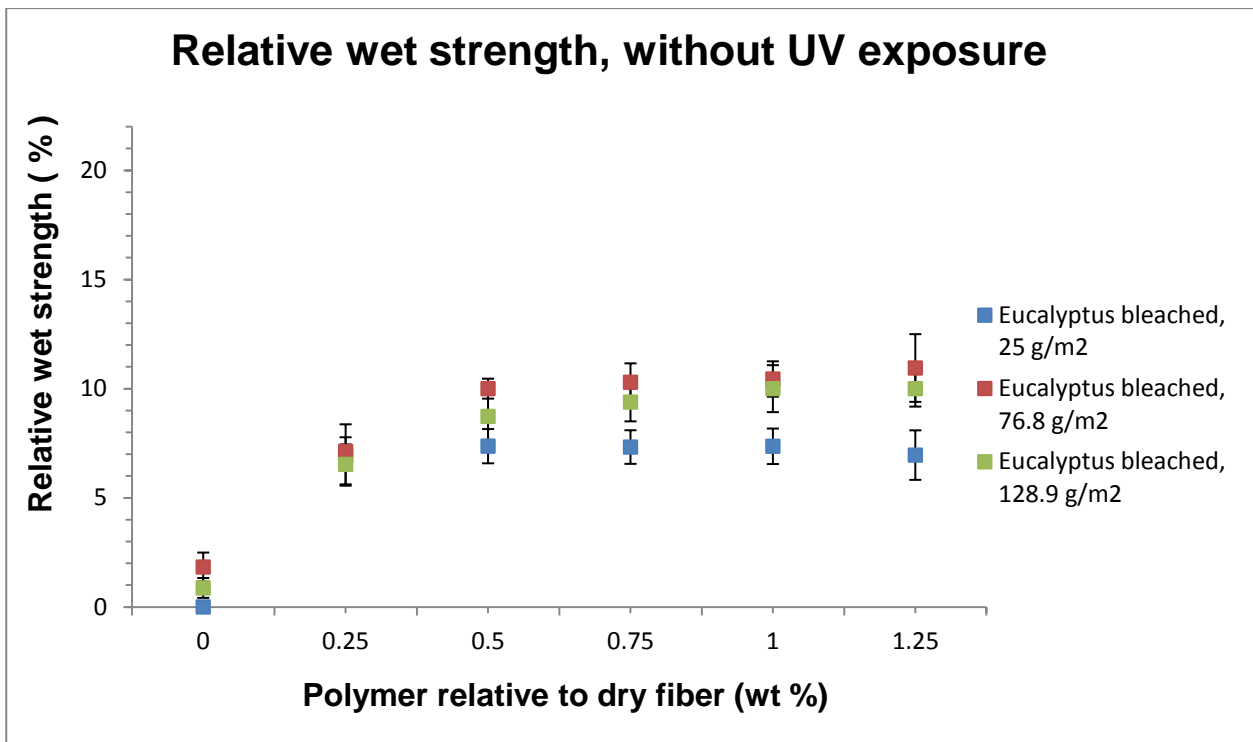


Figure 15 Relative wet strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

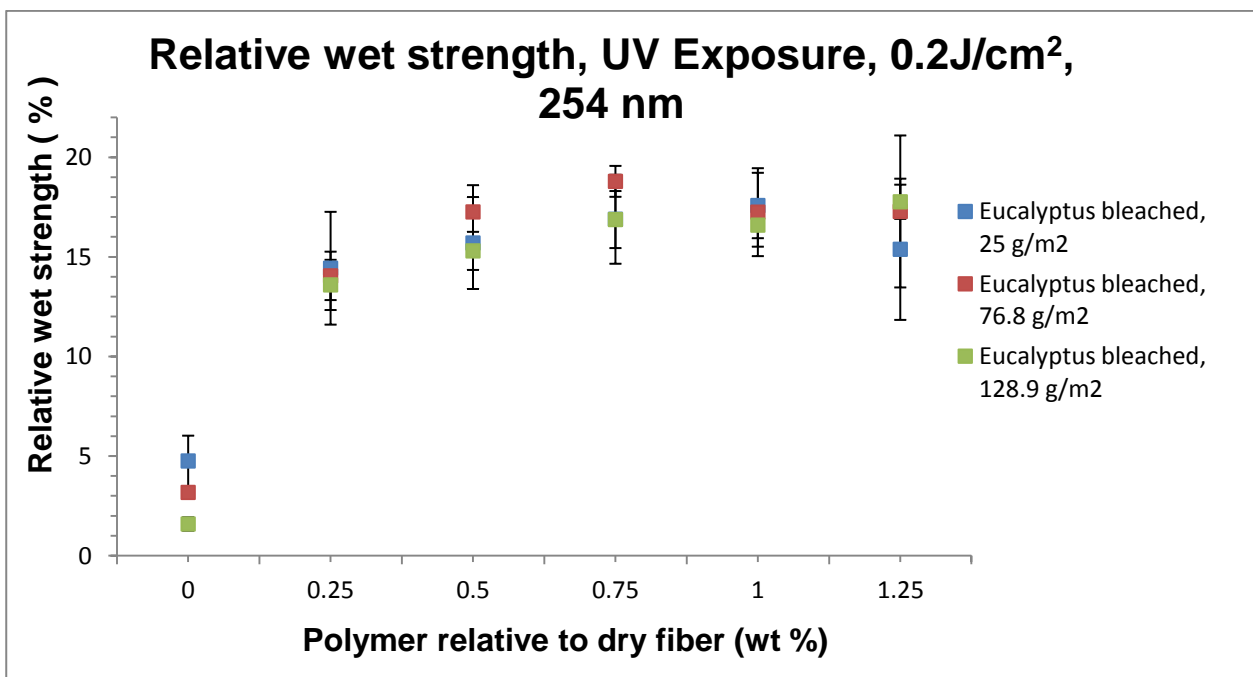


Figure 16 Relative wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 25g/m²(blue), Eucalyptus bleached 76.8g/m²(red), Eucalyptus bleached 128.9g/m²(green).

PVAm-BP can be used for increase relative wet strength which gives wet tensile strength around 17% of its dry tensile strength in presence of UV irradiation to paper substrate. And grammage does not affect the relative wet strength of paper sheet containing photo-reactive polymer.

4.2. Effect of pulp on paper strength (Paper substrate containing PVAm-BP polymer):

4.2.1. Effect on dry tensile strength:

Dry tensile strength values were calculated for different types of pulp (eucalyptus bleached pulp and beech sulphite bleached pulp) with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

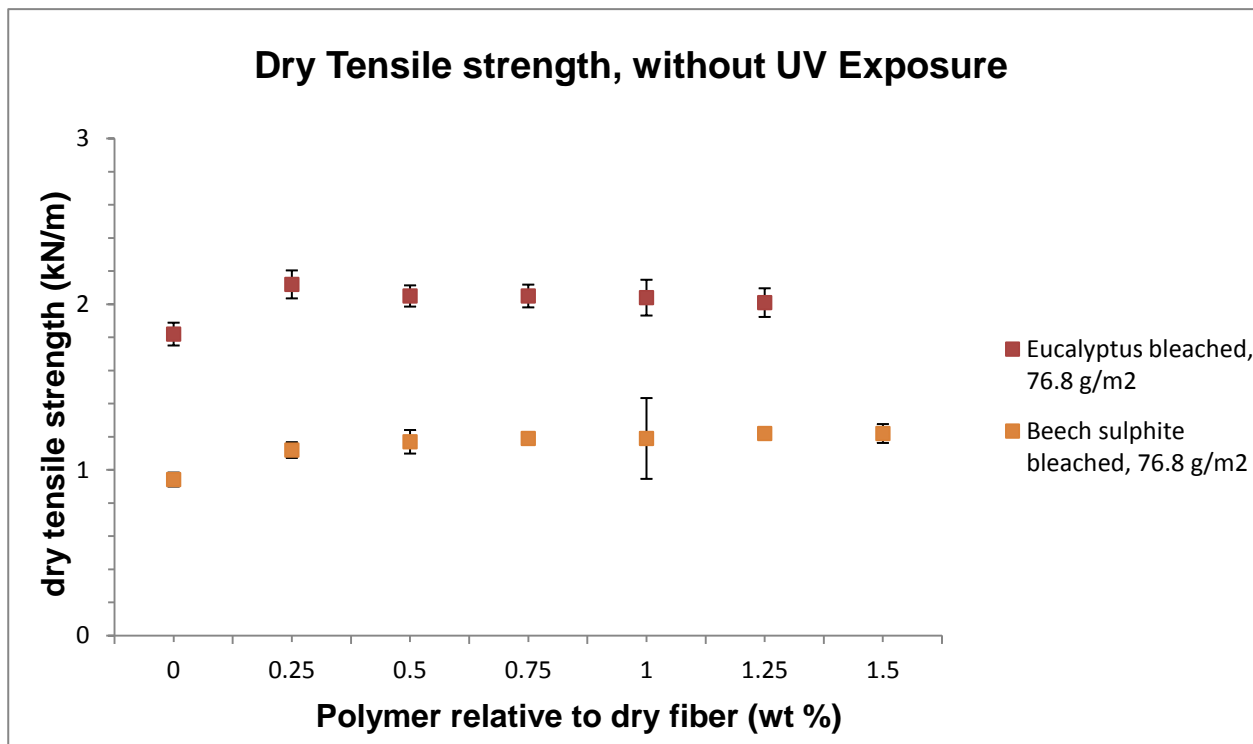


Figure 17 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

From the graphs, there is no significant difference in dry tensile strength by increasing concentration of photo-reactive polymer in paper sheet.

But in comparison between different types of pulp (Eucalyptus bleached and Beech sulphite bleached), Eucalyptus bleached pulp shows higher dry tensile strength.

It can be concluded that eucalyptus bleached pulp shows more dry tensile strength, because eucalyptus pulp was treated with kraft process for pulping whether beech pulp was treated with sulphite process of pulping. And kraft process gives more strength to paper material.

By UV irradiation of paper sheets, it was observed that there is no significance difference in dry tensile strength values.

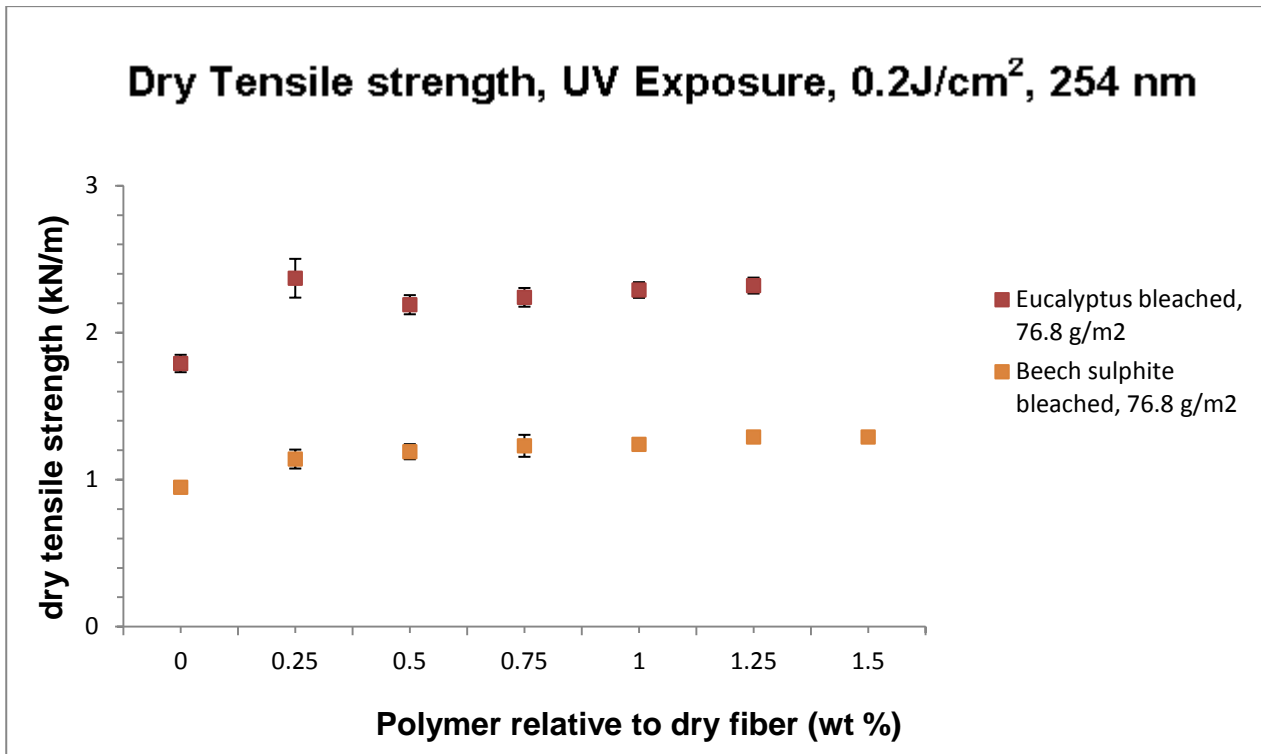


Figure 18 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

4.2.2. Effect on dry elongation at break:

Dry elongation at break values were calculated for different types of pulp (eucalyptus bleached pulp and beech sulphite bleached pulp) with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

From the graphs, there is no significant difference in dry elongation at break by increasing concentration of photo-reactive polymer in paper sheet. But in comparison between different types of pulp (Eucalyptus bleached and Beech sulphite bleached) Eucalyptus bleached pulp shows higher dry elongation at break. By UV irradiation of paper sheets, it was observed that there is no significance difference in dry elongation at break.

