

A Systematic Study of Noncross-linking Wet Strength Agents

Niko Aarne,[†] Arja-Helena Vesterinen,[‡] Eero Kontturi,^{*,†} Jukka Seppälä,[‡] and Janne Laine[†]

[†]Department of Forest Products Technology, School of Chemical Technology, Aalto University, P.O. Box 16300, 00076 Aalto, Finland

[‡]Polymer Technology Research Group, School of Chemical Technology, Aalto University, P.O. Box 16100, 00076 Aalto, Finland

Supporting Information

ABSTRACT: Cellulosic fibers are inherently hydrophilic, and the modification of them to withstand moisture is important both commercially and scientifically. The usual methods are based on the cross-linking chemistry of reactive groups such as epichlorohydrins. Here, we present that it is possible to attain paper with wet strength from a combination of polymers that lack cross-linking chemistry, namely, carboxymethyl cellulose (CMC) and Polybrene. To accomplish this, we first altered the surface charge of the fibers by adsorption of CMC. Subsequent adsorption of Polybrene, forming the fibers as paper sheets, and drying yielded paper with wet strength properties. The wet strengthening was further investigated by (i) varying the molecular weight of the CMC, (ii) varying the cationic polyelectrolyte, and (iii) synthesizing polymers called ionenes to study the structural properties behind the wet strength of Polybrene. The results showed that (i) drying was necessary to obtain wet strength, (ii) wet strength seemed to be a surface effect, (iii) high M_w CMC played an important role in the development of wet strength, and (iv) only asymmetric ionenes ([3,6] and [6,12]-ionenes) could attain wet strength while symmetric [3,3] and [6,6]-ionenes failed to show wet strength properties.

■ INTRODUCTION

Paper and related products, such as consumer packages, are used to store information and valuable goods whether they are books or cardboard boxes. As such, they have tremendous industrial significance. One of the limits of paper has been its hydrophilic nature that hinders its use in wet environments. The use of synthetic and/or polymeric wet strength agents have successfully improved the properties of paper in these humid surroundings. Paper towels, tissues, and packages are common examples of this achievement. However, despite nearly 70 years of active research on wet strength agents, only three classes have been found to be commercially feasible. The classes consist of formaldehyde-derived resins, polyamide-epichlorohydrin resins, and aldehyde (glyoxalated) resins.¹ All three classes have different mechanisms behind the wet strength effect, but all of them are based on cross-linking.² Even though the polymers themselves are not necessarily cationic, the commercial products often are because of the added cationic monomers in the polymerization mixture.² The cationicity helps the wet strength resins to adsorb onto the fibers³ because the cellulosic fibers are anionic. The positive charge itself does not contribute to wet strength.¹ Previously, the mechanisms behind the commercial wet strength resins have been elaborated. The wet strength resins either cross-link the cellulose to strengthen the fiber–fiber bonds or the resin cross-links with itself and forms a protective layer around the fiber–fiber bond.² The coating then inhibits water adsorption and retains some of the existing fiber–fiber bonds. The two mechanisms effortlessly explain the attained wet strength for nearly all wet strength agents.^{4,5} However, there exists a fourth group of commercial wet strength agents, namely, amine containing polymers, such as poly(ethylene imine) (PEI),⁶ chitosan,⁷ and poly(vinylamine) (PVAm).⁸ Their wet strengthening mechanism has remained shrouded even though several

key investigations have been conducted.^{4–6,8–11} These investigations have attributed the wet strength to amine cross-linking chemistry,⁸ and therefore the purported mechanism does not differ substantially from the other commercial wet strength agents.

Here, we demonstrate that it is possible to attain wet strength with cationic polyelectrolytes that lack any cross-linking chemistry. We demonstrate this effect with quaternary amine polymers such as Polybrene and similarly structured ionenes, which have been adsorbed onto carboxymethyl cellulose (CMC) pretreated fibers. This approach is similar to the approach taken by Pelton's group recently where the CMC was seen as an important medium to bring more cationic polyelectrolytes to the fiber–fiber joint. CMC was not a wet strength agent by itself; its adsorption on fibers was merely a method to increase the adsorption of cationic polyelectrolyte.^{12,13} In addition, oxidation of cellulose fibers with 2,2,6,6-tetramethylpiperidine-1-oxy radical (TEMPO) has been shown to improve wet strength with cationic polyelectrolytes.¹⁴ In this work, we explore the structural components of the wet strength inducing cationic polyelectrolyte and the role of anionic groups brought in by CMC. There is not a commonly recognized theory that would explain this kind of wet strength. Therefore, we suggest a mechanism that might explain the unprecedented wet strength behavior based on the asymmetric structure of the polymer.

Received: May 3, 2013

Revised: July 17, 2013

Accepted: July 22, 2013

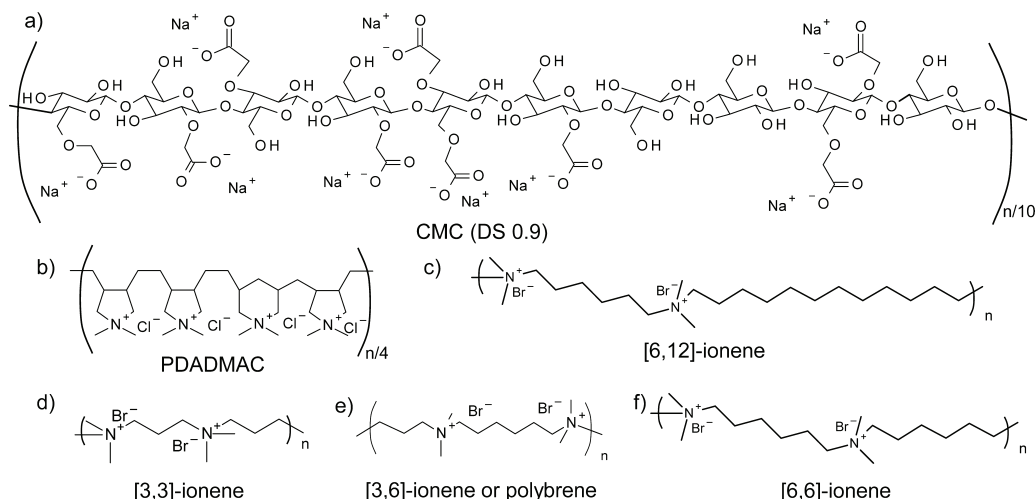


Figure 1. Polymers used and synthesized for this study. (a) Schematic representation of CMC with DS 0.9. (b) Schematic representation of the high M_w PDADMAC. (c–f) Various ionenes synthesized for this study; (c) [6,12]-ionene, (d) [3,3]-ionene, (e) [3,6]-ionene or Polybrene, (f) [6,6]-ionene.

