# The Effects of Certain Polymers on Tensile strength and Tension Relaxation of Wet Web

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## Abstract

The trend in papermaking has been towards lower basis weights, decreased amounts of softwood kraft pulp and an increased use of fillers and recycled fibers. All these changes tend to result in lower strengths of both wet and dry web. To maintain necessary strength in the papers, a greater quantity of strength additives is often required. The effect of different polymers on the dry paper strength has been widely studied and the action of mechanism of different polymers is quite well known. There is much less information of their effect on wet web properties, and especially on the tensile strength and relaxation characteristics.

In this laboratory scale study, the effects of adding different polymers by spraying on wet web tensile and relaxation characteristics at high strain rate were examined. The sprayings were done on wet paper sheets before wet pressing. The results showed that spraying of polymers significantly improves wet and dry paper tensile strength without any increase in dry paper density. The effect of different polymers on wet web mechanical properties was characteristic for each polymer. Carboxymethyl cellulose (CMC) and chitosan improved wet web tensile strength at dryness levels higher than 55%, while polyvinyl alcohol (PVA) improved wet web tensile strength also at lower dryness levels. The most prominent increase in dry and wet web tensile strength was obtained by sequential application of oppositely charged polymers. However, the relative increase of tensile strength was significantly higher for the wet web (80% increase) than for the dry paper (35% increase) compared to the reference without added polymer. Also the mode of polymer addition had a significant effect on wet web tensile strength. Despite a significant increase in the wet web strength, only minor effects on the residual tension (tension after 0.475 s relaxation) was observed. Based on this result, it was concluded that spray addition of the polymers used in this study increased molecular level interactions between fibers but had no effect on the fiber network activation.

**Keywords**
Wet web, polymers, tensile strength & relaxation.

## Introduction

The main target of the paper manufacturer is to make a product with the desired material properties. To do this economically, good runnability of the paper machine is required. Paper machine runnability is often evaluated by the number of web breaks in proportion to the production speed. The practical maximum width of paper machines today is about 11 meters, because increasing the width would require significant investments (increased radius of cylinders) to eliminate vibrations of the cylinders at high speeds. To increase the amount of produced paper on a paper machine, web breaks, broke and downtime in general must be minimized and the production speed maximized [1,2].

The increase of paper machine production speed is often limited by an increase of web breaks and many paper machines are thus forced to run below their design speed. To increase paper machine production speed, the locations and reasons for the web breaks caused by the production speed increase must be identified before they can be reduced. In many cases the bottleneck in the paper machine line is the runnability of the wet web in the press-to-dryer transfer and at the beginning of the dryer section [3-6]. In the open draw, the wet web is transferred from one surface to another without the support of any fabrics. During the open draw, the stability of the running web depends mainly on the web tension. After the press section, the dryness of the wet web varies typically between 40-50%, which means that the tensile stiffness of the web is only 10-15% of the stiffness of dry paper. Accordingly, a considerable speed difference (typically 2-5%) is required to create enough tension to transfer the web and to guarantee a stable run of the paper web in the open draw [3,7,8].

After the open draw, the velocity of the web remains constant for a considerable time. During this time, the tension created in the open draw does not remain constant, but lowers rapidly, i.e. tension relaxation occurs. Typically 50-60% of the tension created in straining is lost during the 0.5 s relaxation time. Lowered tension due to relaxation may lead to slackening of the wet paper. This causes wrinkling, bagging, fluttering and weaving of the web, which can lead to web breaks [3,9]. This means that in order to predict wet web tension behavior at the beginning of the dryer section both tensile strength and relaxation properties of the wet web should be known.

