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Switching off PAE wet strength

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Abstract: The wet strength of cellulose-cellulose joints, reinforced with PAE-loaded microgels, was decreased by nearly a factor of two when the labile disulfide crosslinks on the supporting microgels were exposed to a reducing agent. The supporting microgels were temperature and pH sensitive poly(*N*-isopropylmethacrylamide-co-acrylic acid) microgels, prepared with a disulfide crosslinker. The level of PAE loading increased with the microgel carboxyl content. This work illustrates a new approach to increasing the recyclability and compostability of wet-strength papers made with PAE wet-strength resin.

Keywords: disulfide; microgel; PAE; repulping; wet strength.

Introduction

Many paper products requiring longer term exposure to water are made with PAE wet-strength resin. The backbone of PAE is the polyamide derived from the condensation of adipic acid with diethylenetriamine (Crisp and Riehle 2018). Some of the secondary amines are subsequently converted to azetidinium groups by reaction with epichlorohydrin. A simplified structure of PAE is shown in Figure 1. The cationic azetidinium groups and protonated secondary amine groups promote PAE adsorption onto pulp fiber surfaces; a study of PAE adsorption on regenerated cellulose reported a coverage of $\sim 3 \text{ mg/m}^2$ (Ahola et al. 2008). During heating and drying the reactive azetidinium forms covalent grafts with carboxyl groups on fibers, and crosslinks within and between PAE chains (Espy 1995) (Wagberg and Bjorklund 1993) (Lindström et al. 2005). The result is a crosslinked polymer networks

between contacting fiber surfaces. Cured PAE network are somewhat hydrophobic showing little tendency to swell or hydrolyze in water (Sharma and Deng 2016). This insensitivity to water maintains fiber-fiber joint strength when paper is exposed to water.

Figure 1: PAE crosslinking with itself and grafting to cellulosic carboxyl groups.

An undesirable consequence of high wet strength is the difficulty in repulping broke, recycling, and composting wet-strength paper grades (Su et al. 2012) (Siqueira et al. 2013). Herein we show that PAE wet strength can be reduced significantly by exposure to a reducing agent if the PAE is supported on reductant-responsive microgels.

Repulping wet-strength papers is an old problem that has been addressed in both the scientific and the patent literature. The challenge is to sever enough bonds in the crosslinked PAE network to weaken fiber-fiber joints. Some of the proposed approaches are an oxidation step at low pH, followed by a hydrolysis step at high pH (Fischer 1997); mixtures of peroxide and persulfate at elevated temperatures and high pH (Siqueira et al. 2013); building weak links into the PAE main chain (Dulany et al. 1996); PAE modification with succinic acid; and mixing PAE with temporary (aldehyde-based) wet-strength resins (Staib 2002). This list is representative but by no means complete. Furthermore, we do not know the extent to which any of these technologies has been implemented.

We have been evaluating the potential of microgels as a platform for new dry and wet strength resins. Microgels are crosslinked water-soluble polymer that swell in water

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to give spheres that are typically 100 to 1000 in nm diameter (Pelton 2000). The water content of our microgels is in the range 60–90 wt%, a value that depends upon the temperature, the hydrophobicity of the polymer, the presence of charge groups and the crosslink density.

Our wet strength results with polyvinylamine microgels (Miao et al. 2007b) and with PVAm coated poly(*N*-isopropylacrylamide) microgels (Wen and Pelton 2012) gave intermediate (i. e. about $\frac{1}{2}$ that of PAE) wet strength with TEMPO oxidized cellulose. When comparing linear with microgel forms of PVAm, wet adhesion was the same if the amine contents in cellulose-cellulose joints were the same. However, because the microgels are much larger than linear chains, an adsorbed monolayer of microgels puts much more adhesive into the joints compared to linear PVAm (Miao et al. 2007a).

More recently we have explored the use of microgels as a route to wet-strength resins whose adhesive character can be switched off by a chemical trigger (Yang and Pelton 2017). We prepared microgels with disulfide degradable linkages that are severed in the presence of reducing agents. The microgels also had surface hydrazide groups, capable of forming covalent bonds with aldehyde groups, present on TEMPO oxidized cellulose. The microgels gave significant adhesion and, upon exposure to a reducing agent, the wet strength was greatly reduced because the supporting microgels decomposed. Although this work gave valuable mechanistic information, the exotic home-made microgels coupled with the requirement of having TEMPO oxidized fibers, made commercial adaptation unlikely.