EXPERIMENTAL SECTION

Materials. Pulp. The pulp fibers were obtained from fully bleached (elementary chlorine free bleaching) chemical pulp produced in Botnia, Äänekoski, Finland. Only the long fibers section was used, and the fines were removed from the pulp through 200 mesh with 6.0 g/dm³ consistency, mixing, and a 5.0 dm³/min flow rate for tap water (conductivity 200 μ S/cm) for 1 h 30 min to give a clear filtrate (adapted from SCAN-M 6:69 standard). Furthermore, the carboxylic acid groups found in the fibers were ion-exchanged to Na⁺ to remove interfering metal cations such as Ca²⁺ and Al³⁺.¹⁵ The standard method ensures that all carboxylic acid groups have the same counterion (Na⁺). The counterions of the carboxylic groups in the fibers were first replaced to protons by washing them with deionized water, stirring the mixture for 60 min in 10 mM HCl solution, and finally washing the fibers with deionized water twice to obtain conductivity <5 μ S/cm. The protons were then replaced by sodium ions by using 0.005 M NaHCO₃ and adjusting the pH to >8 by 1 M NaOH. This solution was mixed for 40 min, filtrated, and washed with deionized water until conductivity was again <5 μ S/cm.

Reagents. We used deionized water (conductivity 0.5 μ S/cm). Control of the pH was done with hydrochloric acid (1 M HCl), sodium hydroxide solution (1 M NaOH), and sodium bicarbonate (1 M NaHCO₃) stock solutions, all of analytical grade. Calcium chloride dihydrate (Merck, analytical grade) was used to increase ionic strength during CMC adsorption.

Commercial Polyelectrolytes. The commercially available polyelectrolytes were two CMCs (90 000 g/mol DS 0.7 and 700 000 g/mol DS 0.9, as reported by the producer Sigma-Aldrich), hexadimethrine bromide, (Polybrene, [3,6]-ionene, $\geq 94\%$, Sigma), and polydimethyldiallylammonium chloride, (PDADMAC, Sigma). To determine the charge in polyelectrolyte titrations, sodium polyethanesulfonate (PES-Na, M.W. 19 100 g/mol Oy G.W. Berg & Co. Ab/BTG Müttek GmbH) was used. The PDADMAC was ultrafiltrated before use with Miniset membrane cassette system (300 K Omega 0.75 ft², cut off at >300 000 g/mol, Filtron Technology Corporation,

Northborough, MA, U.S.A.) at 2.0 bar and 1.0 g/dm³. The size exclusion chromatography (SEC) data for these polymers is available elsewhere.¹⁶

Ionenes. Ionenes are polymers of ditertiary amines and dibromides, which polymerize through the Menshutkin reaction. The naming convention is as follows. The length of the linear chain (number of CH₂ groups) of the ditertiary amine is X CH₂ units, and the linear chain of the dibromide has Y CH₂ units. The numbers are written inside the brackets, separated by a comma to form the chemical formula for the monomer and thus the name of the polymer (i.e., [X,Y]-ionene).¹⁷ Note that due to symmetry [X,Y] and [Y,X]-ionenes are, in practical terms, identical even though different monomers have been used. We synthesized several ionenes using acetone as a solvent. In a typical synthesis, 10 g of diamine was dissolved in 150 mL acetone at ambient conditions. Subsequently, the reaction flask was placed in an oil bath, and dibromide was added under continuous stirring. The reaction proceeded 24 h in which time the synthesized polymer precipitated. This precipitate was further purified and analyzed. Polymer formation was confirmed by ¹H NMR as a peak at 3.3 ppm originating from CH₃ groups in the quaternary ammonium ions (see Figure 1 for ionene structures and the Supporting Information for details of synthesis and SEC). ¹H NMR was measured with a 400 MHz NMR (Bruker Ultrashield 400 Plus) using deuterium oxide as a solvent. Some of the polymers [3,3], [6,6], and [6,12]-ionenes polymerized effortlessly, while [1,3] and [2,2]-ionenes did not. They were most probably low molecular mass dimers.¹⁸ Only the polymerized products were used in the adsorption experiments, and the molecular formulas of the polymers are shown in Figure 1.

Methods. Adsorption of CMC. The pulp fibers were treated with CMC to increase the surface charge. CMC was attached to the fibers at conditions of 50 mM CaCl₂, 30 g/L pulp consistency, and 80 °C for 2 h keeping the pH above 8 with 1 M NaOH. The pulp was washed with deionized water until the conductivity of the filtrate was <5 μ S/cm. The pulp was

subsequently washed to the Na-form. This removed part of the adsorbed CMC. Detailed results of the adsorption and charge increase can be found elsewhere.¹⁶

Charge Density Determinations. We determined the charge density of the cationic polymers via polyelectrolyte adsorption with the MÜTEK particle charge detector (PCD-03, Müttek Analytic, Herrsching, Germany). PES-Na was used as the titrant.¹⁹ The polyelectrolyte properties are shown in Table 1.

Table 1. Characteristics of Polyelectrolytes Used^a

polymer	M_w (kDa)	M_w/M_n	CD (meq/g)
low M_w CMC	66	2.7	3.8
high M_w CMC	690	1.9	4.1
PDADMAC	800	12.6	6.2
[3,3]-ionene	17	2.7	6.0
Polybrene i.e. [3,6]-ionene	6.3	1.8	5.3
[6,6]-ionene	25	1.8	4.8
[6,12]-ionene	63	1.2	4.0

^aMolecular weight (M_w), polydispersity index (M_w/M_n), and charge density (CD).

The polymers are all highly charged because each monomer has at least one charged group. However, the ionene series have a decreasing charge density due to the increasing amount of alkyl (CH_2) groups of the monomer. In addition, the adsorption of the synthesized ionenes onto cellulosic fibers was determined.¹⁶ The highly charged polymers should have low molecular weight to access the cell wall.^{20,21} All the synthesized ionenes could titrate the total charge of the cellulosic fibers, and this further indicated that the molecular weights of the ionenes were low.

Adsorption of Cationic Polyelectrolytes. We had earlier determined both the surface and total charge of these fibers with cationic polyelectrolyte adsorption.¹⁶ The acquired adsorption isotherms allowed us to add cationic polyelectrolytes 100% \pm 5% of the total or surface charge of the fibers, depending on the polyelectrolyte used. The experimental scheme is depicted in Figure 2.