To lower the costs in papermaking, the trend is to constantly use less and cheaper raw materials. This results in deteriorated mechanical properties of the wet and dry web. To compensate this, a greater quantity of strength additives is often required. Several wet strength additives are currently used in papermaking to increase the permanent wet strength of dried papers. These additives serve to increase or strengthen existing bonds; to protect existing bonds; to form bonds that are insensitive to water and to produce a network of material that physically entangles with fibers. These traditional wet strength additives do not enhance wet web strength, i.e. the strength of never dried wet webs. This is because wet strength additives require usually heating and curing time [10].

A typical way to improve wet web strength by chemicals is to increase the water removal of pulp, for example, through the use of different retention aids. Increased dryness improves the mechanical properties of the wet web. Another way to improve wet web mechanical properties would be to use chemical additives that increase interactions between fibers in the wet state. In this study, the effects of various polymers on wet web strength and relaxation characteristics were examined.

## Materials and methods

### Pulps and refining

ECF-bleached pine pulp was obtained from a Finnish pulp mill. The pulp was refined (a conical pilot-scale refiner) and dewatered at the mill. The pulp was packed as never-dried into airtight polyethylene bags, and kept at -18°C until used for testing. The Schopper-Riegler value of the pulp after dewatering and freezing was 20.

### Hand Sheets and spraying

Wet and dry handsheets having grammage of 60 g/m$^2$ (base paper without any chemicals) were formed without white water circulation adapting SCAN-CM 26:99.

The principle of the spray device is presented in Figure 1A. In the spraying of polymers, formed handsheets were attached to the wire with a vacuum which also enhanced the penetration of polymers into the paper during spraying. All chemicals were diluted to 0.5% consistency before spraying. Chitosan was dissolved in 1% acetic acid before diluting to 0.5% consistency. The spraying unit consisted of a vacuum box, a screen plate and wire was on a rail, and it was moved with an electric motor. The amount of sprayed chemical was adjusted by changing the speed of the unit, while the flow remained constant. In the case of a dual application of polymers, similar spraying was carried out in two steps. After spraying, the sheets were wet pressed using two different pressure levels (50 kPa and 350 kPa) to reach two different dryness levels for the wet handsheets. Wet samples were cut to a width of 20 mm and dry samples to 15 mm, both with a sample length of 100 mm. In one trial point, the pulp was divided in two fractions (50%/50%) and polymers were added to the pulp fractions. Before forming of sheets the pulps were mixed in a DDJ mixer for 20 s.

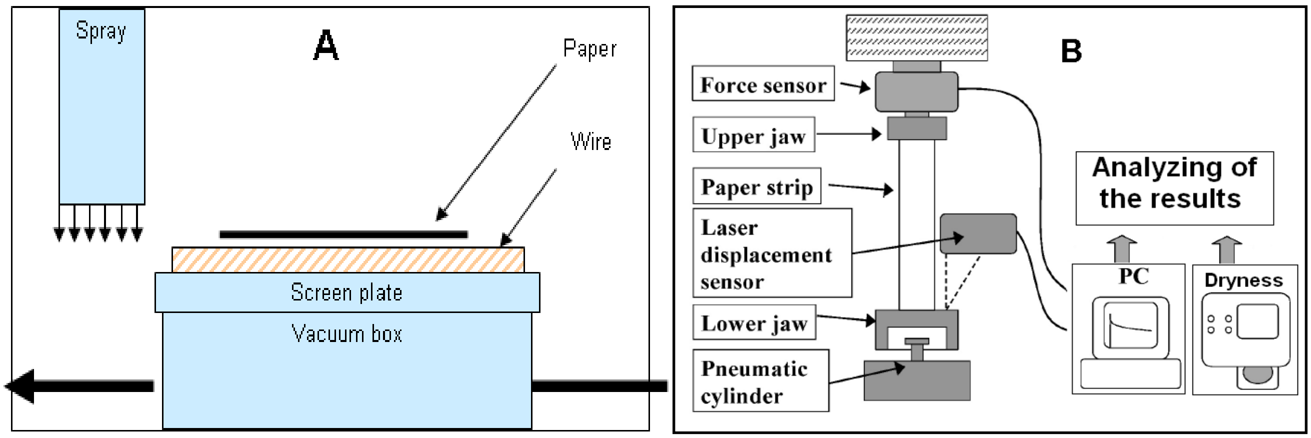


*Figure 1. Schematic illustration of the spray device (figure A)) and IMPACT -fast tensile- and relaxation test rig (figure B)* [3, 11].