Herein we describe a more feasible approach where conventional cationic PAE resins are adsorbed onto reductant sensitive anionic microgels, turning PAE into a switchable wet-strength resin. The concept is illustrated in Figure 2.

Finally, the following wet strength results are not based upon paper testing. Instead, we employ a method we call wet-peeling which is a variation of an approach first described 70 years ago (McLaren 1948). In a wet-peel experiment, two wet, regenerated cellulose membranes are stacked with a thin layer of wet-strength resin between them. The stack is pressed (laminated), dried, and then rewetted. The resulting laminate is a physical model for wet fiber-fiber joints in paper. Wet laminate strength is measured as the 90-degree peel delamination force required to separate the two membranes. We recently described this method in greater detail, including comparing results with conventional paper testing (Yang et al. 2018).

Figure 2: Schematic illustration of PAE-loaded microgel with disulfide linkages that can be severed by the reducing agent DTT.

Materials and methods

Materials

Regenerated cellulose membranes (Spectra/Por2, MWCO 12–14 kDa, product number 132684) were purchased from Spectrum Laboratories, US. TAPPI standard blotter papers were purchased from Labtech Instruments Inc., Canada. PAE was FENNOSTRENGTH 4063 provided by Kemira, US. All other chemicals were purchased from Sigma-Aldrich, Canada. Water type 1 (as per ASTM D1193-6, resistivity 18 MΩ/cm) was used in all experiments.

N-isopropylmethacrylamide (NIPMAm) was recrystallized with toluene/hexane (6/4, v/v) mixture solution and dried under nitrogen gas purge. The inhibitor (monomethyl ether hydroquinone) in acrylic acid (AA) was removed by passing the AA through an inhibitor remover column (Sigma-Aldrich, US). PAE was dialyzed against water for eight hours using Spectra/Por3 dialysis tubes with MWCO 3.5 kDa (Spectrum Laboratories, US) and stored in aqueous solution at 4 °C. PVAm was dialyzed against water for one week and freeze-dried. Other chemicals were used as received.

Supporting microgel preparation

A series of poly(NIPMAm-co-AA) microgels was synthesized by redox-initiated precipitation polymerization. (Gaulding et al. 2012). The recipes are summarized in Table S1. In a typical polymerization, 11.2 mmol NIPMAm, 0.15 mmol sodium dodecyl sulphate (SDS) and 0.56 mmol AA were dissolved in 80 mL water in a 250 mL round bottom flask. The reaction mixture was adjusted to pH 3 with 0.1 M HCl and heated to 50 °C and was agitated with a magnetic stirrer bar for one hour with nitrogen gas purging. Added next was 0.16 mmol *N,N,N',N'*-tetramethylethylenediamine (TEMED) in 10 % aqueous solution. After 10 minutes of agitation, 0.4 mmol ammonium persulfate (APS) in 2 mL water and 0.59 mmol *N,N'*-bis(acryloyl)cystamine (BAC) in 3 mL methanol were added into the mixture. The polymerization proceeded for six hours at 50 °C with nitrogen gas purging. The microgels were purified by dialysis against water for one week and stored in aqueous solution at 4 °C.

PAE loading into supporting microgels

PAE loading recipes are shown in Table S2. In a typical process, 80 mg purified PAE was added in 60 mL 1 mM NaCl solution at pH 7 in a 200 mL beaker. The solution was agitated vigorously with a magnetic stirrer bar for one hour. 50 mg supporting microgels were dispersed in 10 mL 1 mM NaCl solutions at pH 7 in a 20 mL glass vial. Microgel dispersions were slowly added into PAE solutions at a rate of 1 mL/min with strong agitation to minimize aggregation. After the mixing, the mixture solution was agitated mildly overnight. Unbound PAE in the supernatant was removed by decantation after ultracentrifugation at 45,000 rpm for 30 minutes. The microgels were re-dispersed in 1 mM NaCl solution at pH 7. The centrifugation and re-dispersion were repeated three times. PAE-loaded microgel solutions (Py-Ax) with a concentration of ~5 g/L were stored in aqueous solution at 4 °C. The PAE contents of PAE-loaded microgels were calculated from the quantities of unretained PAE.