Paper Testing. Laboratory sheets were prepared according to SCAN-C 26-67, with the following modifications: 60 g/m² sheets were done, deionized water was used, and the drying was done in press with 1.0 ± 0.1 kg/cm² pressure (~ 0.1 MPa) and temperature 130 ± 1 °C in both press plates for 3 min (dry matter content was 90–91%). Paper testing was done according to the following standards: Grammage ISO 536, thickness ISO 534, and tensile testing SCAN-P 38:80.

Wet Strength Measurements. The wet strength was measured according to SCAN-P 20:95 with several modifications. We used the same apparatus (Alwetron TH1 Tensile Tester, Lorentzen & Wettre, Sweden) to measure the physical properties of the paper sheets in the dry state as well as in the wet state. This allowed us to calculate the wet/dry strength ratios, which otherwise would be difficult due to differences in span length and pulling velocity when two different types of equipment are used to measure the dry and wet strengths. The lowest tensile strength measurable was $\sim 1.8 \pm 0.2$ N m/g. Some of the samples (reference and CMC treated samples) did not necessarily show appreciable wet tensile strength but disintegrated upon contact or when inserted in to the tensile strength tester. Therefore, soaking times were kept minimal (30 s), and the dry matter contents of each test piece were measured directly after the measurement. However, the samples that demonstrated wet strength held the wet strength

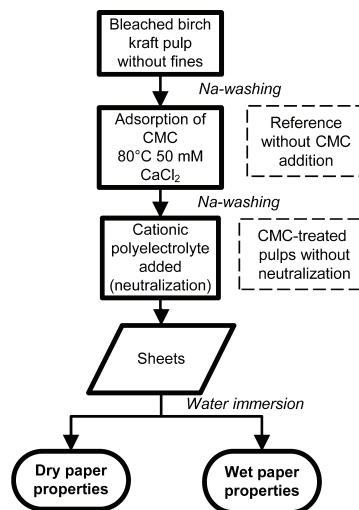


Figure 2. Scheme for the wet strength experiments. The addition of CMC was deemed necessary based on earlier research. Subsequently, cationic polyelectrolyte (ionenes) was added to neutralize the anionic charge. The treated fibers were formed into paper sheets and analyzed for their physical properties in dried formed and after immersed in water.

for a longer time. The relatively short time was chosen to obtain comparable values for the reference samples. The wetting was complete for all samples as the dry matter content of the soaked samples were always lower than water retention value. Higher dry matter contents were obtained by letting the samples dry a period of time before measuring. The measured dry matter contents enabled deeper discussion about the wet strength mechanism. No size or other hydrophobizing treatments were used.

RESULTS

The wet strength measurements were performed on an already formed paper that had been rewetted (Figure 2). This drying and rewetting was necessary to obtain the wet strength values as none of the cationic polyelectrolyte-treated fibers exhibited wet strength upon forming the test sheets. Figure 3 presents the wet tensile strength of paper when using different dosages of CMC and Polybrene. The effect is the most pronounced when high M_w CMC is neutralized with Polybrene. The effect is much smaller for low M_w CMC treated with Polybrene but still measurable. The surface modification of fiber with CMC is therefore an important initial step to attain the wet strength. However, the cationic polyelectrolyte is necessary for wet strength because CMC addition on fibers alone does not exhibit any wet tensile strength (Figure 3a.) The type of the cationic polyelectrolyte is decisive. For example, the use of PDADMAC as the cationic polyelectrolyte does not give any wet strength (Figure 3b).

There is a notable discrepancy between the wet strengths of Polybrene and PDADMAC-treated fibers after high M_w CMC adsorption, which is not surprising because it is well known that cationic polyelectrolytes with quaternary amines do not give wet strength.¹ However, the origin of these differences in wet strength might be because Polybrene adsorbs on the fibers to a

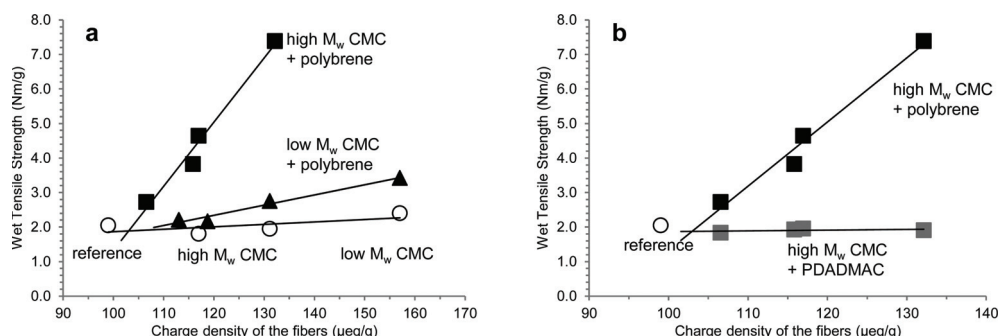


Figure 3. (a) Effect of molecular weight of CMC for the wet strength of paper using Polybrene. (b) Use of PDADMAC does not give any wet strength. Higher charge density of the fibers corresponds linearly with the adsorbed amount of CMC. (Adsorption can be calculated from the values in Table 1, e.g., high M_w CMC [(33 μeq/g)/(4.1 meq/g) = 8.1 mg/g] neutralized with Polybrene [(133 μeq/g)/(5.3 meq/g) = 25 mg/g] or PDADMAC [(33 μeq/g)/(6.2 meq/g) = 5.3 mg/g].) In all experiments, the cationic polyelectrolyte was fully adsorbed.

much greater extent than PDADMAC due to the molecular weight differences. Here, we have to assess the importance of the amount of the added polyelectrolyte. It is generally accepted that increasing the amount of wet strength agent increases wet strength. Therefore, the amount of added Polybrene should play an important role in the development of wet strength. If the wet strength is high at substantial additions of Polybrene, the neutralization of the whole fiber is essential to develop wet strength. On the other hand, if the wet strength is attained at low additions, the effect is more likely to be a surface effect. We tested this hypothesis with high M_w CMC surface-treated fibers because these fibers possessed a higher wet strength than the low M_w CMC-treated fibers or the reference sample (Figure 3). The amount of Polybrene was gradually increased, and the wet strength was measured at each addition (Figure 4). Previously, we had determined the surface charge of the fibers by the polyelectrolyte titration method.¹⁶ This information was used to give the 100% surface