**List of samples**

- Reference with no chemicals
- CMC (DS 0.7, DP 140) added by spraying, 1 g/m$^2$
- CMC (DS 0.7, DP 140) added by spraying, 2 g/m$^2$
- Chitosan (made from crab shells, with a relative molecular weight of 400 000 g/mol, and 19% acetylation) added by spraying, 1 g/m$^2$
- CMC (DS 0.7, DP 140) + chitosan (made from crab shells, with a relative molecular mass of 400 000 g/mol, 19% acetylation) both added by spraying, 1 g/m$^2$ + 1 g/m$^2$
- PVA (degree of hydrolysis 99%, DP 1800) added by spraying, 1 g/m$^2$
- CMC (DS 0.7, DP 140) + C-PAM (cationic polyacrylamine) (molecular weight 10-12 Mg/mol, charge density 2 meq/g) both added by spraying, 1 g/m$^2$ + 0.5 g/m$^2$
- (C-PAM) (molecular weight 10-12 Mg/mol, charge density 2 meq/g) + A-PAM (anionic polyacrylamine) (molecular weight 8-9 Mg/mol, charge density -1 meq/g) both added by spraying, 0.5 g/m$^2$ + 0.5 g/m$^2$
- C-PAM (molecular weight 10-12 Mg/mol, charge density 2 meq/g) + A-PAM (molecular weight 8-9 Mg/mol, charge density -1 meq/g) both added to pulp, 5 kg/t + 5 kg/t

**Measurements**

Grammage of the handsheets were measured according to SCAN-P 6:75, thickness of handsheets according to SCAN-P 7:75 and air permeance according to SCAN-P 26:78. IMPACT-fast tensile test rig (Figure 1B) was applied for paper tensile strength and relaxation tests. The strain rate used in this study was 1 m/s. The tension relaxation of paper was evaluated as the tension remaining after 0.475 s of relaxation (residual tension). In addition to the tensile- and relaxation test instrument, an essential instrument in the test procedure is a moisture analyzer, with which the dryness of wet paper samples was measured after tests.

## Results

### Strength and density of dry paper

Figure 2A shows that spraying CMC on wet handsheets before wet pressing increased the tensile index of dry handsheets by 25% at both addition levels (1 g/m$^2$ and 2 g/m$^2$). This result is in line with several studies published on the wet end addition of CMC (see for example [12-14]). Addition of CMC has been expected to break the weak bonding between agglomerated fibrils and induce electrostatic stabilization. As a result of this, CMC disperses fibrils on the fiber surface which leads to increased interactions between fibers [12, 15].

The addition of polyvinyl alcohol also increased dry paper strength, which is in line with the earlier studies [16, 17]. Polyvinyl alcohol is a hydrophilic polymer carrying hydroxyl group on its each repeating unit, which permits the development of hydrogen bonds with hydroxyl and carboxylic groups of cellulose fibers, thus enhancing the tensile strength of dry paper [18]. The addition of chitosan improved dry paper tensile index by 13%. The structural similarity of chitosan to cellulose and the electrostatic interactions, as well as the possibility of covalent bonds forming between chitosan and cellulose have been proposed as explanations for the increase in dry paper strength [19].