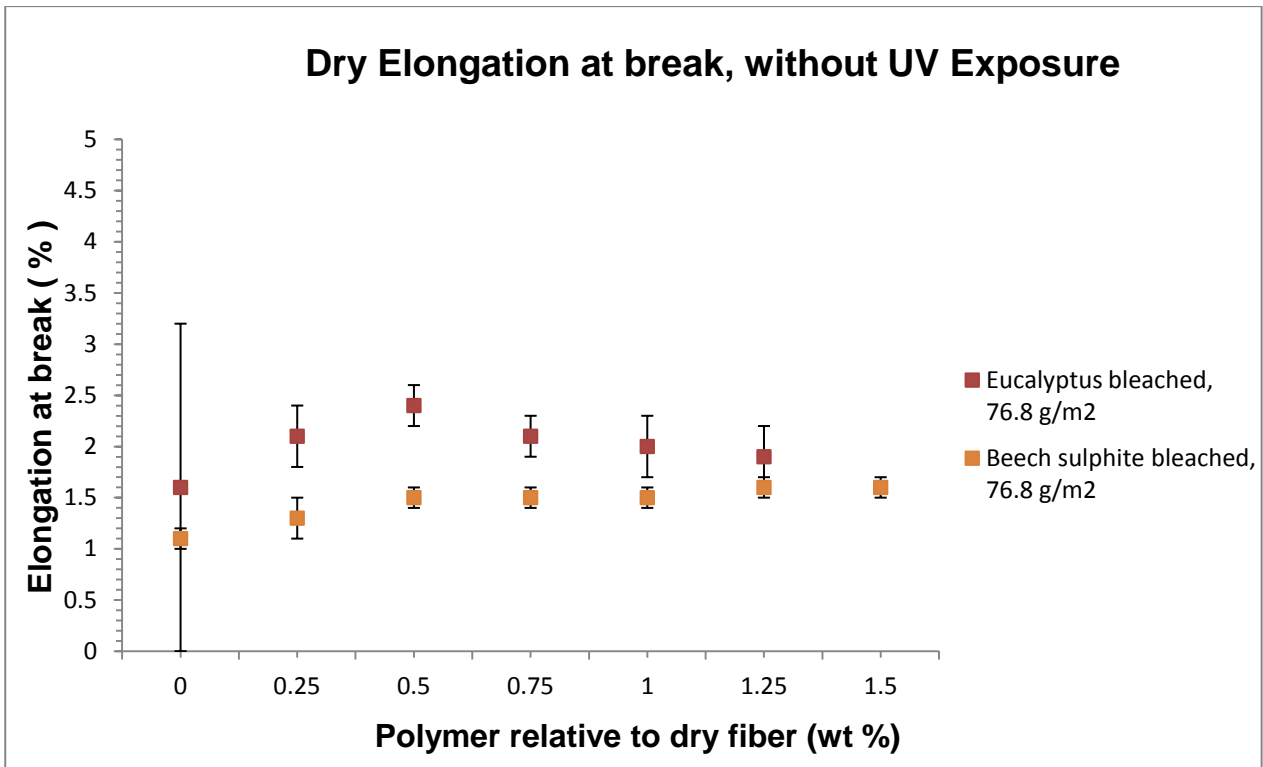


Figure 19 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

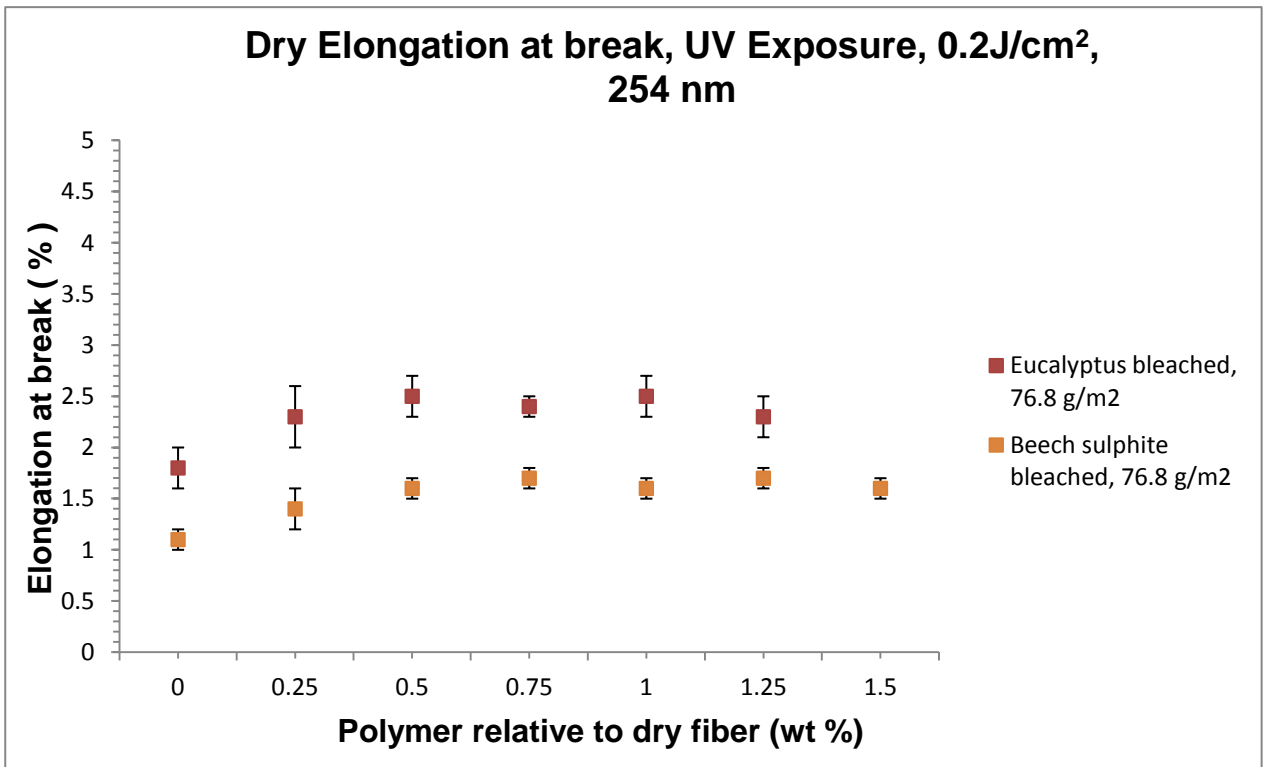


Figure 20 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

4.2.3. Effect on wet tensile strength:

Wet tensile strength values were calculated for different types of pulp (eucalyptus bleached pulp and beech sulphite bleached pulp) with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

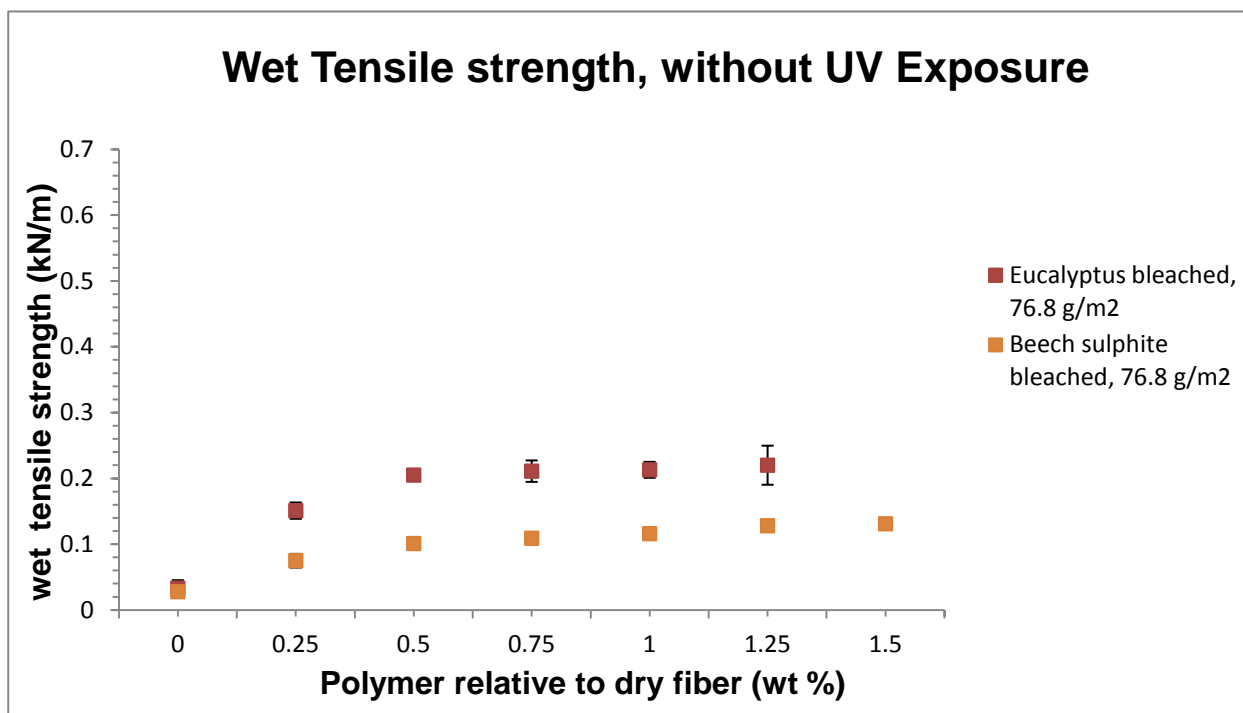


Figure 21 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

In presence of photo-reactive polymer in paper substrate, it has been observed that significant increase in wet tensile strength within range of 0% to 0.25% of photo-reactive polymer concentration. But further more increase in polymer concentration, it shows slightly increase in wet tensile strength. In comparison between different types of pulp (Eucalyptus bleached and Beech sulphite bleached) Eucalyptus bleached pulp shows higher wet tensile strength. By UV irradiation of paper sheets, it was observed that there is no significance difference in wet tensile strength.

From the UV exposed graph, when paper sheets were UV irradiated at 0.2J/cm² inside 254nm UV chamber, it was observed that wet tensile strength values increase more in compare to unexposed paper. And eucalyptus bleached pulp shows show higher wet tensile strength.

It can be concluded that PVAm-BP with UV exposure gives paper sheet a high wet tensile strength in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets.

PVAm-BP can be used for increase wet tensile strength of paper substrate. And UV irradiation to paper substrate containing photo-reactive polymer, gives high wet tensile strength.

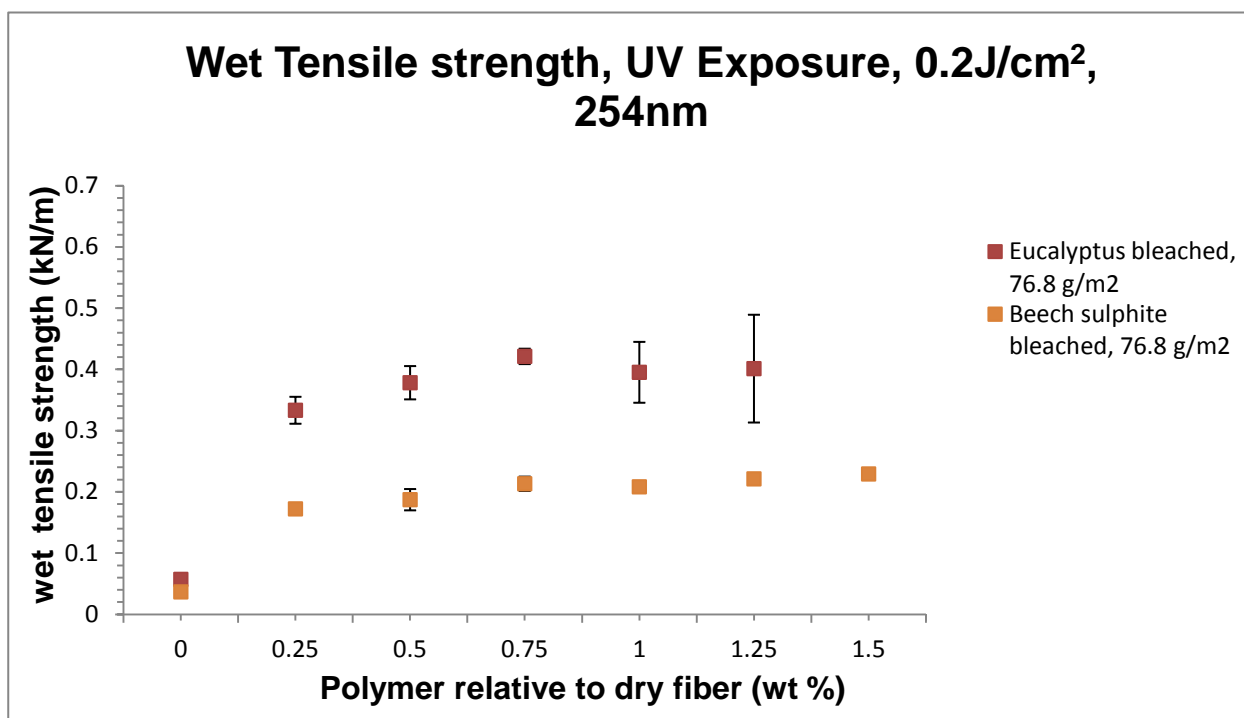


Figure 22 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

4.2.4. Effect on wet elongation at break:

Wet elongation at break values were calculated for different types of pulp (eucalyptus bleached pulp and beech sulphite bleached pulp) with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

In presence of photo-reactive polymer in paper substrate, it has been observed that significant increase in wet elongation at break within range of 0% to 0.25% of photo-reactive polymer concentration. But further more increase in polymer concentration, it shows slightly increase in wet tensile index.

Wet elongation at break increases in presence of UV exposure, because fibres get covalently attach to the photo-reactive polymer in presence of UV light. But in comparison between different types of pulp

(Eucalyptus bleached and Beech sulphite bleached) Eucalyptus bleached pulp shows higher wet elongation at break.