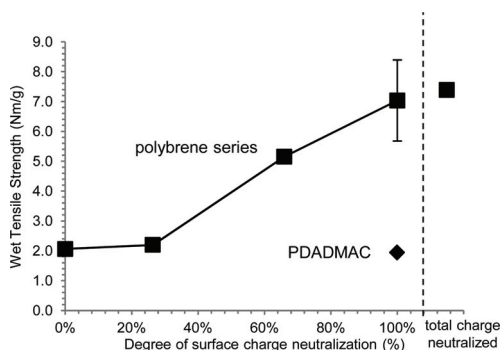


Figure 4. Wet strength development with Polybrene additions. The surface charge of high M_w CMC-treated fibers (8.1 mg/g) is gradually neutralized with Polybrene. (PDADMAC was used to obtain the surface charge 100% point (33 μeq/g). The 100% surface neutralized point for Polybrene is an average of 5 measurements that had surface charge neutralized and partial neutralization of the cell wall.) The last point corresponds to the total charged neutralized sample where Polybrene has been added substantially more (133 μeq/g) than the amount needed for surface neutralization (33 μeq/g). In all experiments, the cationic polyelectrolyte was fully adsorbed.

neutralization point in the graph in Figure 4. We assumed that the surface charge will be neutralized first and that only after the surface is fully adsorbed with cationic polyelectrolyte does the adsorption to the fiber interior occur. In Figure 4, the increase in surface neutralization corresponds to the appearance of wet strength. At roughly the midpoint of surface neutralization (~50%), the wet strength is starting to develop. A fully developed wet strength is attained at complete surface neutralization, and increasing the amount of Polybrene does little to further improve the wet strength in Figure 4. This clearly demonstrates that the wet strength is a surface effect, i.e., it is not necessary to neutralize the fiber completely to attain a wet strength effect.

We hypothesize that the unique wet strengthening effect of Polybrene is due to a structural difference with respect to many other cationic polyelectrolytes. In Polybrene, the charge is an integral part of the polymer backbone, and thus the functional group bearing the charge is not free to rotate like it is in the cationic side groups in most other cationic polymers. We earlier demonstrated that Polybrene-treated samples, after high M_w CMC adsorption, had unique wet strengthening behavior that was not possible to attain with other cationic polyelectrolyte with quaternary amines (e.g., PDADMAC, Figure 3b). The wet strength was likely a surface effect involving high M_w CMC and Polybrene (Figure 4). However, the molecular weights of Polybrene and PDADMAC differ substantially. Therefore, it is interesting to compare the wet strength results of similarly structured polymers that share the molecular weight and linear structure of Polybrene. Several ionenes were prepared, and their wet strength results are shown in Figure 5. It shows that the prepared ionenes differ substantially in their behavior to induce wet strength. The striking feature of the results is that the [3,3]- and [6,6]-ionene treated papers do not demonstrate wet strength. This is important because these ionenes are made from the constituent pieces of Polybrene ([3,6]-ionene). Therefore, the distance between the charges in the molecule does not explain the wet strength. However, a [6,12]-ionene has the same wet strength effect as Polybrene. The common feature of these molecules is their asymmetric charge distribution—the distance between the charges alternates in a 1:2-ratio. Although the only polymers with asymmetric charge distribution were of a 1:2-ratio asymmetry ([3,6] and [6,12]-ionenes), we hypothesize that the asymmetric charge

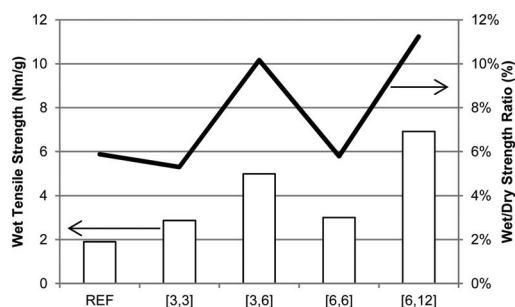


Figure 5. Wet strengths of different ionenes. Only [3,6] and [6,12]-ionenes show appreciable wet strength. (High M_w CMC pre-adsorbed pulp, 8.1 mg/g).

distribution along the polymer chain is responsible for the effect.

Finally, it is long known that some wet strength can also be attained with sizing chemicals, e.g., alkenyl succinic anhydrides (ASA) and alkyl ketene dimers (AKD). However, these chemicals are not considered to be wet strength chemicals because they merely prevent the wetting of the fibers rather than increasing the fiber–fiber bond strength. Therefore, the mechanism behind the wet strength of asymmetric ionenes may simply originate from the increased hydrophobicity of the Polybrene and [6,12]-ionene compared to, e.g., [3,3]-ionene. We concluded that sizing (hydrophobizing) the fibers was not the reason behind the wet strength by comparing the dry matter contents of the Polybrene-treated samples against the wet strength curve for fibers that do not wet (Figure 6). The wet strength development follows a completely different route for Polybrene ([3,6]-ionene) and [6,12]-ionene than for the reference and [3,3] and [6,6]-ionenes (Figure 6).

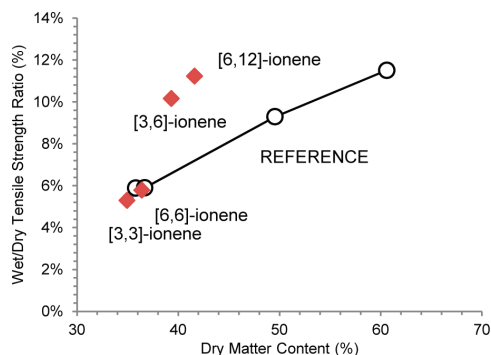


Figure 6. Wet strength effect of ionenes is shown in diamonds (high M_w CMC pre-adsorbed pulp, 8.1 mg/g). A wet strength curve for reference is shown (circles) to demonstrate that the wet strength of the ionenes is not due to increased dry matter content of the samples.

We summarize the obtained results as follows: (i) Drying was necessary to obtain wet strength. (ii) No amine chemistry was present when using ionenes to obtain the wet strength. (iii) The wet strength seemed to be a surface effect. (iv) High M_w CMC played an important role in the development of wet strength. (v) Asymmetric cationic ionene was needed. (vi) The

increased wet strength was not due to a decreased wetting (sizing effect).