The highest tensile index was achieved by a dual application of CMC and chitosan. The dual application of C-PAM and A-PAM also increased tensile index significantly, but the dual application of CMC and C-PAM had no effect on the dry paper tensile index. This result partly concurs with previous findings on polyelectrolyte multilayers (oppositely charged polymers added sequentially to pulp (see for example [20-25])). Polyelectrolyte multilayers have been found to increase the molecular contact area in the fiber-fiber joints [20]. These multilayers were also found to create a larger number of fiber-fiber contacts in the sheet [25]. The use of polyelectrolyte multilayers has been shown to increase dry paper strength with only a minor decrease in density, light scattering or impaired formation of the sheet [24]. The increase of strength has been demonstrated to be greatly dependent on the adsorption of polymers, which is affected by several parameters, such as electrolyte concentration, the type of electrolyte and the charge density [21]. The adsorption of the polymers was not determined in this study.

The spraying of different polymers had no effect on the density of dry paper (Figure 2B) despite the high increase in the tensile index. This indicates that addition of different polymers increased the strength of fiber-fiber bonds but did not increase the number of these bonds. Increased tensile strength with constant density is beneficial form many paper grades (especially for wood-free paper grades) and boards, where the bulk is important for the final product functionality [26].

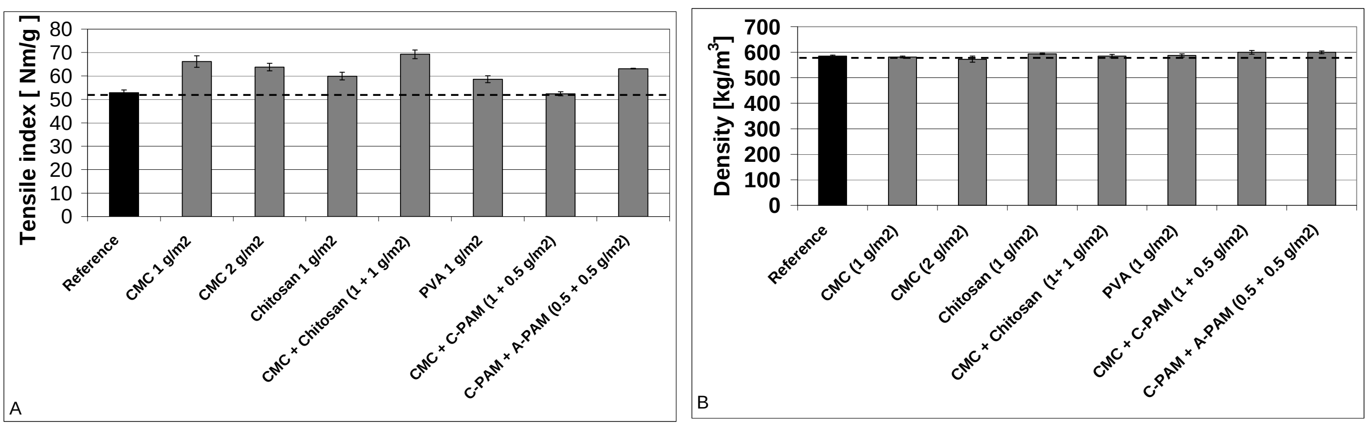


*Figure 2. The effect of adding different polymers by spraying to formed handsheets on tensile index (figure A) measured by the Impact test rig at strain rate 1 m/s and density (figure B) of dry handsheets made from softwood kraft pulp. Error bars show a 95% confidence interval of the mean of the measurement.*

### Mechanical Properties of Wet Web

The effect of the studied polymers on wet web tensile strength is presented in Figure 3A. CMC increased the wet web tensile strength similarly for both addition levels (1 g/$m^2$ and 2 g/$m^2$). The dispersion of fibrils when CMC is added to pulp is believed to increase molecular level interactions between fibers due to the increased surface area (due to hydration of fibrils on the fiber surface) [15,27]. It is worth noting that CMC had no effect on the wet web strength at lower dryness levels (at a given dryness), but a clear increase in wet web strength was obtained at dryness levels above 55%. The development of wet strength with increasing dryness is quite similar with CMC and chitosan. Chitosan is also known to disperse fibrils, but the effect is smaller than with CMC [19]. Chitosan is believed to increase the wet web tensile strength through covalent bonding between cellulose and chitosan. As the chitosan is dissolved in mild acetic acid, the amine group protonates and thus has a cationic charge. Therefore, it is possible that electrostatic interactions between cationic amine groups of chitosan and the anionic fiber surface are also involved, which may also affect on the wet web tensile strength [19].