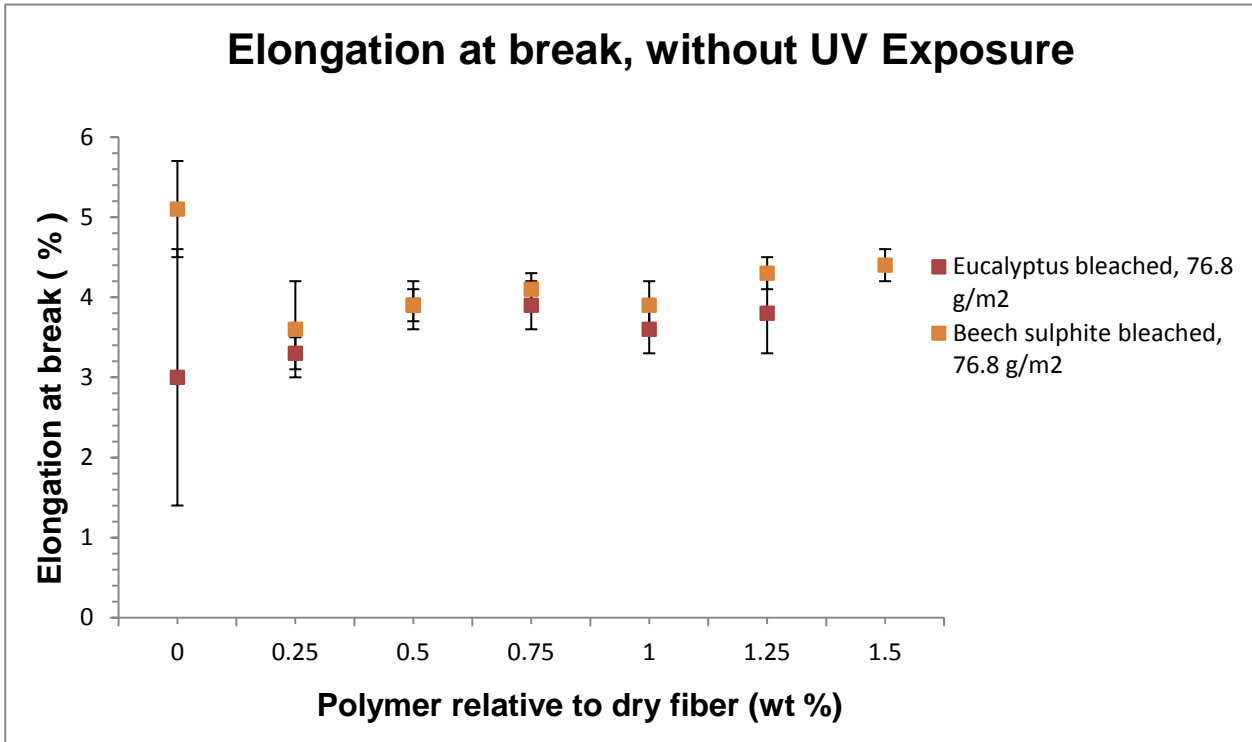


Figure 23 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

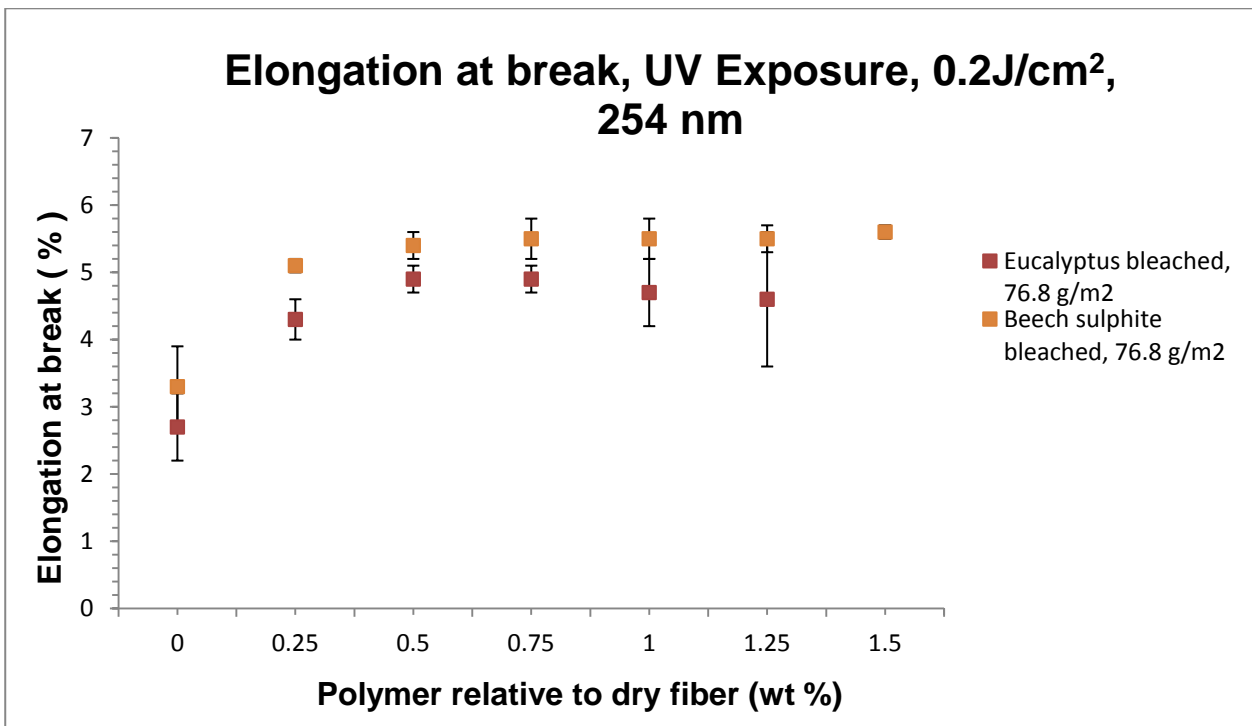


Figure 24 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

4.2.5. Effect on relative wet strength:

Relative wet strength values were calculated for different types of pulp (eucalyptus bleached pulp and beech sulphite bleached pulp) with varying PVAm-BP polymer concentration (wt %) in absence and presence of UV irradiation.

In presence of photo-reactive polymer in paper substrate, it has been observed that significant increase in relative wet strength within range of 0% to 0.25% of polymer. But further more increase in polymer concentration, it shows slightly increase in relative wet strength values.

It has been observed that photo-reactive paper substrate with UV exposure shows wet tensile strength of around 17% of its dry tensile strength, and without UV exposure it was around 10% (At 1.25% polymer concentration). Relative wet strength increases in presence of UV exposure, because fibres get covalently attach to the photo-reactive polymer in presence of UV light.

It was observed that Eucalyptus bleached and Beech sulphite bleached show almost same relative wet strength values.

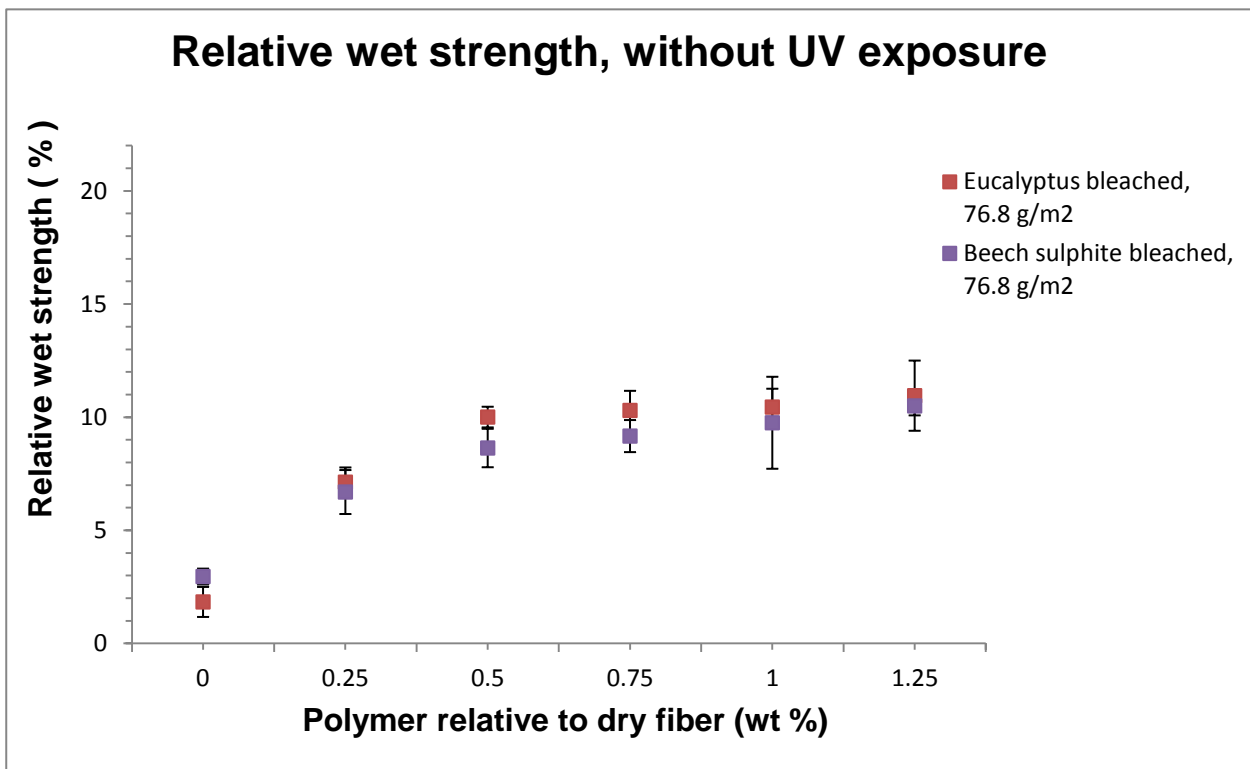


Figure 25 Relative wet strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

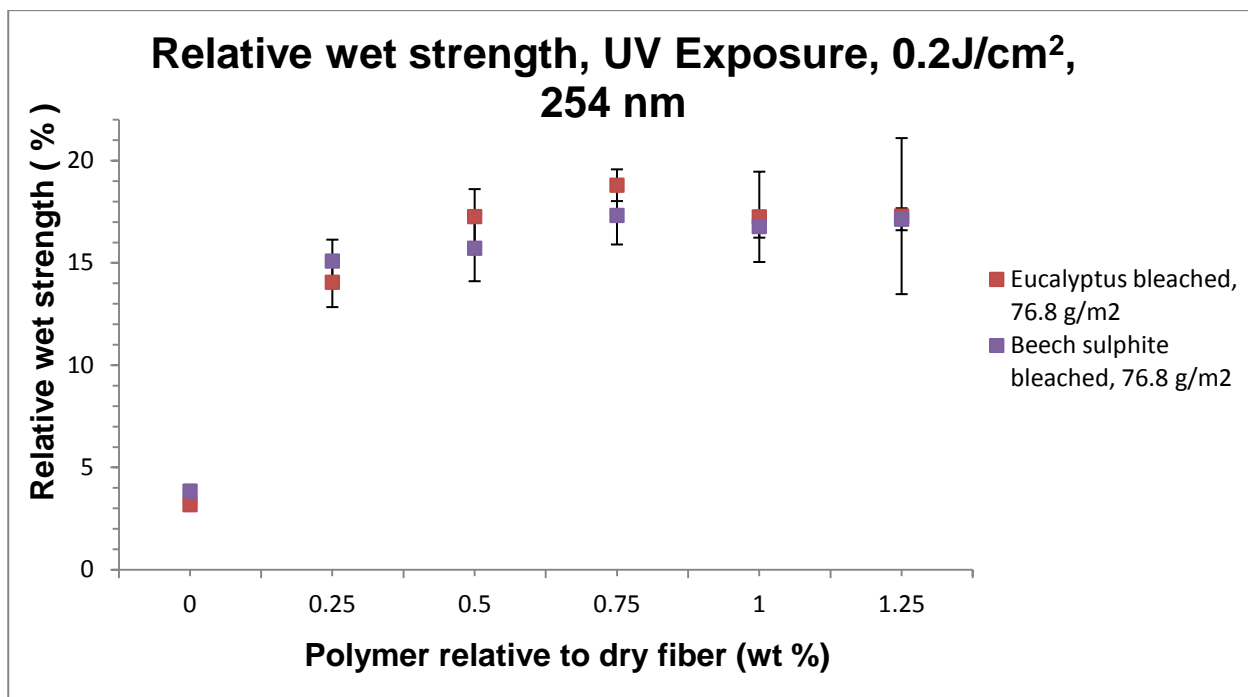


Figure 26 Relative wet strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for Eucalyptus bleached 76.8g/m²(red), Beech sulphite bleached 76.8g/m²(orange).

4.3. Effect of filler on paper strength (Paper substrate containing PDMAA-co-MABP):

4.3.1. Effect on dry tensile strength:

Dry tensile strength values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying PDMAA-co-MABP polymer concentration (wt %) in absence and presence of UV irradiation.

From the graphs, there was a decrease in dry tensile strength values by increasing in filler content in surface applied photo-reactive polymer on paper substrate by size press. (It has been seen that we obtained very low dry strength values in absence of fillers in paper, and it was suggested that we didn't add retention aid into filler free paper and in other filler containing paper we added some retention aid to stock solution in paper making and this retention aid gives some strength to the paper sheets because in presence of retention aid retention of fibre and fines get increases)

Fillers containing paper shows almost same dry tensile strength values in presence or absence of UV exposure to paper substrate containing photo-reactive polymer. So it can be concluded that there is no significant effect of photo-reactive polymer sized paper containing filler on dry tensile strength values.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), Talcum and GCC fillers give more dry tensile strength to the paper sheet at lower concentration of filler (3.08 wt%) but in presence of talcum filler there was high decrease in tensile strength values when we increased filler concentration from 7.94wt% to 15.4wt%.

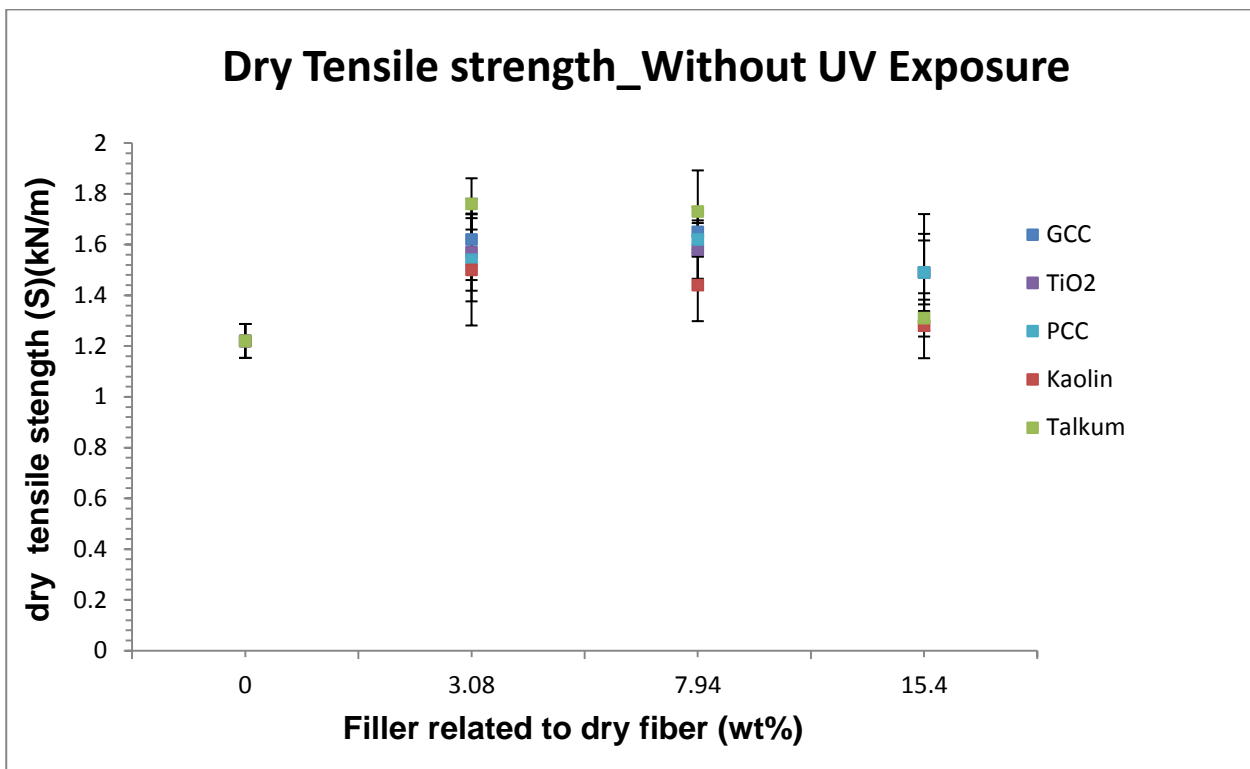


Figure 27 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

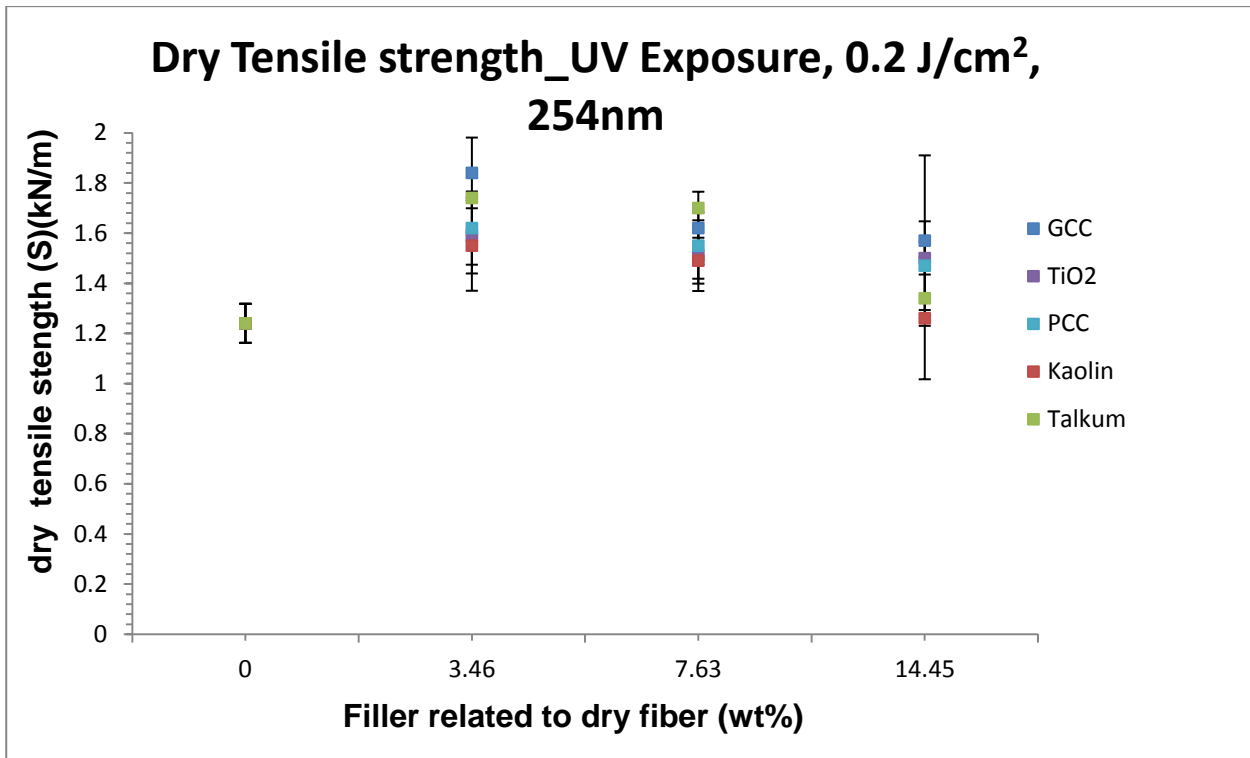


Figure 28 Dry tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

4.3.2. Effect on dry elongation at break:

Dry elongation at break values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying PDMAA-co-MABP polymer concentration (wt %) in absence and presence of UV irradiation.