DISCUSSION

Background. The Two Mechanisms. We will start the discussion on how the ionenes impart wet strength by briefly stating the existing methods that are known to impart wet strength on fibers. For increased wet strength, two generally accepted mechanisms exist. The first one is called the *protection mechanism*, and it is based on the fact that if the fiber–fiber bond is covered with hydrophobic material the resulting covering material resists water intrusion and keeps the fibers bonded by protecting the existing fiber–fiber bonds (Figure 7a).² The other mechanism is known as the *reinforcement mechanism*. As the name suggests, it functions by strengthening the existing fiber–fiber bonds through new—usually covalent—bonds between the fibers themselves. The resulting covalent fiber–fiber bonds resist the dispersing effect of water, resulting in increased wet strength (Figure 7a,b).² We have summarized examples of commercially available wet strength treatments and their primary mechanism and reactions (Table S1, Supporting Information). These are vegetable parchenting, acidic wet strengthening, basic or neutral wet strengthening, temporary wet strengthening, and cationic polyamine wet strengthening. In vegetable parchment, the wet paper is welded together with sulfuric acid treatment that gelatinizes the surface of cellulose. Subsequent washing and drying forms paper with good wet resistance properties, as the dissolved and gelatinous cellulose polymers dry on the surface and form a dense film that is impenetrable to both water and even oil.^{22,23} Therefore, vegetable parchenting can be considered to function via protection mechanism. Acidic wet strengthening relies on polymers such as urea–formaldehyde or melamine–formaldehyde that are impregnated to fiber webs, which are cured at high temperature.^{2,24} As an example, urea–formaldehyde (or rather the urea–methylol structure) polymerizes to form low M_n linear polymers that cross-link at high temperature (Figure 7a). The cross-linking can continue days, even weeks, in the dry state. Basic or neutral wet strengthening functions via PAE and other epichlorohydrin polymers that react on the surface of the fiber (Figure 7b). The polymer adsorbs on the surface of the fibers and mainly reacts with itself, even though the few carboxyl groups found in the fibers participate in the reactions.² In temporary wet strengthening, glyoxalated polymer reacts with the hydroxyl groups of cellulose to form hemiacetals or acetals (pH <4.5) or reacts with the amide groups of the wet strength agent to form amides (pH ~5–6).² A typical example is the glyoxal-reacted PAM (G-PAM). Both temporary wet strengthening and basic or neutral wet strengthening are considered to reinforce the fiber–fiber bonds and thus give wet strength. In cationic polyamine wet strengthening, a polyamine such as PEI, chitosan, or PVAm react with each other at room temperature and form imine and aminal bonds. To a large extent, the primary and secondary amines probably react to form imine and aminal bonds while the few aldehyde groups found in the fibers forms fiber–fiber cross-links. The additional contribution from electrostatic interaction between the polymer and fiber has been argued to form fiber–fiber bonds that do not wet, but the mechanism has remained unknown.^{7,8,25} In short, the four commercial wet strength resins have mainly cross-linking reactivity, while vegetable parchment (butter wrap) and our CMC+asymmetric ionene treatment work according to a different mechanism. Here, we explore the effect of this

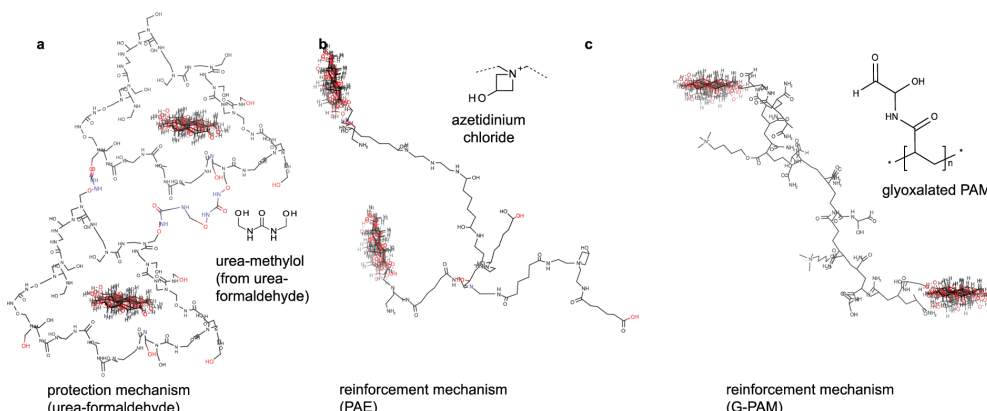


Figure 7. Two types of wet strength mechanisms and three commercially available wet strength resins. (a) Protection mechanism with urea-formaldehyde forms closely networked structures around cellulose but does not react with it. (b) PAE reacts with itself forming complex cross-linked forms. Some of the chains react with the carboxylic groups found in the hemicelluloses or in the oxidized end groups of cellulose. (c) Glyoxalated polyacrylamide forms complex networks by reacting with the hydroxyl groups in the polymer or with cellulose. Cationic groups dispersed in the structure help to concentrate the cross-linking near the anionic fibers. The illustrations are schematic and assume that the fibers consist only of a single cellulose chain. In reality the structures are 3 orders of magnitude larger. However, the chemistry is correctly depicted and is according to the literature.^{1,2,24} The molecular structure insets show the reactive cross-linking group. (Supporting Information has .mol files of these structures.).

fundamental difference when discussing the proposed mechanism for the asymmetric ionenes.

The Four Attributes of Wet Strength Agents. Espy summarized the four attributes for a wet strength agent suitable for commercial papermaking: water-solubility, cationicity, polymeric nature, and reactivity.¹ The reactivity refers to the cross-linking tendency of a wet strength agent. From these four parameters, the reactivity is the only attribute that lacks in ionenes. Therefore, we believe that ionenes can be used to study the effect of the other three parameters on wet strength.

Three Classes of Wet Strength Adhesion. On the basis of his extensive research on wet strength,^{8,10–12,26–30} Pelton has suggested that the wet strength adhesion could be separated to three classes: heat curing, damp dried, and instantaneous wet adhesion. Of these, the heat curing polymers are added before the fiber web has formed, and they are activated by a heat treatment afterward. This is usually done in the drying section of a paper machine and is therefore most commonly encountered in practice. PAE and UF resins are examples of heat curing polymers. In contrast, damp dried systems do not need heat activation. Treating an already formed fiber web with a wet strength agent and subsequently drying the paper to activate the wet web yields damp-dried wet strength. PVAm and PEI, as well as our ionenes, belong to the damp-dried class. Finally, the instantaneous wet adhesion demands that the wet strength is already attained when the fibers are in low concentration in the solution, i.e., before the formation of the fiber web. Instantaneous wet adhesion has been difficult to achieve, and scientifically advanced concepts such as PVAm boronate³¹ or bioconjugation³² are needed.