The amount of unretained PAE collected from the washing the microgels was determined by polyelectrolyte titration performed with a Mutek PCD T3 titrator fitted with a Mutek PCD 03 streaming current detector (SCD). In a typical experiment, a 10 mL sample of PAE in 1 mM NaCl was adjusted to neutral pH and was placed in the Mutek cell. After 5 min equilibration, the mixture was titrated with 1 meq/L polyvinyl sulfate potassium salt (PVSK) standard solution (BTG, US). The apparatus automatically added 0.02–0.10 mL of PVSK per injection, and the SCD signal

was recorded when the drift rate was below 8 mV in 10 seconds. The titration ended once the SCD signal was lower than zero. The PVSK consumption at end point was recorded. Reported values are averages of three repeated experiments and the standard deviation is reported. PAE content was determined based on a calibration curve. The calibration curve and calculation details are shown in Figure S1 in the supporting information.

Microgel characterization

The electrophoretic mobilities of microgels were measured with a ZetaPlus analyzer (Brookhaven Instruments, US) using the phase analysis light scattering mode. Microgels were dispersed in 1 mM NaCl solution at neutral pH 7 at 23 °C. Reported values were averaged over 10 cycles with 10 scans for each cycle. The standard error is reported for each result.

Hydrodynamic diameters of microgels were measured by dynamic light scattering (Model BI-APD, Brookhaven Instruments, US) at 23 °C with software version 1.0.0.1. The detection angle was 90°, and we used a 633 nm wavelength laser. At least three runs were recorded for each sample, and the standard deviation is reported. The polydispersity index was provided by the software. Microgels were measured in 1 mM NaCl solution at pH 7, unless specified.

Microgel carboxyl contents were determined by conductometric titrations, carried out with a Burivar-I2 automatic burette (ManTech Associates, Canada). 50 ± 2 mg of microgels was dispersed in 50 mL 1 mM NaCl with initial pH 2.7 ± 0.1. All samples were titrated by 0.1 M NaOH with an increment of 0.05 pH units/injection. The corresponding injection volumes were in the range of 5–100 µL. The interval between injections was 90 seconds. An example conductometric titration curve is shown in Figure S2.

The degree of swelling of the supporting microgels is pH and temperature dependent. Figure S3 in the appended supporting information show example microgel diameters as functions of pH and temperature. The mass of polymer in a shrunken supporting microgel was calculated from the diameters at pH 3, 55 °C (Table S3), assuming the water mass fraction of 29 % (Lele et al. 1997). The water contents under other conditions were calculated from the swelling ratios and polymer mass per particle.

Wet adhesion measurements

Wet, oxidized, regenerated cellulose membranes were treated with PAE or PAE-loaded microgels. Stacked pairs

of membranes were pressed (laminated), with or without heating and the laminates were conditioned for 24 h in at 23 °C and 50 % relative humidity. The laminates were rewetted in aqueous solution for thirty minutes and gently blotted giving a laminate water content of around 50 %. Adhesion was measured as the 90° wet-peel force required to separate the wet membranes. A detailed review of this method was recently published (Yang et al. 2018) and many of the experimental details are given in the supporting information.

Results

Supporting microgels

Our supporting microgels were based on Lyon's research, which showed that disulfide crosslinked *N*-isopropyl-methacrylamide microgels were completely degraded to water-soluble polymers in the presence of a reductant (Gaulding et al. 2012). We prepared a series of four microgels, A1, A3, A8, and A12 each with disulfide crosslinks and some acrylic acid monomer to introduce carboxyl groups. Some properties of the A series of supporting microgels are summarized in Table 1.

All the supporting microgels were prepared with 5 mol% of crosslinker. Microgel water content depends upon the temperature, the crosslinker density, the carboxyl contents and the pH (Pelton 2000). Figure S3 (in the supporting information) shows an example of the influence of temperature and pH on microgel swelling.

The major difference among the supporting microgels was the carboxyl content, which varied over an order of magnitude. The carboxyls promoted PAE sorption (see below) and were available to condense with PAE groups upon drying and heating.

Figure 3: Supporting microgel dispersions (2 g/L in 1 mM NaCl) before and after 30 min reduction in 10 mM DTT at pH 9.