From the graphs, there was a decrease in dry elongation at break by increasing in filler content in surface applied photo-reactive polymer on paper substrate by size press.

Filler containing papers show almost same dry elongation at break in presence or absence of UV exposure to paper substrate containing photo-reactive polymer. So it can be concluded that there is no significant effect of photo-reactive polymer sized paper containing filler on dry elongation at break values.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), Talcum and GCC fillers give more elongation at break to the paper sheet at lower concentration of filler (3.08 wt%) but in presence of talcum filler there was high decrease in elongation at break values when we increased filler concentration from 7.94wt% to 15.4wt%.

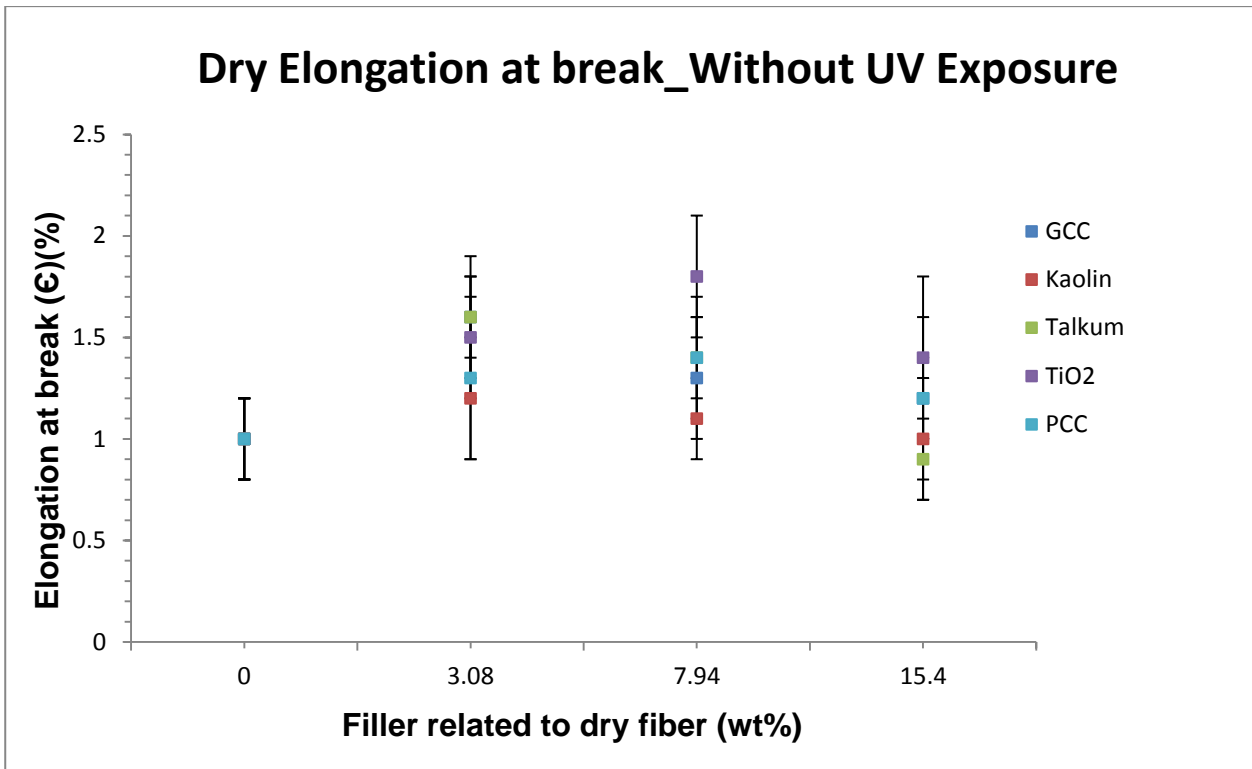


Figure 29 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for GCC (blue), TiO2 (purple), PCC (sky blue), Kaolin (red), Talcum (green).

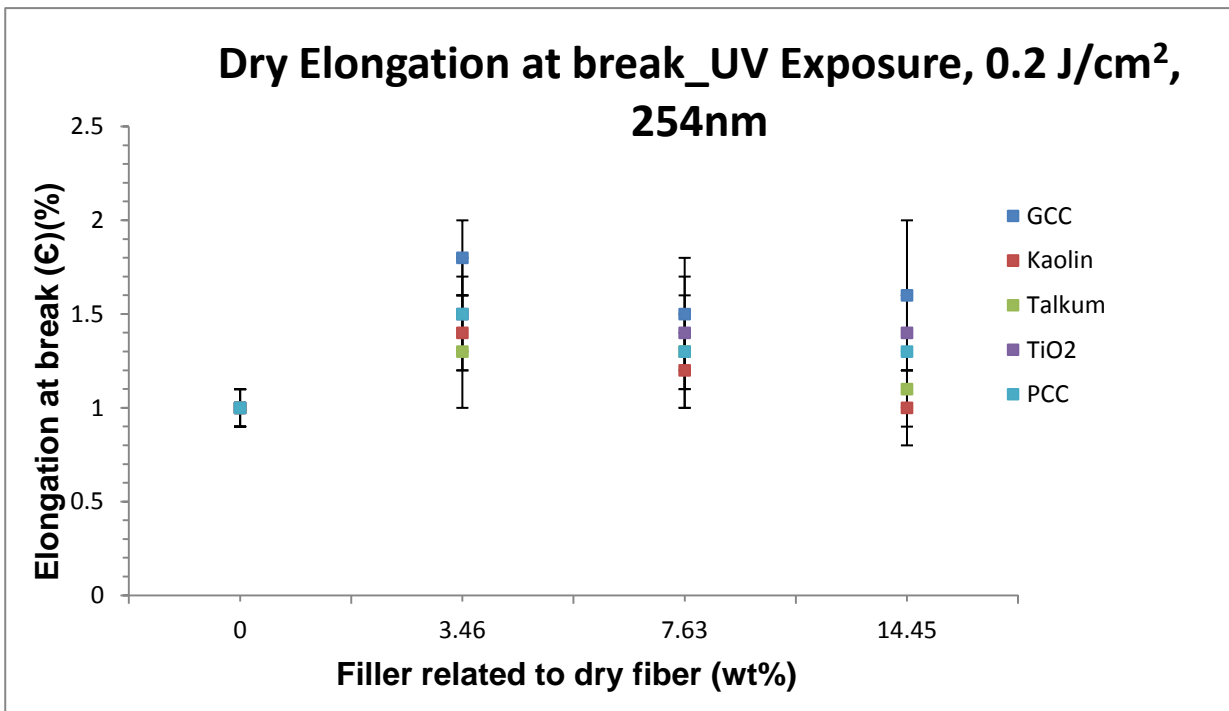


Figure 30 Dry elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for GCC (blue), TiO2 (purple), PCC (sky blue), Kaolin (red), Talcum (green).

4.3.3. Effect on wet tensile strength:

Wet tensile strength values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying PDMAA-co-MABP polymer concentration (wt %) in absence and presence of UV irradiation.

From the graphs, there was a decrease in wet tensile strength by increasing in filler content in surface applied photo-reactive polymer (1.05% ± 0.014 wt %) on paper substrate by size press.

It has been observed that wet tensile strength values increase in presence of UV exposure to fillers containing paper substrate.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), GCC filler gives more wet tensile strength values to the paper sheet at lower concentration of filler (3.08 wt%) and kaolin, talcum and TiO₂ fillers shows almost same impact on wet tensile strength values.

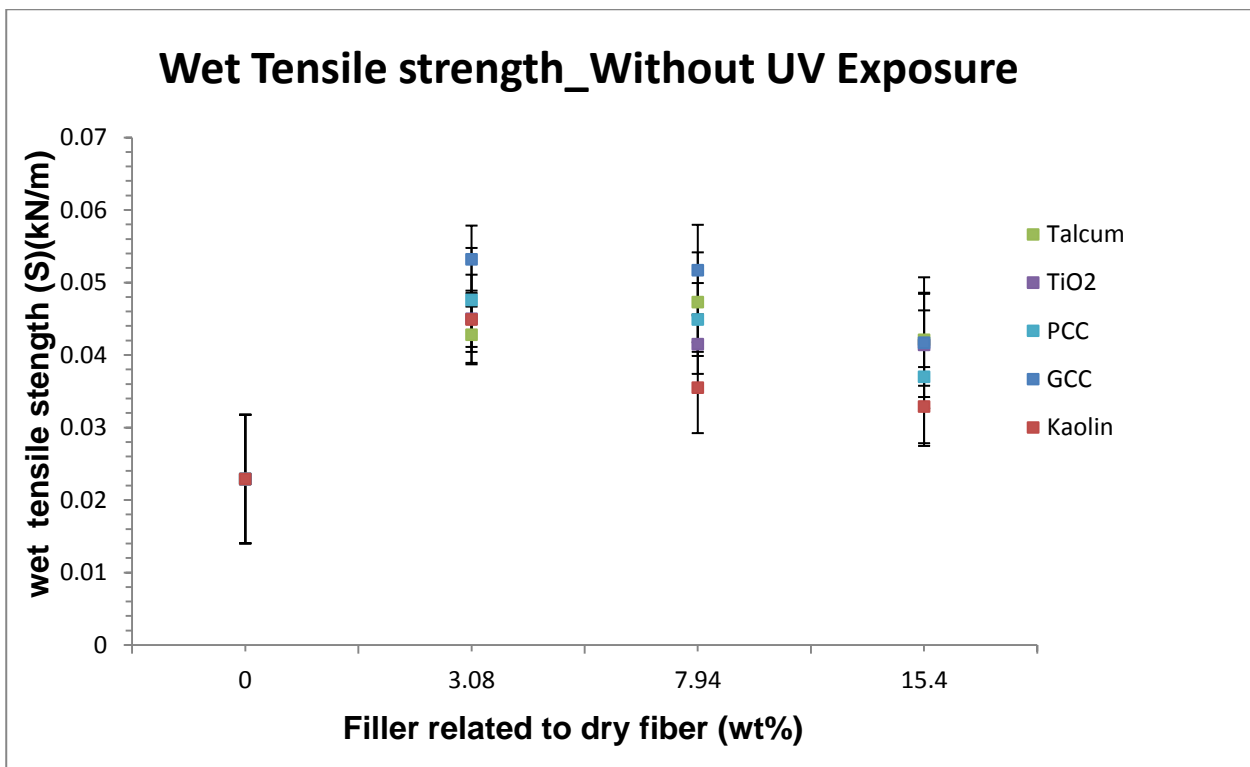


Figure 31 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

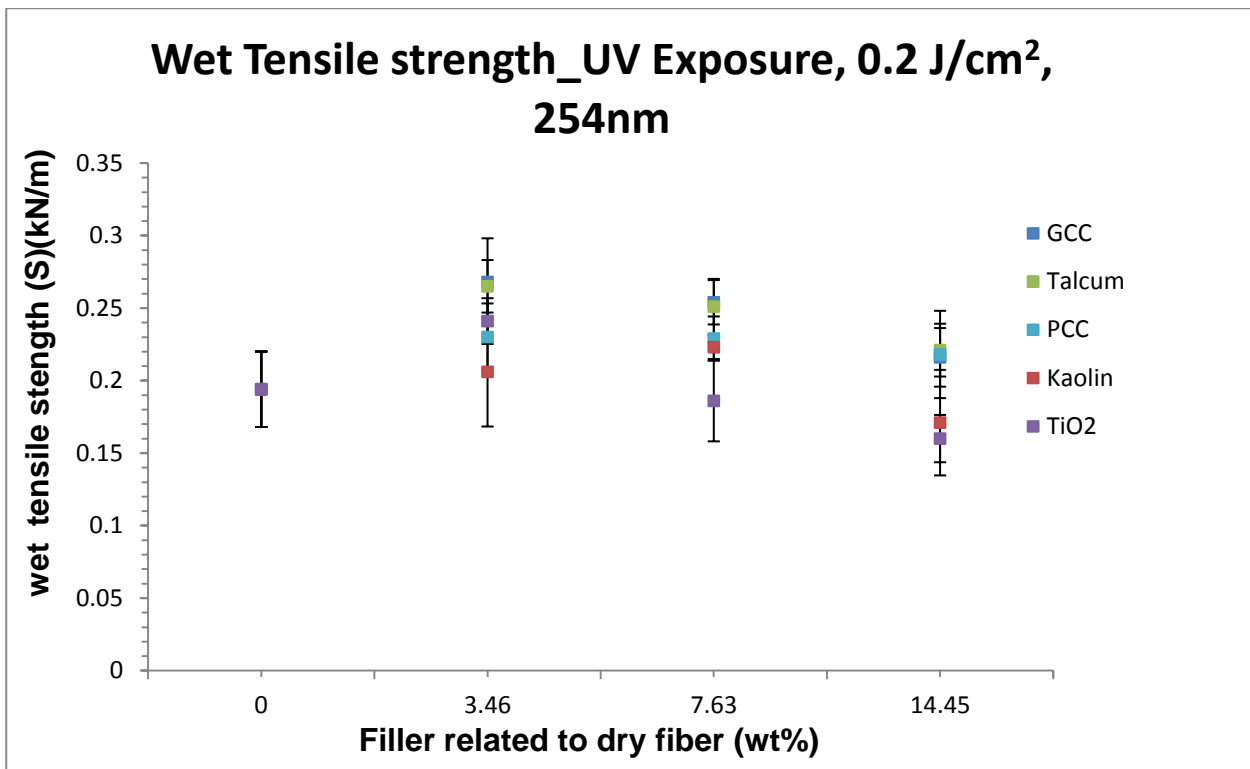


Figure 32 Wet tensile strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

4.3.4. Effect on wet elongation at break:

Wet elongation at break values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying PDMAA-co-MABP polymer concentration (wt %) in absence and presence of UV irradiation.