Proposed Mechanism. Before we can assess the wet strength mechanism in our samples, we would like to review an excellent case in wet strength enhancement whose chemical nature only constitutes cellulose, namely, vegetable parchment. Vegetable parchment is prepared by dipping cellulosic fibers in concentrated sulfuric acid, and because it contains only cellulose, no cross-linking chemistry is available. The origin of the wet strength arises probably from dissolved cellulose on the

surface of the fibers that has dried between two fibers. This fiber-fiber bond is shown in the SEM images of the cross-section of fibers.^{22,23} The characteristic water resistance of vegetable parchment can be attributed to a crystalline structure that resists water intrusion and a structure that is formed from cellulose upon a strong acid treatment. In the case of CMC + asymmetric ionene, no cross-linking is to be expected either. Some ionic cross-links at fiber-fiber interface are possible in the dry state and probably help improve strength as shown in the ionic multilayer studies where dry tensile strength of the subsequent paper can be easily doubled.¹⁶ The ionic interactions compete with hydration in the wet state and usually do not give wet strength, as shown in Figures 3b and 5. However, when the structure is dried, the capillary forces pull the fibers into contact forming weak fiber-fiber bonds. If this fiber-fiber bond contains hydrophobic areas that the water cannot penetrate, the fiber-fiber bond can remain intact when the paper is immersed in water. Therefore, we suggest that the fiber-fiber bond is protected by the hydrophobic areas of the CMC + asymmetric ionene complex akin to the dense cellulose gel layer in vegetable parchment (Figure 8). The critical dependence of the wet strength effect on the molecular weight of the CMC (Figure 3) demonstrates that the hydrophobic contact between fibers is not easy to attain. The asymmetric ionenes are small in size, and therefore, a highly swollen gel (high M_w CMC) is needed to maximize the fiber-fiber contact.

It is not easy to explain with these results why only asymmetric ionenes seem to impart wet strength. In ionenes, the positive charges are part of the chain, and they are not free to rotate around the chain. The simplest explanation comes from the hypothetical difference of the conformation of the asymmetric and symmetric ionenes. Because an equally spaced charge in a polymer chain forces the conformation to take a stiff linear form, probably the alternating short and long distances between charges allow a spiral form for the asymmetric ionenes. This would allow the ionenes with different charge distributions to have fundamentally different conformations in the solution as well as on the surface of cellulosic fibers when adsorbed.

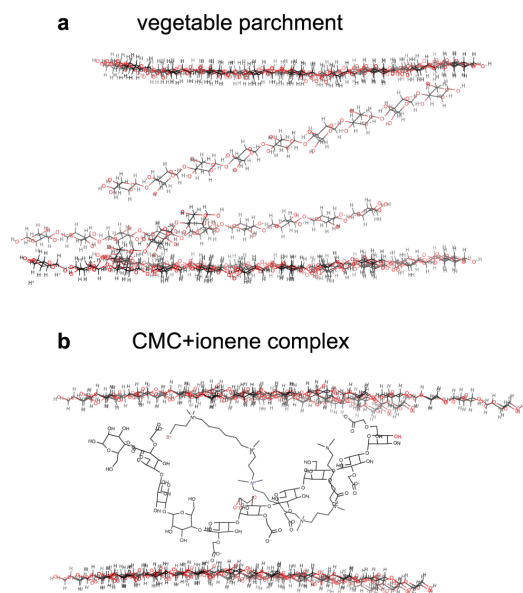


Figure 8. (a) Treatment with H_2SO_4 (vegetable parchenting) dissolves cellulose and forms a gel between adjacent fibers. Drying the dissolved cellulose gel between the fibers forms strong fiber–fiber bonds that resists water intrusion. (b) CMC+ionene complex adsorbed between two fibers. Anionic CMC acts like a cellulose gel while the asymmetric ionene hydrophobizes the CMC. The resulting hydrophobic CMC+ionene complex resists water intrusion, and wet strength is attained (after drying). The illustrations are schematic. In reality the structures are 3 orders of magnitude larger. (Supporting Information has .mol files of these structures.).

Finally, we would like to mention that the price of Polybrene is prohibitively high for actual papermaking applications (ca. 4000 USD/kg). However, this study demonstrates that a systematic synthetic approach to strength agents is likely to increase the level of understanding in strength enhancement of paper. Thereby, this approach may eventually lead to new and more cost efficient methods for developing paper strength agents.

CONCLUSIONS

The systematic study of various ionenes that induce wet strength on paper was demonstrated. The origin of the wet strength was attributed to the asymmetric charge distribution that enabled the hydrophobic domains to fuse together, thus forming van der Waals bonds between cellulosic fibers. The hydrophobic domains resisted water intrusion, and the papers exhibited wet strength. The ionenes also serve as a model system to separate the electrostatic effect of wet strength from the cross-linking effect. The asymmetric charge distribution is also an important design parameter that should be taken into account, e.g., when a cross-linking chemical such as PAE is synthesized and the stabilizing polymer in the commercial mixtures is chosen.

ASSOCIATED CONTENT

Supporting Information

Size exclusion chromatograms for ionenes and a table describing the commercial wet strength mechanisms for paper as well as downloadable files for the structures found in Figures 7 and 8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: eero.kontturi@aalto.fi. Phone: +358 503442978. Fax: +358 945124259.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the financers of ChAD project: Botnia, Kemira, UPM, Andritz, and Finnish Centre for Technology and Innovation (TEKES).

REFERENCES

- (1) Espy, H. H. The mechanism of wet-strength development in paper: A review. *Tappi J.* **1995**, 78, 90–99.
- (2) Lindström, T.; Wågberg, L.; Larsson, T. On the Nature of Joint Strength in Paper: A Review of Dry and Wet Strength Resins Used in Paper Manufacturing. In *13th Fundamental Research Symposium*; The Pulp and Paper Fundamental Research Society: Cambridge, U.K., 2005; pp 457–562.
- (3) Laine, J.; Lindström, T.; Nordmark, G. G.; Risinger, G. Studies on topochemical modification of cellulosic fibres Part 3. The effect of carboxymethyl cellulose attachment on wet-strength development by alkaline-curing polyamide-amine epichlorohydrin resin. *Nord. Pulp Pap. Res. J.* **2002**, 17, 57–60.
- (4) Stannett, V. T. The Mechanism of Wet-Strength Development. In *Wet Strength in Paper and Paperboard*; Weidner, J. P., Ed.; TAPPI Monograph Series No. 29; Technical Association of the Pulp and Paper Industry: New York, 1965; Vol. 43, pp 85–104.
- (5) Stannett, V. T. Mechanisms of Wet-Strength Development in Paper. In *Surfaces and Coatings Related to Paper and Wood: A Symposium [held At] State University College of Forestry at Syracuse University*; Syracuse University Press: Syracuse, NY, 1967; pp 269–300.
- (6) Sarkanen, K. V. Polyethyleneimine Resins. In *Wet Strength in Paper and Paperboard*; Weidner, J. P., Ed.; TAPPI Monograph Series No. 29; Technical Association of the Pulp and Paper Industry: New York, 1965; pp 38–49.
- (7) Laleg, M.; Pikulik, I. I. Wet-web strength increase by chitosan. *Nord. Pulp Pap. Res. J.* **1991**, 6, 99.
- (8) DiFlavio, J.-L.; Bertoia, R.; Pelton, R.; Leduc, M. The Mechanism of Polyvinylamine Wet-Strengthening. In *13th Fundamental Research Symposium*; The Pulp and Paper Fundamental Research Society: Cambridge, U.K., 2005; pp 1293–1316.
- (9) Trout, P. E. The mechanism of the improvement of the wet strength of paper by polyethylenimine. *Tappi* **1951**, 34, 539–544.
- (10) DiFlavio, J.-L.; Pelton, R.; Leduc, M.; Champ, S.; Essig, M.; Frechen, T. The role of mild TEMPO–NaBr–NaClO oxidation on the wet adhesion of regenerated cellulose membranes with polyvinylamine. *Cellulose* **2006**, 14, 257–268.
- (11) Wen, Q.; Pelton, R. Microgel adhesives for wet cellulose: Measurements and modeling. *Langmuir* **2012**, 28, 5450–7.