Addition of polyvinyl alcohol increased the wet web strength (also at dryness levels below 55%). It is likely that polyvinyl alcohol as a high-molar-mass polymer having high affinity to fibers may increase molecular level interaction between fibers at wet state. The dual application of CMC and chitosan increases wet web tensile strength significantly more than the addition of CMC or chitosan alone. Based on the earlier studies published in the literature [28,19], it could be suggested that wet web strength results from a combination of covalent bonding (due to chitosan) and increased fibril dispersion, which could lead to greater molecular level interaction between fibers. However, since similar increase in the wet web strength is obtained also with a combination of CMC and C-PAM and the combination of C-PAM and A-PAM than with CMC and chitosan, it seems more likely that increased molecular level interaction between fibers (weather they are or electrostatic of chemical nature) explains the strength increase of wet web rather than formation of covalent bonds.

The addition of different polymers had only a marginal effect on residual tension (Figure 3B) of the wet web. The increase in residual tension is below 10% with all polymers compared to the reference point with no polymers. This result indicates that residual tension of wet web is more affected by the ability of fiber segments to carry load at small strain levels, rather than magnitude of interactions between fibers.

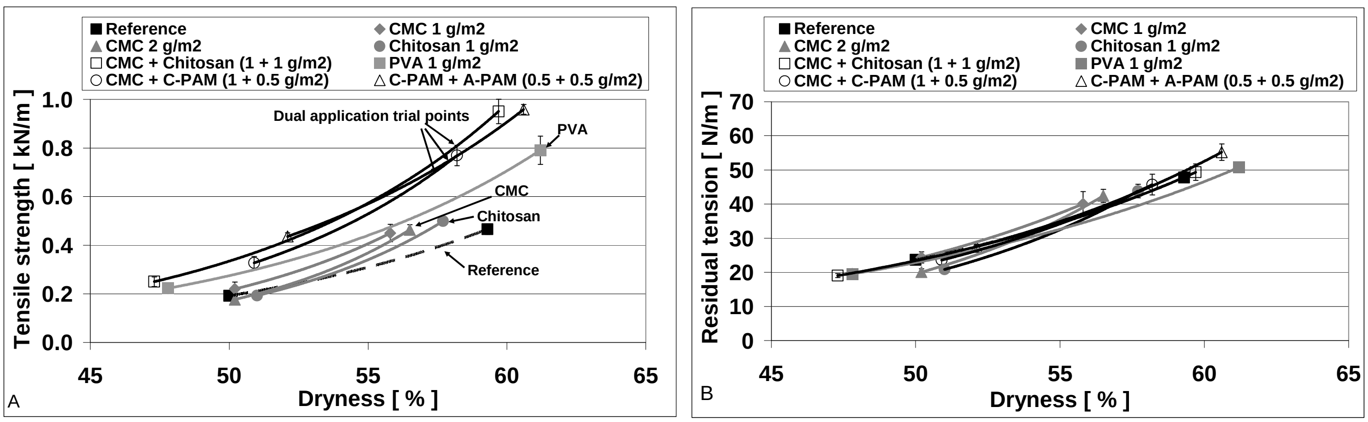


*Figure 3. The effect of spraying different polymers on formed handsheets on tensile strength (figure A) and residual tension (figure B) of wet handsheets (made from kraft pine) as a function of dryness. An exponential fit is used to describe the effect of dryness. The measurements were made by Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement.*

**Mode of addition**

Figures 4A and 4B show how the mode of addition of oppositely charged polymers (C-PAM and A-PAM) affected the dry and wet tensile strength. The addition of C-PAM to one part of the pulp and A-PAM to the other part before mixing the pulps had almost no effect on dry and wet web strength (compared to the trial point with no polymers), whereas the sequential addition of polymers (similar amount as in pulp addition) through spraying results in a marked improvement of dry and wet web strength. This result shows that the interactions between fibers, especially at wet web can be greatly affected by the location of different polymers in the fiber network.