From the graphs, there was a decrease in wet elongation at break by increasing in filler content in surface applied photo-reactive polymer (1.05% ± 0.014 wt %) on paper substrate by size press.

It has been observed that wet elongation at break values increase in presence of UV exposure to fillers containing paper substrate.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), PCC and GCC fillers give more wet elongation at break values to the paper sheet at lower concentration of filler (3.08 wt%) and kaolin filler shows lowest wet tensile strength values among all used fillers (at any concentration of filler).

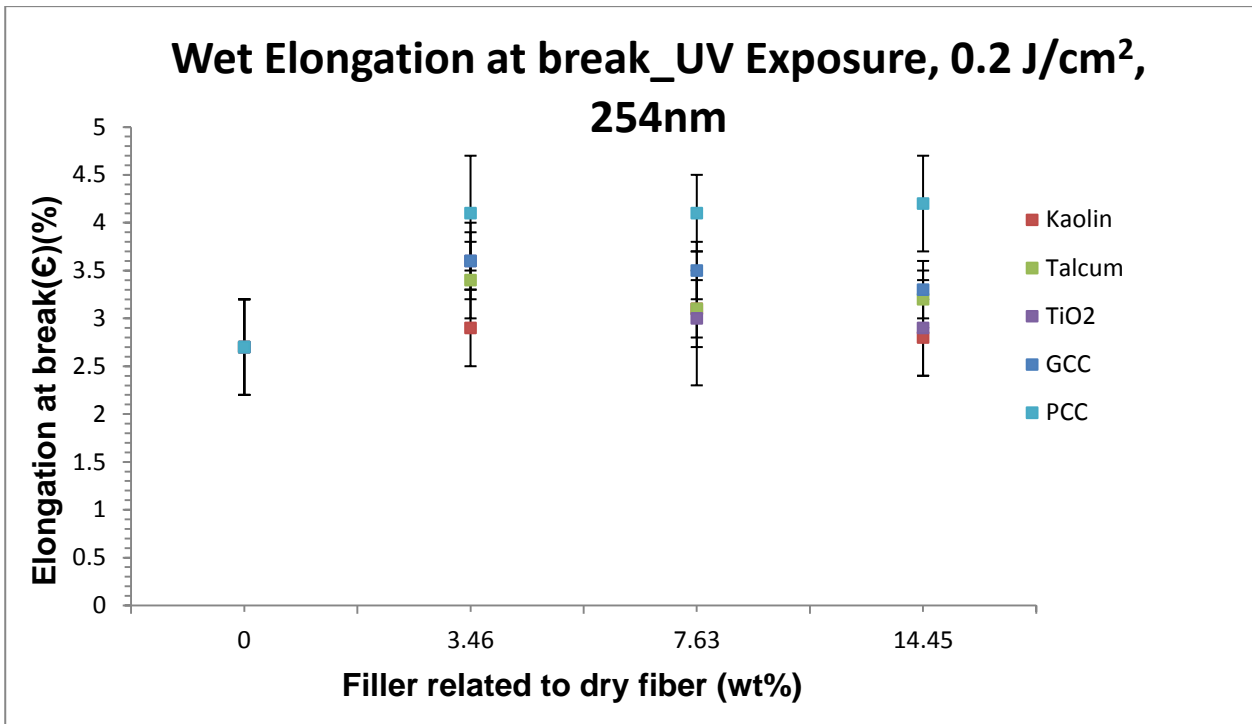


Figure 33 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

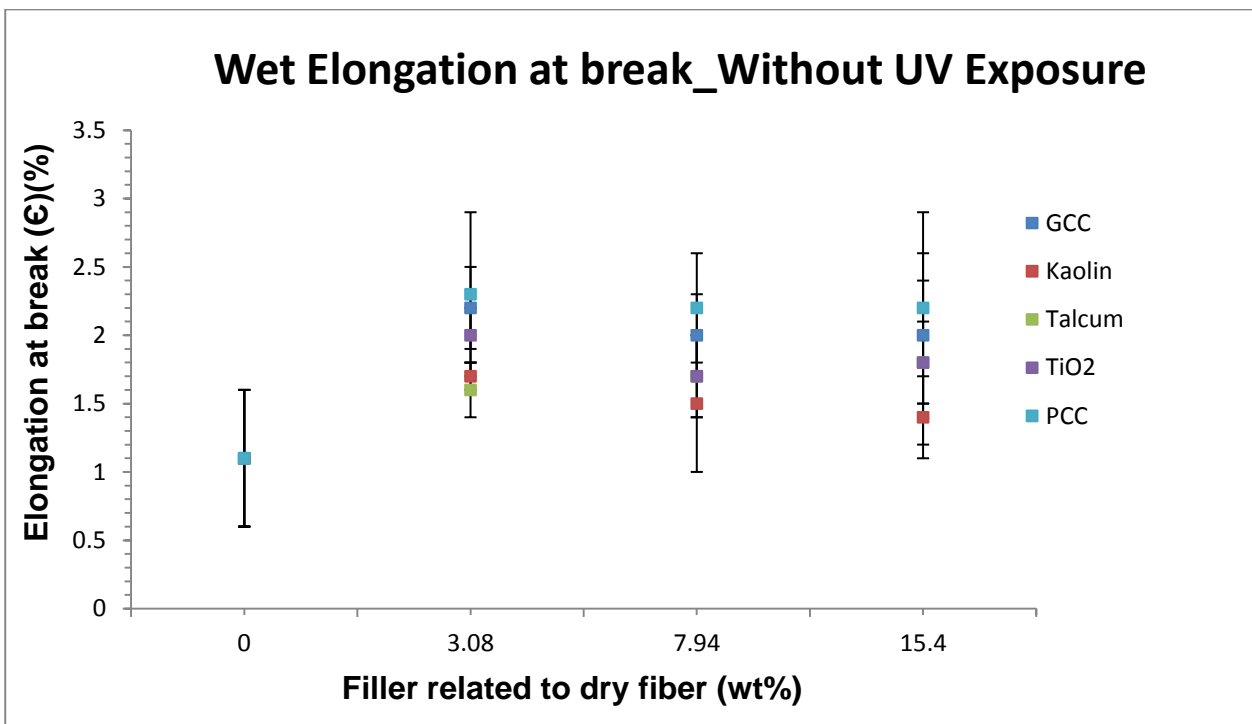


Figure 34 Wet elongation at break, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

4.3.5. Effect on relative wet strength:

Relative wet strength values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying PDMAA-co-MABP polymer concentration (wt %) in absence and presence of UV irradiation.

In presence of photo-reactive polymer (1.05% ± 0.014 wt %) in paper substrate with UV exposure, it has been observed that no significant effect of fillers on strength properties of Photo-reactive polymer containing paper materials except TiO₂ filler. For TiO₂, decrease in relative wet strength by increasing filler concentration.

It has been observed that paper substrate containing photo-reactive polymer with fillers in it, shows wet tensile strength in range of 12 to 16% of its dry tensile strength in presence of UV exposure, but without UV exposure it was around 2%, because in this strength measurement we applied photo-reactive polymer on surface, and without UV exposure it couldn't attach to the paper substrate and it loses its surface applied polymer while watering of these paper materials. And relative wet strength increases in presence of UV exposure, because fibres get covalently attach to the polymer in presence of UV light.

In presence of UV exposure, Talcum and GCC give the higher relative wet strength to the paper substrate.

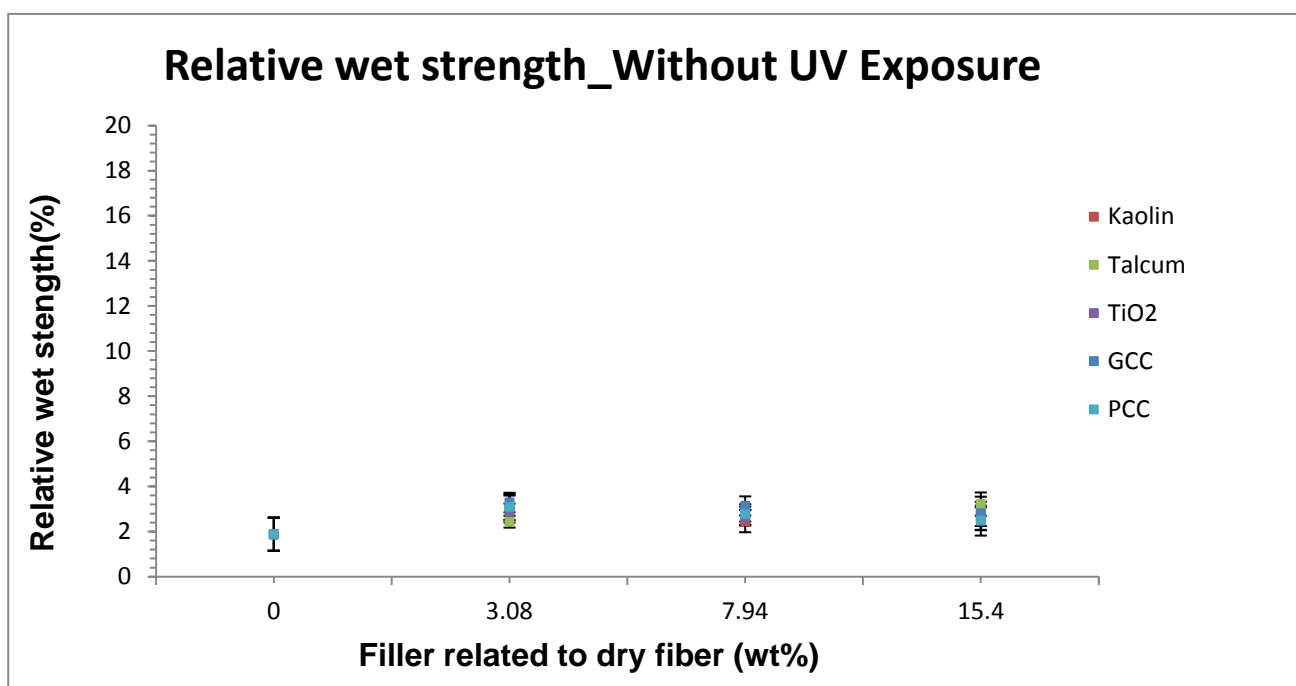


Figure 35 Relative wet strength, as a function of polymer concentration relative to dry fibre (wt %) in absence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

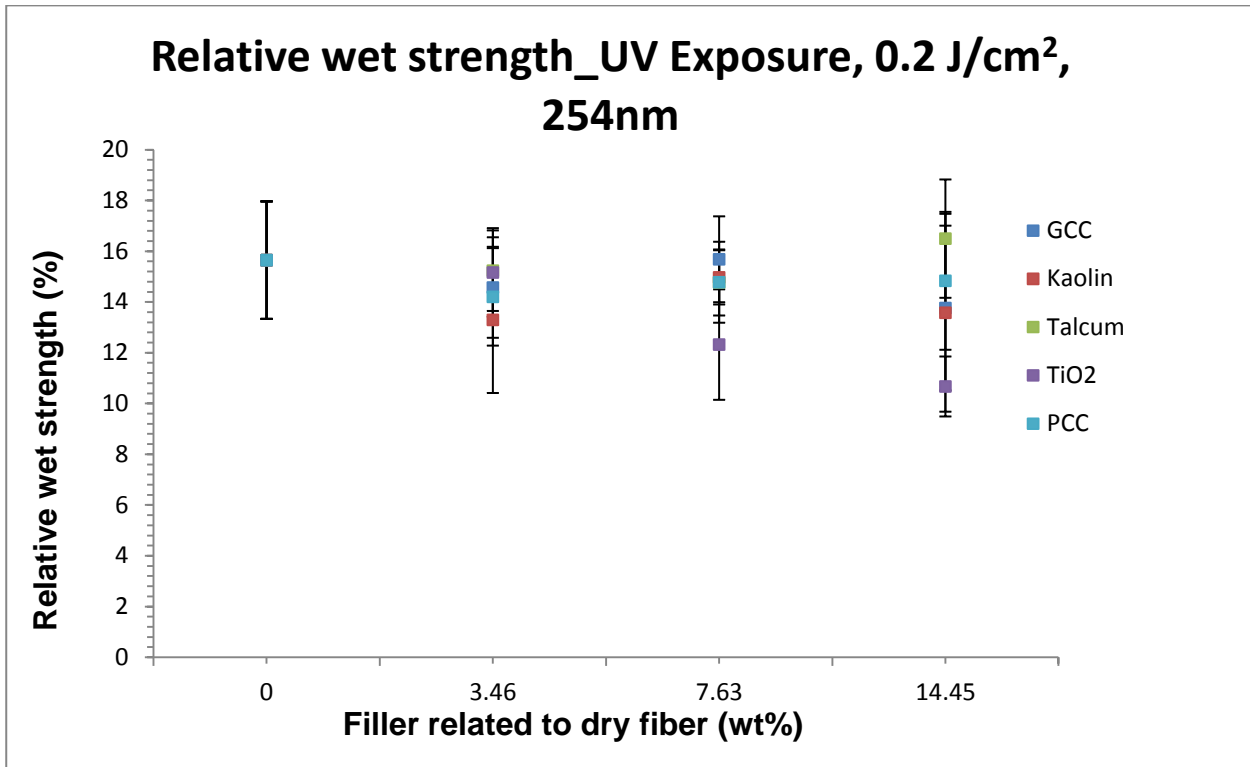


Figure 36 Relative wet strength, as a function of polymer concentration relative to dry fibre (wt %) in presence of UV exposure for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

4.4. Effect of intensity of UV irradiation on paper strength (Paper substrate containing PDMAA-co-MABP):

4.4.1. Effect on dry tensile strength and dry elongation at break:

Dry tensile strength and dry elongation break values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying intensity of UV irradiation to paper sheet contains PDMAA-co-MABP polymer in absence and presence of UV irradiation.

In presence of PDMAA-co-MABP polymer in paper substrate, it has been observed that no significant increase in dry tensile strength, dry tensile index and dry elongation at break values. Dry strength properties do not change in presence of variable intensity of UV exposure.

From the graphs, there was a no significance difference in dry strength properties by increasing in intensity of UV exposure on surface applied photo-reactive polymer (1.05% ± 0.014 wt %) on paper substrate by size press. But comparison in between different type of fillers (GCC, kaolin, talcum,

TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), TiO₂ filler gives more dry strength to the paper sheet at any intensity of UV exposure.