- (12) Feng, X.; Pelton, R.; Leduc, M.; Champ, S. Colloidal complexes from poly(vinyl amine) and carboxymethyl cellulose mixtures. *Langmuir* **2007**, *23*, 2970–6.
- (13) Feng, X.; Pouw, K.; Leung, V.; Pelton, R. Adhesion of colloidal polyelectrolyte complexes to wet cellulose. *Biomacromolecules* **2007**, *8*, 2161–6.
- (14) Saito, T.; Isogai, A. Wet strength improvement of TEMPO-oxidized cellulose sheets prepared with cationic polymers. *Ind. Eng. Chem. Res.* **2007**, *46*, 773–780.
- (15) Wågberg, L.; Ödberg, L.; Glad-Nordmark, G.; Odberg, L. Charge determination of porous substrates by polyelectrolyte adsorption Part 1. Carboxymethylated, bleached cellulosic fibers. *Nord. Pulp Pap. Res. J.* **1989**, *4*, 71.
- (16) Aarne, N.; Kontturi, E.; Laine, J. Carboxymethyl cellulose on a fiber substrate: The interactions with cationic polyelectrolytes. *Cellulose* **2012**, *19*, 2217–2231.
- (17) Rembaum, A.; Baumgartner, W.; Eisenberg, A. Aliphatic ionenes. *J. Polym. Sci. Part B: Polym. Lett.* **1968**, *6*, 159–171.
- (18) Rembaum, A.; Noguchi, H. Reactions of N,N,N',N'-Tetramethyl- α,ω -diaminoalkanes with α,ω -Dihaloalkanes. II. x-y Reactions. *Macromolecules* **1972**, *5*, 261–269.
- (19) Aarne, N.; Kontturi, E.; Laine, J. Influence of adsorbed polyelectrolytes on pore size distribution of a water-swollen biomaterial. *Soft Matter* **2012**, *8*, 4740.
- (20) Horvath, A. T.; Horvath, A. E.; Lindstrom, T.; Wågberg, L. Diffusion of cationic polyelectrolytes into cellulosic fibers. *Langmuir* **2008**, *24*, 10797–10806.
- (21) Horvath, A. T.; Horvath, A. E.; Lindström, T.; Wågberg, L. Adsorption of highly charged polyelectrolytes onto an oppositely charged porous substrate. *Langmuir* **2008**, *24*, 7857–7866.
- (22) van der Reyden, D.; Hofmann, C.; Baker, M. Effects of aging and solvent treatments on some properties of contemporary tracing papers. *J. Am. Inst. Conservation* **1993**, *32*, 177.
- (23) Cartier, N.; Escaffre, P.; Mathevet, F.; Chanzy, H.; Vuong, R. Structure and recycling of vegetable parchment. *Tappi J.* **1994**, *77*, 95–101.
- (24) Brent, E. A.; Drennen, T. J.; Shelley, J. P. Urea-Formaldehyde Resins. In *Wet Strength in Paper and Paperboard*; Weidner, J. P., Ed.; Tappi Monograph Series No. 29; Technical Association of the Pulp and Paper Industry: New York, 1965; pp 9–19.
- (25) Myllytie, P.; Yin, J.; Holappa, S.; Laine, J. The effect of different polysaccharides on the development of paper strength during drying. *Nord. Pulp Pap. Res. J.* **2009**, *24*, 469–477.
- (26) Pelton, R. On the design of polymers for increased paper dry strength: A review. *Appita* **2004**, *57*, 181–190.
- (27) Feng, X.; Zhang, D.; Pelton, R. Adhesion to wet cellulose – Comparing adhesive layer-by-layer assembly to coating polyelectrolyte complex suspensions 2nd ICC 2007, Tokyo, Japan, October 25–29, 2007. *Holzforschung* **2009**, *63*, 28–32.
- (28) Wen, Q.; Pelton, R. Design rules for microgel-supported adhesives. *Ind. Eng. Chem. Res.* **2012**, *51*, 9564–9570.
- (29) Wen, Q.; Vincelli, A. M.; Pelton, R. Cationic polyvinylamine binding to anionic microgels yields kinetically controlled structures. *J. Colloid Interface Sci.* **2012**, *369*, 223–30.
- (30) Pelton, R. Some properties of newsprint impregnated with polyvinylamine. *Tappi J.* **2002**, *1*, 21–26.
- (31) Chen, W.; Leung, V.; Kroener, H.; Pelton, R. Polyvinylamine-phenylboronic acid adhesion to cellulose hydrogel. *Langmuir* **2009**, *25*, 6863–8.
- (32) Tejado, A.; Antal, M.; Liu, X.; van de Ven, T. G. M. Wet cross-linking of cellulose fibers via a bioconjugation reaction. *Ind. Eng. Chem. Res.* **2011**, *50*, 5907–5913.

Supporting Information for

A Systematic Study of Non-crosslinking Wet Strength Agents

This Supporting Information consists of the experimental details of the ionene synthesis and their size exclusion chromatographs as well as a large table that describes various commercial wet strength methods and their mechanisms and primary reactions. (Table S1)

S1 Ionene synthesis

3,3-ionene was synthesized using N,N,N',N'-tetramethyl-1,3-propanediamine and 1,3-dibromopropane. After polymerization the precipitate was washed with ethanol. 6,6-ionene was synthesized using N,N,N',N'-tetramethyl-1,6-hexanediamine and 1,6-dibromohexane. After polymerization the precipitate was washed with pentane. 6,12-ionene was synthesized using N,N,N',N'-tetramethyl-1,6-hexanediamine and 1,12-dibromododecane. After polymerization acetone was added to the reaction mixture to induce further precipitation. The precipitate was washed with pentane.