Figure 3 illustrates that the turbid microgels dispersions were converted to polymer solutions by 30 min exposure to the reducing agent dithiothreitol (DTT) at pH 9.

PAE properties

Although very effective as a wet-strength resin, PAE is a difficult polymer for mechanistic studies because: it has a broad molecular weight distribution (Obokata et al. 2005); it is partially branched/crosslinked; the extent of secondary amine conversion to azetidinium groups is a variable; and PAE properties change with storage time – the

Table 1: Summary of microgel properties.

Microgel	PAE content		Diameter (nm)	PDI	E.M ($10^{-8} \text{ m}^2/\text{Vs}$)	Total COOH (meq/g)	Water content (%)
	Mass (%)	Excess charge (meq/g)					
A1	0	–	292 ± 2	0.20	−0.84 ± 0.07	0.11 ± 0.00	80
A3	0	–	446 ± 8	0.06	−1.57 ± 0.05	0.33 ± 0.01	84
A8	0	–	407 ± 8	0.03	−1.83 ± 0.07	0.81 ± 0.05	88
A12	0	–	293 ± 2	0.04	−2.27 ± 0.09	1.15 ± 0.01	88
P9-A1	8.7 ± 2.9	+0.19	249 ± 3	0.24	+1.69 ± 0.11	–	67
P25-A3	25.4 ± 1.7	+0.54	415 ± 14	0.12	+2.42 ± 0.17	–	75
P35-A8	34.6 ± 2.6	+0.74	461 ± 8	0.14	+2.52 ± 0.13	–	–
P41-A12	40.9 ± 3.5	+0.88	395 ± 10	0.18	+2.70 ± 0.09	–	–

All measurements were conducted in 1 mM NaCl at neutral pH and at room temperature. PDI is the polydispersity index and E.M. is the electrophoretic mobility. The microgel nomenclature, Ax, reflects the carboxyl content of the dry microgels where x is meq/10 g. For the PAE-loaded microgels, Py-Ax, y is mass fraction of PAE in the dried microgels.

half-life of azetidinium groups with respect to ring opening is about 10 years (Obokata and Isogai 2005). Of these characteristics we were most concerned with the low molecular weight fractions for the following reasons.

Our goal was to prepare microgel-PAE complexes where most of the PAE was located on the exterior surface. The penetration of low molecular weight PAE chains into the microgel interior could further crosslink the microgels via the interior carboxyl groups. Unlike disulfide crosslinks, the PAE crosslinks would not degrade in the presence of a reducing agent. We dialyzed the commercial PAE solution against water for 8 h using a 3.5 kDa membrane to remove any very low molecular weight components. The dialyzed PAE was used for all experiments and we did not evaluate the impact of the dialysis.

PAE-loaded microgels

PAE-loaded microgels were prepared by exposing the supporting microgels to a solution containing excess PAE – details of the loading experiments are summarized in Table S2. The properties of the cleaned PAE-loaded microgels are summarized in Table 1. Except for the low carboxyl content A1 microgel, the polydispersity indices, measured by dynamic light scattering, increased with PAE treatment. This suggests there was some aggregation which is inevitable when a dispersion is taken through the isoelectric point. The particle size distributions for A12 and P68-A12, in Figure S4, show the broadening of the particle size distribution, typical of aggregation.

In all cases the cationic charge content from adsorbed PAE was greater than the content of anionic carboxyl groups in the supporting microgel. The excess cationic charge was estimated as shown in Table 1. Therefore the resulting cationic PAE-loaded microgels spontaneously adsorb on the anionic cellulose surfaces.

Finally, the PAE treated microgel dispersions were treated with DTT, however we did not observe the complete loss of turbidity seen with the supporting microgels alone in Figure 3. Polyelectrolyte complexation between PAE and the anionic microgel chains was sufficient to prevent complete microgel dissolution.