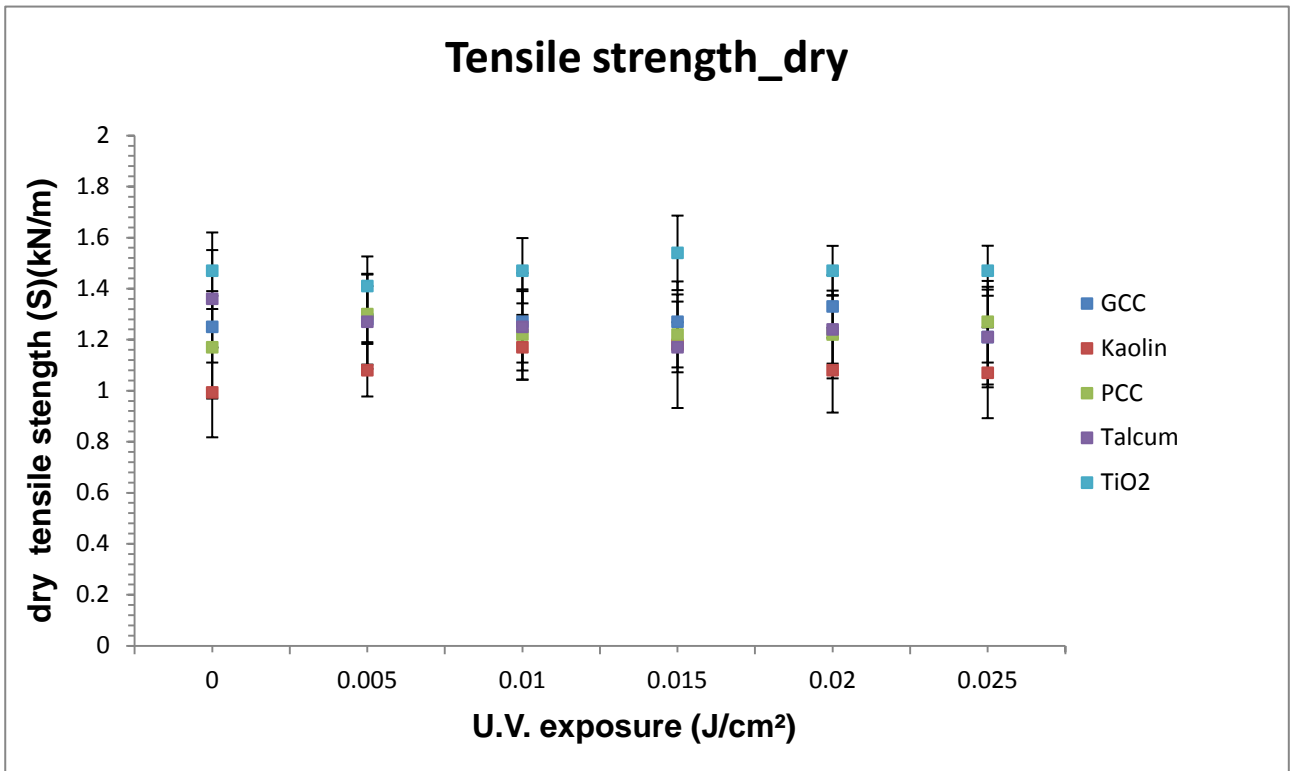


Figure 37 Dry tensile strength, as a function of intensity of UV exposure (J/cm²) for GCC (blue), TiO₂ (purple), PCC (sky blue), Kaolin (red), Talcum (green).

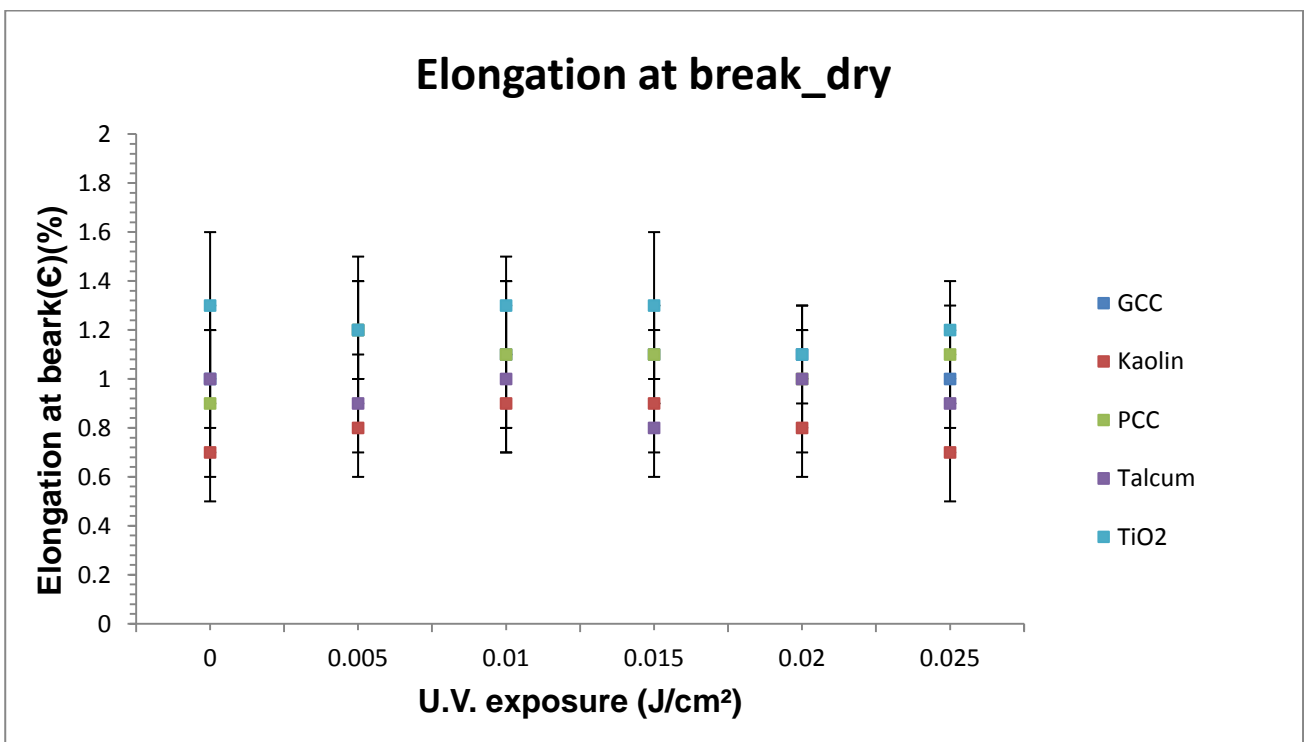


Figure 38 Dry elongation at break, as a function of the intensity of UV irradiation (J/cm²) for GCC (blue), Kaolin (red), PCC (green), Talcum (purple) and TiO₂ (black).

4.4.2. Effect on wet tensile strength and wet elongation at break:

Wet tensile strength and wet elongation break values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying intensity of UV irradiation to paper sheet contains PDMAA-co-MABP polymer in absence and presence of UV irradiation.

In presence of PDMAA-co-MABP polymer in paper substrate, it has been observed that there was significant increase in wet tensile strength; wet tensile index and wet elongation at break values.

From the graphs, there was a very low wet strength into paper substrate at no UV exposure to paper substrate but increasing intensity of UV exposure, it has been seen that there was significant increase in wet strength in range of 0 to 0.025 J/cm² of surface applied photo-reactive polymer (1.05% ± 0.014 wt %) on paper substrate by size press.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), Talcum, TiO₂ and GCC fillers give more wet strength to the paper sheet at any intensity of UV exposure (in range of 0 to 0.025 J/cm²).

It was also observed that TiO₂ filler affect the relative wet strength properties in presence of UV irradiation to paper substrate containing photo-reactive polymer. There was less increase in wet strength values in presence of TiO₂ as filler in compare to other fillers.

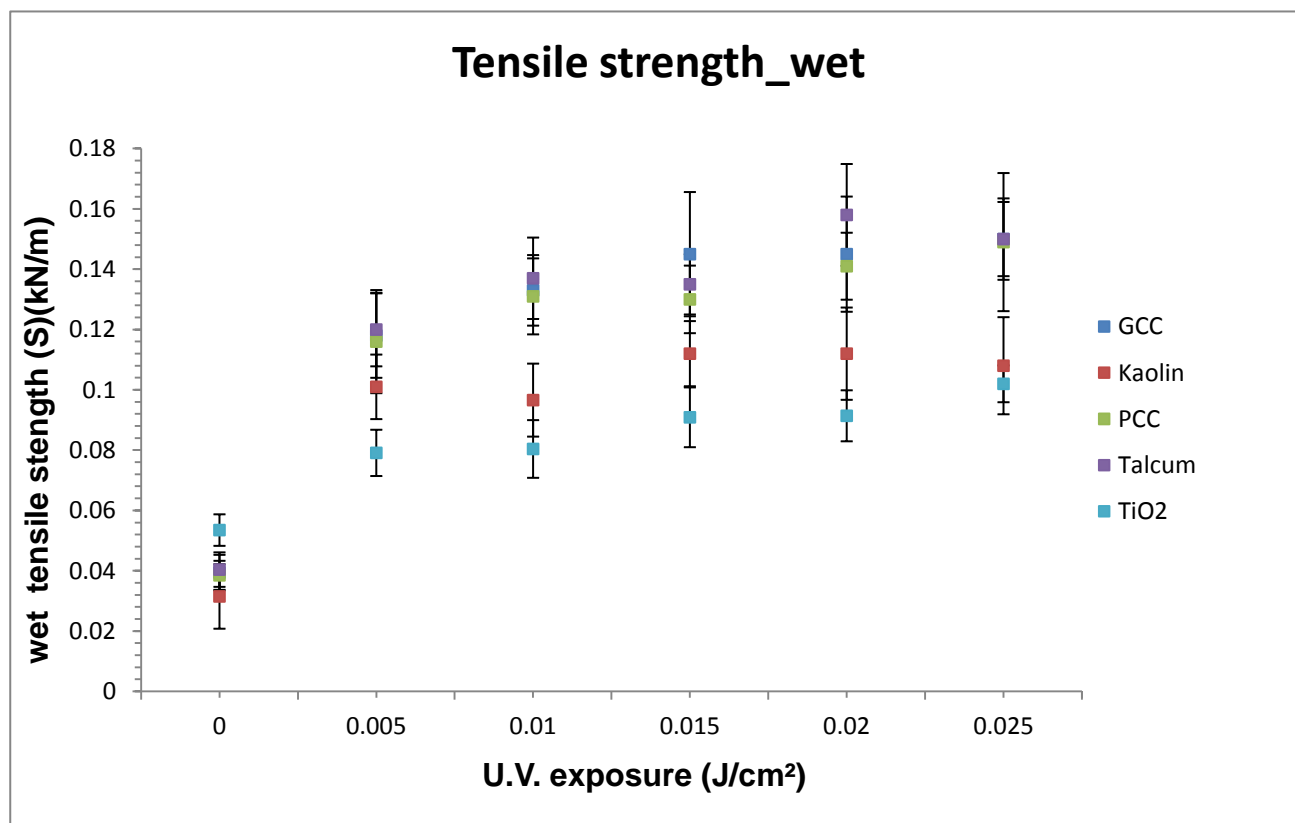


Figure 39 Wet tensile strength, as a function of intensity of UV exposure (J/cm²) for GCC (blue), TiO₂ (sky blue), PCC (green), Kaolin (red), Talcum (purple).

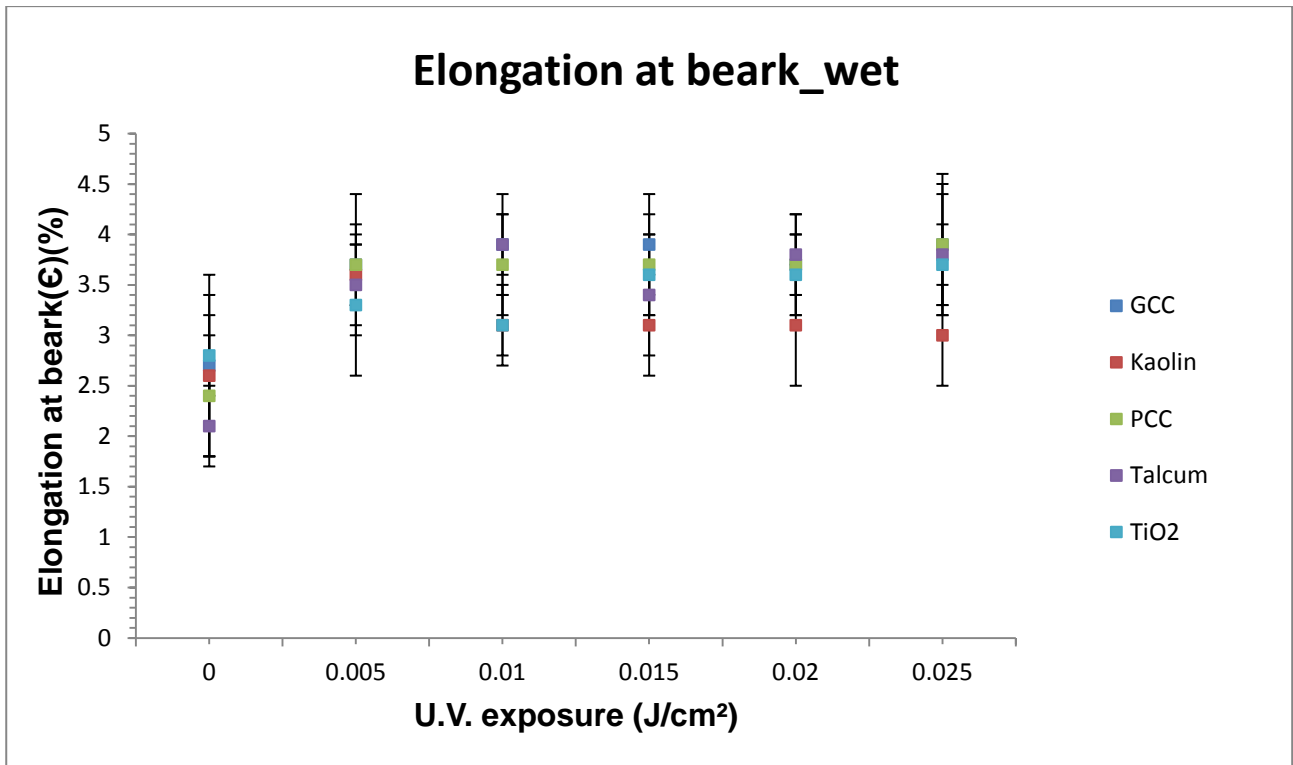


Figure 40 Wet elongation at break, as a function of the intensity of UV irradiation (J/cm²) for GCC (blue), Kaolin (red), PCC (green), Talcum (purple) and TiO₂ (black).

4.4.3. Effect on relative wet strength:

Relative wet strength values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) with varying intensity of UV irradiation to paper sheet contains PDMAA-co-MABP polymer in absence and presence of UV irradiation.

In presence of PDMAA-co-MABP polymer in paper substrate, it has been observed that there was significant increase in relative wet strength values.

From the graphs, there was a very low relative wet strength in paper substrate at no UV exposure to paper substrate but increasing intensity of UV exposure, it has been seen that there was significant increase in relative wet strength in range of 0 to 0.025 J/cm² of surface applied photo-reactive polymer (1.05% ± 0.014 wt %) on paper substrate by size press.

But comparison in between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), Talcum, PCC and GCC fillers give more wet strength to the paper sheet at any intensity of UV exposure (in range of 0 to 0.025 J/cm²), because increasing intensity of UV exposure gives more number of covalent bond attachment of surface applied polymer to cellulose in paper material.

It was also observed that TiO₂ filler affect the relative wet strength properties in presence of UV irradiation to paper substrate containing photo-reactive polymer. There was less increase in relative wet strength values in presence of TiO₂ as filler in compare to other fillers.