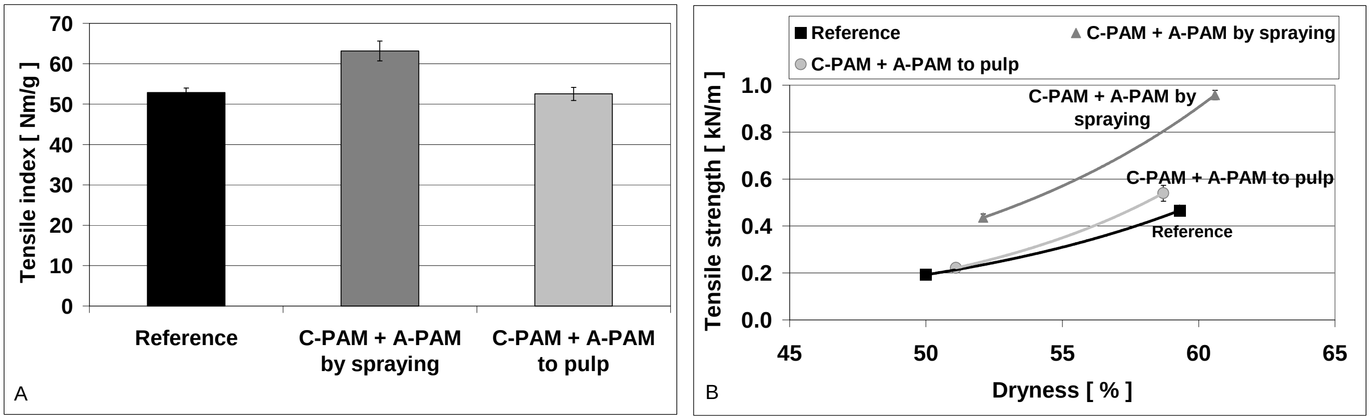


*Figure 4. The effects of using different adding strategies of C-PAM and A-PAM on tensile index of dry(Figure A) handsheets and tensile strength of wet handsheets (Figure B) (made from softwood kraft pulp) as a function of dryness. An exponential fit is used to describe the effect of dryness with wet samples. The measurements were made by the Impact test rig at strain rate 1 m/s. Error bars show a 95% confidence interval of the mean of the measurement.*

## Summary & Conclusions

The results showed that tensile strength of dry and wet paper can be improved by spraying polymers on the wet web before wet pressing. Spraying of CMC and chitosan improved wet web strength at dryness levels higher than 55%, while PVA improved wet web strength also at lower dryness levels. Layering of oppositely charged polymers improved, both dry and wet paper tensile strength, but the effect was significantly higher for wet web. This shows that the layering of polymers increased interactions between fibers at dry and wet state. The addition of polymers probably increased the strength of fiber-fiber joints, which augments wet web tensile strength. However, adding polymers had no effect on wet web residual tension, which is more affected by the readiness of fiber segments to carry load than on the strength of fiber-fiber joints. It is also plausible that the spraying of anionic polymer to the outermost layer could reduce the adhesion between the wet web and the anionic centre roll on a paper machine. In practice, the generation of polymer multilayers or even a bi-layer on the paper machine by spraying can be challenging due to the air flow that travels with the web. This air flow may cause chemicals to spread, thus affecting the evenness of the spray and leading to contamination issues. Therefore the amount added polymers should be minimized and further development of spraying technology, or some other new application method, is required.

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