S2 Size Exclusion Chromatography

Polymer molecular weight was analyzed with size exclusion chromatography (SEC) using following elution solvent: 1 M acetate buffer pH 4.62 (136g sodium acetate·3 H₂O + 60g acetic acid / 1 L; FF-Chemicals FF992) was mixed with distilled water 1:1 ratio. Subsequently 10 vol-% methanol was added. Elution speed was 0.8 ml/min (Waters 510 HPLC Pump and Waters 717plus Autosampler) through the

following column system: Ultrahydrogel 6*40mm Guard Column and Ultrahydrogel Linear Column 7.8*300mm (Waters). Detection was done by combining signals from a refractive index (RI) detector (Waters 2414) and a light-scattering (LS) detector (Wyatt Dawn 8+). Both molecular weight and size of the polymer were analysed. The difference in refractive index between eluent and polymer (dn/dc) used for molecular weight determination was $0.152 \text{ cm}^3/\text{g}$.

S3 Size exclusion chromatographs

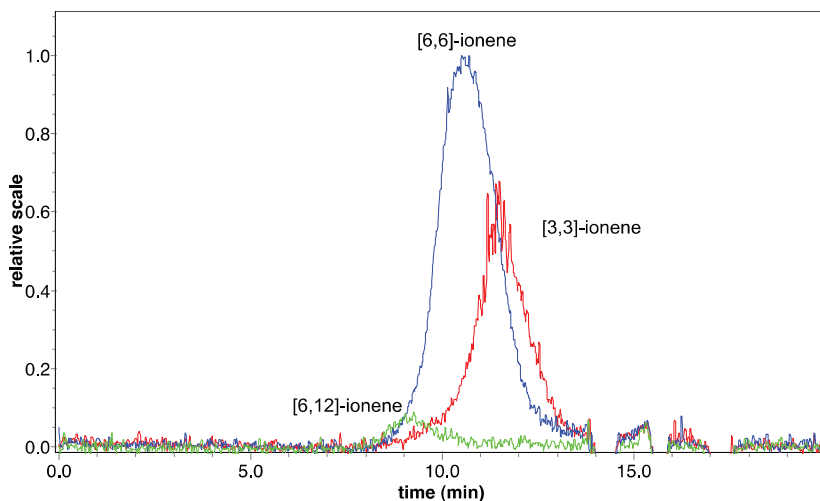


Figure S1. Size exclusion chromatographs for the synthesized ionenes.

Table S1. Commercial wet strength methods and their mechanisms and primary reactions.

Method	Mechanism	Reactions	Chemical
Vegetable parchmenting ^{S1,S2}	<i>Protection mechanism</i> Wet paper is welded together with acid and subsequent drying.	Gelatinization of the surface cellulose by conc. acid. The <i>dissolved and gelatinous</i> cellulose polymers dry on the surface and form a dense film that is impenetrable to both water and even oil.	Conc. H ₂ SO ₄
Acidic wet strengthening ^{S3,S4}	<i>Protection mechanism</i> Polymer impregnated fiber webs are cured at high temperature.	Urea-methylol polymerizes to form low M _w linear polymers that crosslink at high temperature. Cross-linking continues days, even weeks in the dry state.	Urea-formaldehyde or melamine-formaldehyde
Basic or neutral wet strengthening ^{S4}	<i>Reinforcement mechanism</i> Surface adsorbed fibers react with the wet strength agent.	The polymer adsorbs on fibers and mainly reacts with itself. The few carboxyl groups found in the fibers participate in the reactions.	PAE and other epichlorohydrin polymers
Temporary wet strengthening ^{S4}	<i>Reinforcement mechanism</i> Surface adsorbed fibers react with the fiber.	The glyoxalated polymer reacts with the hydroxyl groups of cellulose to form hemiacetals or acetals (pH <4.5) or reacts with the amide groups of the wet strength agent to form amides (pH ~5-6).	Glyoxal reacted PAM (G-PAM)
Cationic polyamine wet strengthening ^{S5-S7}	<i>Mechanism type unknown</i> Surface adsorbed fibers react with each other at room temperature and form imine and aminal bonds.	To large extent the primary and secondary amines probably react to form imine and aminal bonds with the aldehyde groups found in the fibers to form fiber-fiber crosslinks. In addition, electrostatic interaction between the polymer and fibers forms bonds that do not wet, because of an unknown mechanism.	PEI, chitosan and PVAm
Ionene wet strengthening	<i>Mechanism type unknown</i> CMC pre-treated and surface adsorbed fibers form electrostatic bonds that are not rewetted after drying.	The structures of the polyelectrolytes allow only electrostatic interaction. The high M _w CMC allows fiber-fiber interaction and cationic polymer with asymmetric charge distribution probably provides necessary hydrophobicity to resist wetting of the fiber-fiber bonds. Structure of the layer is probably comparable to vegetable parchment.	Ionenes with asymmetric charge distribution (e.g. polybrene or [6,12]-ionene)

References

- (S1) van der Reyden, D.; Hofmann, C.; Baker, M. Effects of Aging and Solvent Treatments on Some Properties of Contemporary Tracing Papers. *Journal of the American Institute for Conservation* **1993**, 32, 177.
- (S2) Cartier, N.; Escaffre, P.; Mathevet, F.; Chanzy, H.; Vuong, R. Structure and recycling of vegetable parchment. *Tappi J.* **1994**, 77, 95–101.
- (S3) Brent, E. A.; Drennen, T. J.; Shelley, J. P. Urea-Formaldehyde Resins. In *Wet Strength in Paper and Paperboard Tappi Monograph Series No. 29*; Weidner, J. P., Ed.; Technical Association of the Pulp and Paper Industry: New York, 1965; pp. 9–19.
- (S4) Lindström, T.; Wågberg, L.; Larsson, T. On the Nature of Joint Strength in Paper - A review of Dry and Wet Strength Resins used in Paper Manufacturing. In *13th Fundamental Research Symposium*; The Pulp and Paper Fundamental Research Society: Cambridge, UK, 2005; pp. 457–562.
- (S5) Laleg, M.; Pikulik, I. I. Wet-web strength increase by chitosan. *Nord. Pulp Pap. Res. J.* **1991**, 6, 99.
- (S6) Myllytie, P.; Yin, J.; Holappa, S.; Laine, J. The effect of different polysaccharides on the development of paper strength during drying. *Nord. Pulp Pap. Res. J.* **2009**, 24, 469–477.
- (S7) DiFlavio, J.-L.; Bertoia, R.; Pelton, R.; Leduc, M. The Mechanism of Polyvinylamine Wet-Strengthening. In *13th Fundamental Research Symposium*; The Pulp and Paper Fundamental Research Society: Cambridge, UK, 2005; pp. 1293–1316.