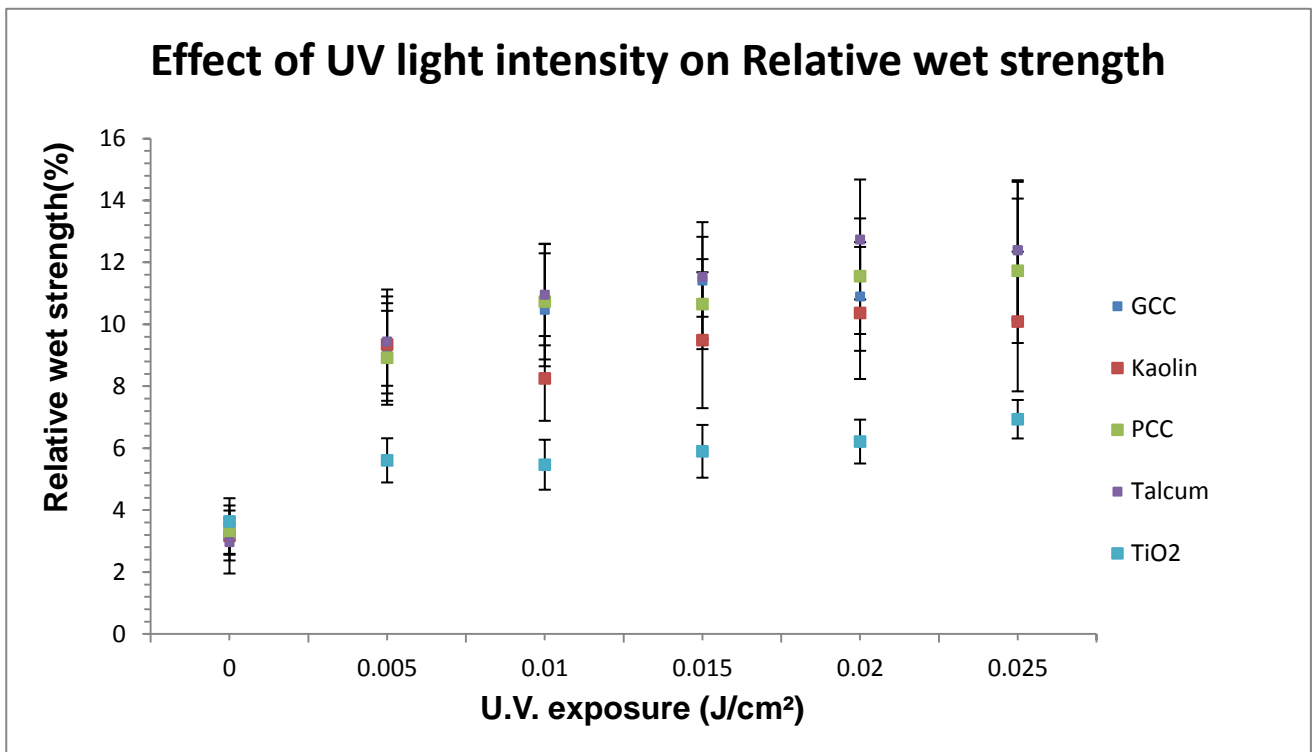


Figure 41 Relative wet strength, as a function of the intensity of UV irradiation (J/cm²) for GCC (blue), Kaolin (red), PCC (green), Talcum (purple) and TiO₂ (black).

4.5. Effect on brightness and whiteness of used paper substrates:

Brightness and whiteness values were calculated for different types of filler (GCC, PCC, Talcum, TiO₂ and Kaolin) containing paper with PDMAA-co-MABP polymer and different types of pulp (eucalyptus bleached and beech sulphite bleached pulp) containing PVAm-BP polymer, in absence and presence of UV irradiation.

In order to measure Brightness and whiteness of paper substrate which were used in experiments, Technidyne colourtouch PC spectrophotometer was used to complete this operation.

Brightness of paper is defined as amount of light, of a prescribed single wavelength (457nm), reflected by paper substrate to the amount that is reflected by an arbitrary standard having 100 reflectance at this wavelength (TAPPI method T452).

Whiteness of paper substrate is measured by reflectance from a paper substrate for all visible spectrums.

In comparison between UV exposed and unexposed paper with different pulp (Beech sulphite bleached and Eucalyptus bleached), it has been observed that after UV exposure to paper substrate, papers with photo reactive polymer inside it become little yellowish in color.

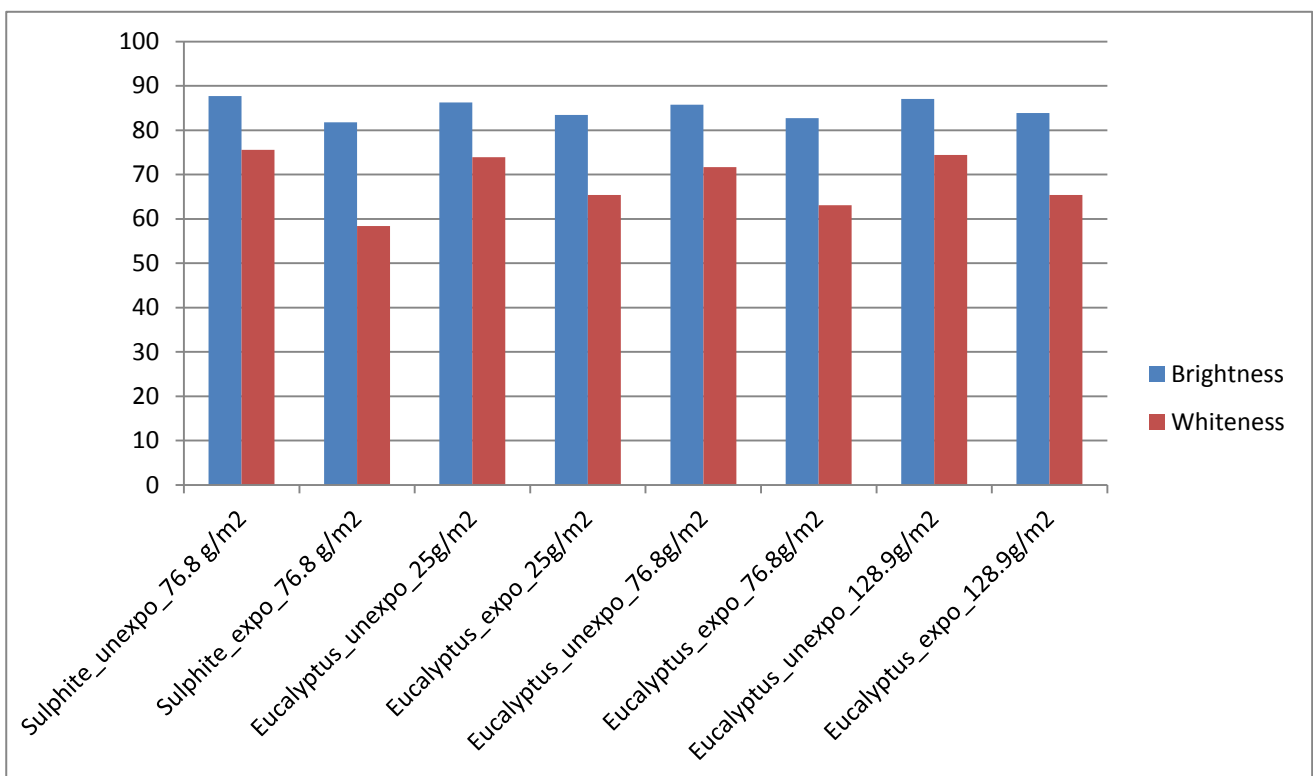


Figure 42 Brightness (blue) and whiteness (red) whiteness of Beech sulphite bleached 76.8g/m² unexposed, Beech sulphite bleached 76.8g/m² exposed, Eucalyptus bleached 25g/m² unexposed, Eucalyptus bleached 25g/m² exposed, Eucalyptus bleached 76.8g/m² unexposed, Eucalyptus bleached 76.8g/m² exposed, Eucalyptus bleached 128.9g/m² unexposed, Eucalyptus bleached 76.8g/m² exposed (left to right).

From the graph, brightness decreases but not as much of decreases in whiteness when papers exposed to UV irradiation.

In comparison between UV exposed and unexposed paper with different type of fillers (GCC, Talcum, TiO₂, PCC, Kaolin), it has been observed that after UV exposure to paper substrate, papers with photo reactive polymer inside it become little yellowish in color.

From the graph, it can be concluded that brightness decreases but not as much of decreases in whiteness when papers exposed to UV irradiation.

It was observed that PCC filler shows more decrease in brightness as well in whiteness after UV light irradiation.

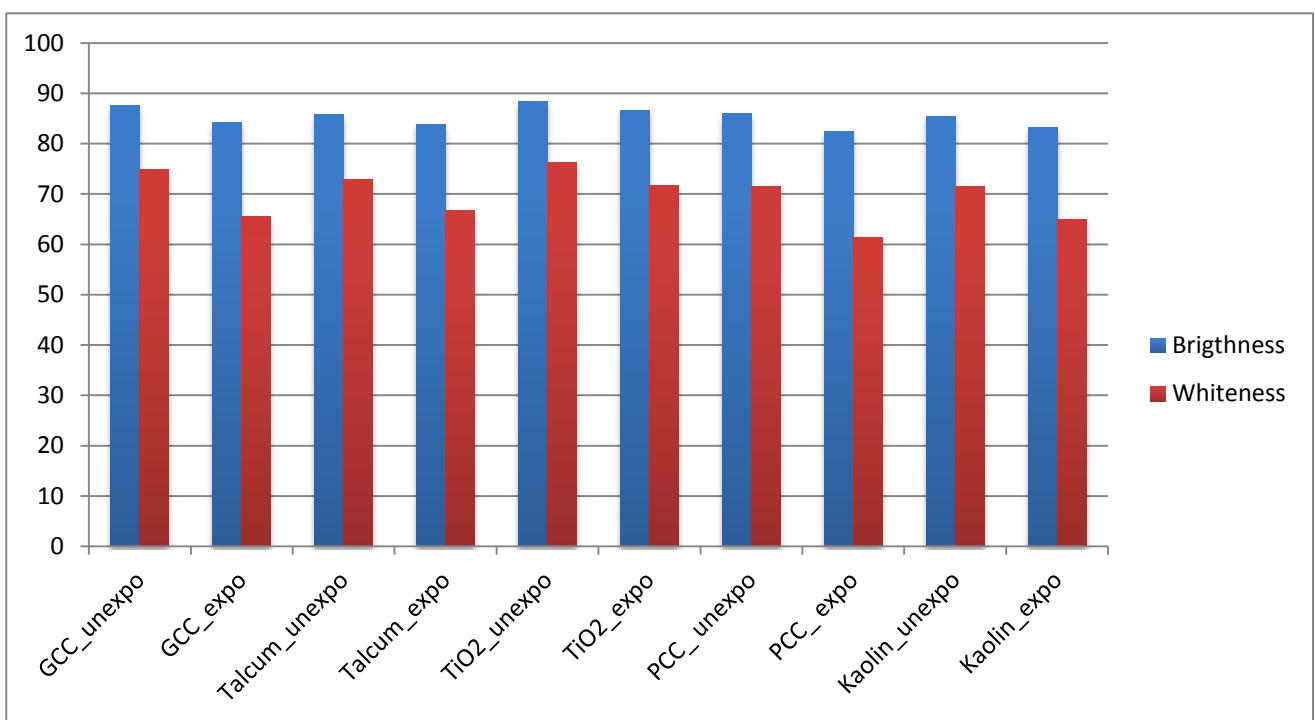


Figure 43 Brightness (blue) and whiteness (red) of GCC unexposed, GCC exposed, Talcum unexposed, Talcum exposed, TiO₂ unexposed, TiO₂ exposed, PCC unexposed, PCC exposed unexposed, Kaolin unexposed, Kaolin exposed (left to right).

5. Summaery

In presence of PVAm-BP polymer in paper substrate, it has been observed that there was a significant increase in relative wet strength within range of 0% to 0.25% of polymer concentration. But further more increase in polymer concentration, it shows slightly increase in relative wet strength values. And there was no impact of grammage of paper sheet on relative tensile strength. But when higher wet tensile strength is required for some final paper product then a higher grammage of paper material can be used. It can be concluded that PVAm-BP with UV exposure gives paper sheet a high relative wet strength in compare to unexposed paper sheet. Because polymer get adsorbed to fibre and while exposing with UV light, polymer attach to the fibres covalently. And covalently attach polymer gives more wet strength to paper sheets.

It has been observed that Eucalyptus bleached and Beech sulphite bleached show almost same relative wet strength values, so in comparison between these two pulp it can be concluded that pulp type doesn't affect relative wet strength of photo-reactive polymer containing paper material.

In presence of PDMAA-co-MABP polymer ($1.05\% \pm 0.014$ wt %) in paper substrate with UV exposure, it has been observed that no significant effect of fillers on strength properties of Photo-reactive polymer containing paper materials except TiO₂ filler. For TiO₂, decrease in relative wet strength by increasing filler concentration.

It has been observed that paper substrate containing PDMAA-co-MABP photo-reactive polymer with fillers in it, shows wet tensile strength in range of 12 to 16% of its dry tensile strength in presence of UV exposure, but without UV exposure it was around 2%, because in this strength measurement we applied photo-reactive polymer on surface, and without UV exposure it couldn't attach to the paper substrate and it loses its surface applied polymer while watering of these paper materials. And relative wet strength increases in presence of UV exposure, because fibres get covalently attach to the polymer in presence of UV light.

In presence of UV exposure, Talcum and GCC give the higher relative wet strength to the paper substrate. It has been observed that there was a very low relative wet strength in paper substrate in absence of UV exposure to paper substrate but increasing intensity of UV exposure, it has been also seen that there was significant increase in relative wet strength in range of 0 to 0.025 J/cm² of surface applied photo-reactive polymer ($1.05\% \pm 0.014$ wt %) paper substrate, because increasing intensity of UV exposure gives more number of covalent bond attachment of surface applied polymer to cellulose in paper material.

In comparison between different type of fillers (GCC, kaolin, talcum, TiO₂, PCC) with same type of pulp (eucalyptus bleached pulp) and same grammage (76.8), Talcum, PCC and GCC fillers give more wet strength to the paper sheet at any intensity of UV exposure (in range of 0 to 0.025 J/cm²).

It was also observed that TiO₂ filler affect the relative wet strength properties in presence of UV irradiation to paper substrate containing photo-reactive polymer. There was less increase in relative wet strength values in presence of TiO₂ as filler in compare to other fillers.

In comparison between UV exposed and unexposed paper with different pulp (Beech sulphite bleached and Eucalyptus bleached), it has been observed that after UV exposure to paper substrate, papers with photo reactive polymer become little yellowish in color so it can be concluded that brightness decreases but not as much of decreases in whiteness when papers exposed to UV irradiation.

6. Instrumentation:

6.1. Technidyne color-touch PC spectrophotometer:

CIE whiteness, brightness, L*a*b* color and opacity are all measured using a Technidyne Color-touch PC spectrophotometer with a range of light sources.

These optical properties are useful to define the visual aspects of plastic, paper and paper-board and paper for printing applications. (Technidyne Color Touch PC,)



Figure 44 Technidyne Color-touch PC spectrophotometer.

6.2. SZP system Zeta-Potential:

Zeta potential is a surface charge on suspended particles (fibre, filling material). This charge determines the interaction between particles. To allow coagulation or flocculation, chemicals are used to influence the charge so that coagulation and/or flocculation occur. For instance in the paper industry, many chemicals are used to allow dewatering, but also to give paper certain qualities such as printability or mechanical strength, both in wet and dry conditions. The charge is also important for the adherence of colours to the fibres. The zeta potential cannot be measured directly, but it can be calculated using the Helmholtz-Smoluchowski comparison.



Figure 45 SZP system Zeta-Potential

Using the zeta potential gauge, a wad of suspension is created by vacuum against the sieve electrode. The liquid slowly flows at various speeds through the wad. This results in shearing forces that cause the mobile opposite charge to stream from the particle. This results in a potential difference that is measured by the instrument. This is the streaming potential. At the same time, the pressure difference over the wad is measured. Following these measurements, the conductivity of the wad is determined and using these data, the zeta potential can be calculated. The measurement is very simple to carry out and takes approximately 1.5 min. using various sieve electrodes; suspensions varying from very fine up to very coarse can be measured. (Magendas B.V.)

6.3. Size press:

Size press is made as two-roll press with hydraulic or pneumatic loading. Press rolls are settled horizontally and its movable roll (in paper run direction).

The rolls are dynamically balanced on demanded speed and can be covered with different coats (rubber, ceramics) depending on produced kind of paper and type of sizing agent. The sizing agent proceeds between the rolls. Volume of sizing slurry can be controlled through set of valves, which are regulated either manually or electric-pneumatically under pressing part onto spreader roll.

Rolls rotation speed of 13 m/min with 4.5 bar pressure between the rolls was used.



Figure 46 size press

6.4. Drum dryer:

Fabric dryer was used to give dryness to the paper sheets after apply polymer by surface operation by size press. Paper sheets were dried by drum drier under condition 100 °C temperature and 20 rotations per minutes.

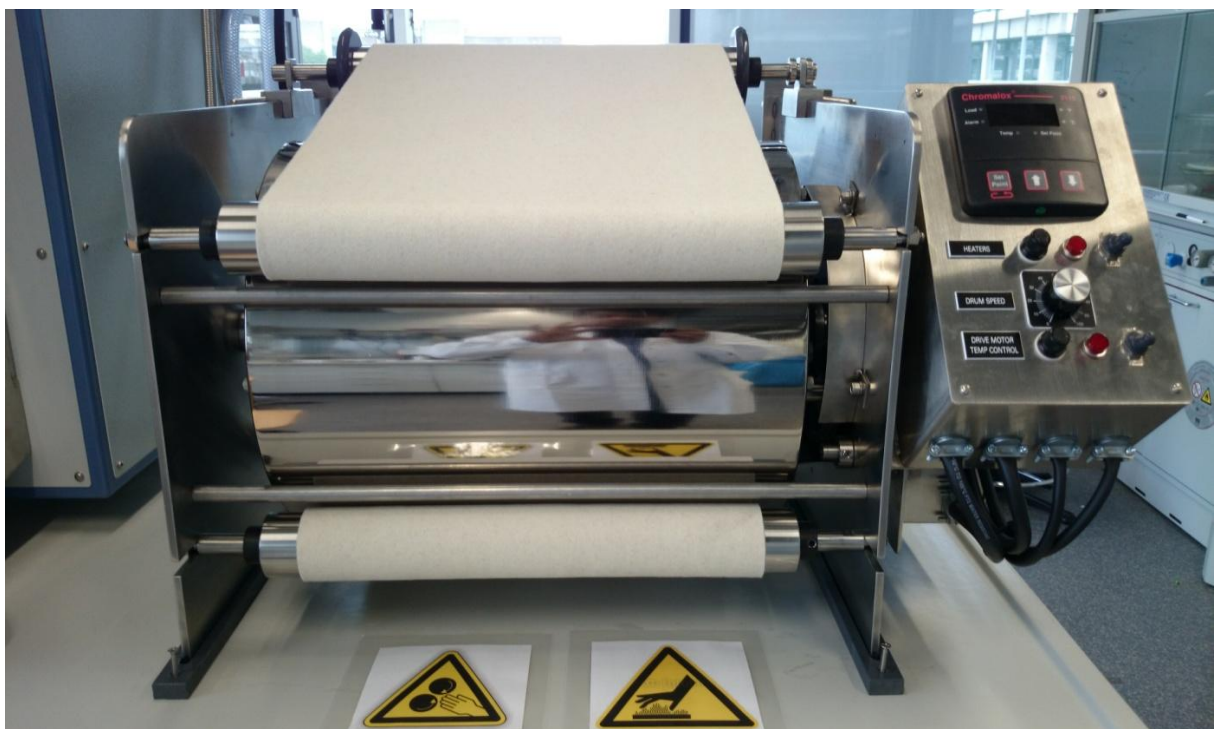


Figure 47 Drum dryer

6.5. UV Chamber:

An UV chamber (254nm wavelength) was used to expose the paper sheets by UV irradiations. An intensity of $2 \times 0.2 \text{ J/cm}^2$ was used and for observation of effect UV exposure on strength properties of paper, paper sheets were irradiated with different intensity of UV exposure like 0.005, 0.010, 0.015, 0.020, and 0.025 J/cm^2 in UV chamber.

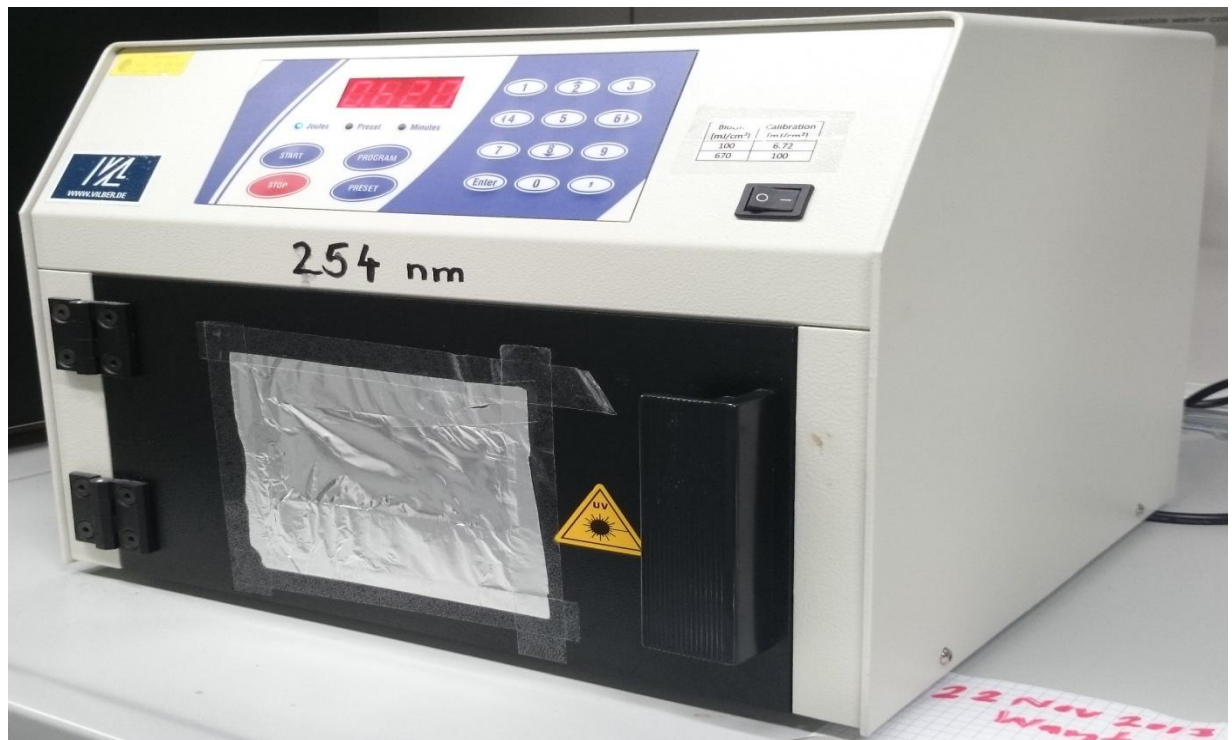


Figure 48 UV Chamber

6.6. Zwick Roll Tensile Tester:

For strength measurement, Zwick Roell tensile tester was used and Tensile strength, Tensile index, Elongation at break (Muchorski, Tensile properties of paper and paperboard [TAPPI T 494], 2006) [TAPPI T 494] were measured by this.

A common tensile test can be performed by this Zwick Roll to provide valuable information about properties such as stiffness modulus, tensile strength, tensile index, elongation at break and energy absorption.

Zwick Roll can be operated with standard commercial PCs or laptops and a software calls testXpert® can be used to get many results from one test. (Zwick Material Testing)



Figure 49 Zwick Roll Tensile Tester

6.7. Freeness tester (Schopper-Reiglar type):

The Schopper-Riegler test quickly provides an idea of the refining degree relating to the speed of the drainage of the diluted paper suspension. The speed of drainage is related to the surface conditions and the expansion of fibres and provides a useful indicator, of the amount of mechanical treatment (refining) of the cellulose paste. This method is applicable to all types of pastes in watery suspension, except for extremely short fibre pastes. (Freeness of pulp (T 227 om-99), 1999)

The scale of measurement in degrees SR.:

- Drainage of **1000 ml** corresponds to **0 °SR**
- Drainage of **0 ml** corresponds to **100 °SR**
- Drainage of each **10 ml** of water corresponds to **1 °SR**.



Figure 50 Freeness tester (Schopper-Reiglar type)

6.8. Dry solid content balance:

Special balance to analyze the solid content of different dispersions and solutions by heating up the samples until a constant weight is achieved.



Figure 51 Dry solid content balance

6.9. Sheet former: The Rapid-Köthen (RK) hand sheet former were used to make paper sheets at laboratory scale.



Figure 52 Rapid-Köthen (RK) hand sheet former.

6.10. Ultrasonic Bar: Ultrasonic bar for homogenization of dispersions of both small and large volume samples.

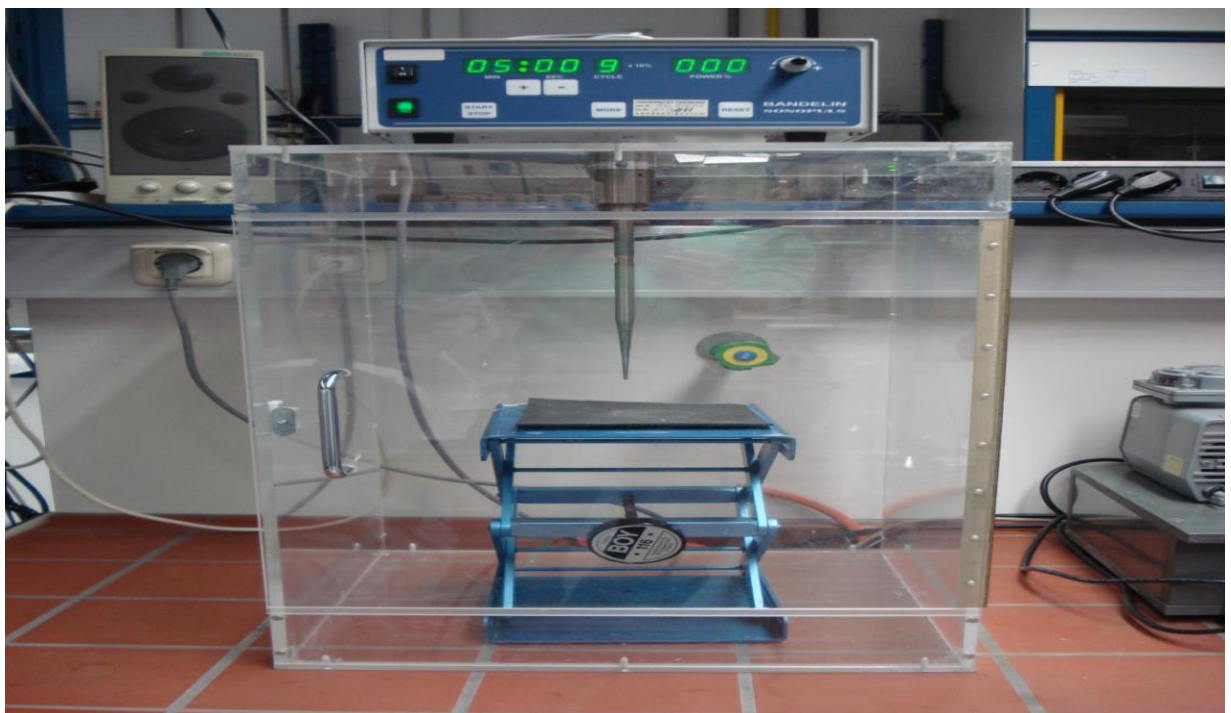


Figure 53 Ultrasonic Bar

6.11. HYLAC Pulp disintegrator:

Before making hand sheets pulp was prepared with disintegration of 35gm of pulp and rest water in each run of Hylec Pulp Disintegrator for making good pulp suspension in water.



Figure 54 HYLAC Pulp disintegrator

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8. Appendix

General definitions:

A. Tensile strength: The maximum tensile force developed in a test specimen before rupture on a tensile test carried to rupture under prescribed conditions. Tensile strength (as used here) is the force per unit width of test specimen.

Tensile strength is indicative of the strength derived from factors such as fibre strength, fibre length, and bonding. For quality control purposes, tensile strength has been used as an indication of the serviceability of many papers which are subjected to a simple and direct tensile stress. Tensile strength can also be used as an indication of the potential resistance to web breaking of papers such as printing papers during printing on a web fed press or other web fed converting operations. (Muchorski, Tensile properties of paper and paperboard(T 494 om-01), 2006)

B. Tensile index: The tensile strength in N/m divided by grammage. (Muchorski, Tensile properties of paper and paperboard(T 494 om-01), 2006)

C. Elongation at break: In general, it is a value of elongation of a paper strip until this paper strip breaks. It shows flexibility of paper.

D. Wet strength: It is more or less a common definition that a paper product which retains more than 15 % of its original dry strength when it is completely soaked in water should be considered as wet strengthened paper product.

In general a wet strength chemicals in paper products should at least be capable of one of these four mechanisms to give wet strengthens to paper:

- Adding to or strengthen existing bonds.
- Protection of existing bonds from loosening caused by water.
- Formation of bonds those are insensitive to water.
- Formation of a network of material that physically entangles with the fibre.

E. Relative wet strength:

$$\text{Relative wet strength (\%)} = \frac{\text{wet tensile strength}}{\text{dry tensile strength}} \times 100$$

- F. Brightness:** Brightness of paper is defined as amount of light, of a prescribed single wavelength (457nm), reflected by paper substrate to the amount that is reflected by an arbitrary standard having 100 reflectance at this wavelength. (Brightness of pulp, paper, and paperboard (T 452 om-08), 2008)
- G. Whiteness:** Whiteness of paper substrate is measured by reflectance from a paper substrate for all visible spectrums (400nm to 700nm).
- H. Freeness of pulp (Canadian standard method):** The freeness of pulp is designed to give a measure of the rate at which a dilute suspension of pulp (3 g of pulp in 1 L of water) may be drained. The freeness, or drainage rate has been shown to be related to the surface conditions and swelling of the fibres. Besides these factors, the result is dependent also on conditions under which the test is carried out, such as stock preparation, temperature, and water quality. (Freeness of pulp (T 227 om-99), 1999)