PAE adhesion

As a benchmark, we measured the adhesion between wet TEMPO oxidized, regenerated cellulose membranes, laminated with adsorbed layers of PAE. Unlike wood pulp fibers, untreated regenerated cellulose has essentially no

carboxyl groups to promote PAE adsorption, or to act as PAE grafting sites with drying. Therefore our standard procedure was to introduce surface carboxyl groups ($\sim 1.3 \times 10^{-4}$ meq/m²) by TEMPO oxidation (Saito and Isogai 2006, Yang et al. 2018). Figure 4 shows the wet-peel delamination forces for two curing temperatures. Before wet-peeling, the laminates must be rewetted. Figure 4 compares results for two rewetting solutions, dilute salt and the reducing agent DTT. Within experimental uncertainty the two rewetting solutions gave the same adhesion, confirming PAE reinforced cellulose-cellulose joints are insensitive to the presence of a reducing agent. Furthermore, we see as a benchmark that PAE gives a wet-peel force on 40 N/m when cured at 70 °C.

Figure 4: The wet-peel force for rewetted laminates made with TEMPO oxidized regenerated cellulose membranes, with an adsorbed layer of PAE. The laminates were press-dried between blotters either at 23 or 70 °C. Before peel testing the laminates were soaked either in 1 mM NaCl or in the reducing agent 10 mM DTT, 1 mM NaCl at pH 9.

Adhesion with PAE-loaded microgels

Figure 5 summarizes our wet-peel adhesion results obtained with PAE-loaded microgels. In all cases, the higher lamination temperature 85 °C gave the highest wet-peel adhesion, which is consistent with the literature (Devore and Fischer 1993).

The extent to which PAE adhesion was “switched off” is illustrated by comparing the adhesion of samples rewetted with DTT reductant, to those rewetted with 1 mM NaCl. The red numbers give the percentage decrease in wet-peel adhesion with DTT exposure. The most dramatic decrease was 46 % corresponding to the microgel with the highest PAE loading.

How weak do joints have to be for easy repulping? Recent results from Monash University show that sheets with

Figure 5: Wet adhesion of laminates rewetted with or without reductants. The control group (black) was rewetted in 1 mM NaCl at pH 9, while the DTT group (white) was rewetted in 10 mM DTT, 1 mM NaCl at pH 9. Red numbers represent the percentage decrease in wet adhesion of the DTT group compared to the control group.

a tensile index of 2 Nm/g were low enough to give good repulpability. {Su et al. 2012} Our own work showed that a tensile index of 2 Nm/g, very roughly corresponds to a wet-peel of 10 N/m. {Yang et al. 2018} Therefore the extent of joint weakening with disulfide cleavage, shown in Figure 5, is not enough to promote easy repulping.

Discussion

This work describes a proof of concept and is not a description of a new product. Specifically, we have shown that the strength of PAE reinforced wet cellulose joints can be decreased by nearly a factor of two when the PAE is supported on a reductant-degradable microgel. The scientific aspects are now discussed, followed by the technological implications.

Figure 2, illustrating the PAE-loaded microgel structure, is aspirational in that we show the PAE to be located on the microgel exterior. We do not know how much PAE is present in the microgel core. PAE present in the microgel interior will introduce PAE crosslinks that are not degradable, negating the function of the disulfide links. Based on the literature, (Bradley and Vincent 2005) (Eichenbaum

Figure 6: The evolution of laminate joint structure with drying and rewetting.

et al. 1999) (Sierra-Martin et al. 2014) we estimate the mesh sizing within the microgel to be of the order 10 nm. Only the lowest molecular PAE fractions, not removed by dialysis, could enter the microgels. Therefore we believe that most of the PAE is present as a shell on the exterior surface of the microgels. The adhesion results support this conclusion because we would not achieve 46 % reduction in strength with DTT rewetting if there were many new, non-degradable crosslinks.

Figure 6 summarizes our vision of the formation of a wet cellulose-cellulose joint, reinforced with PAE-loaded microgels. The positively charged PAE microgels spontaneously adsorb, giving a randomly packed monolayer. Therefore when two wet membranes are pushed together, the initial joint structure includes two layers of roughly spherical microgels (Figure 6). With drying and heating, the microgels, that are mainly water, collapse to become disks. PAE on the exterior of disk surfaces will graft to microgel carboxyls and the cellulose carboxyls (see Figure 1). PAE in the interior of the microgels will form new, non-degradable crosslinks. With rewetting, Figure 6 some PAE induced interior crosslinking will prevent complete reswelling of the microgels.

In addition to providing degradable disulfide linkages, the microgels carry more PAE to the adhesive joint. For example, when PAE adsorbs from solution onto a cellulose surface, the literature suggests that the coverage of adsorbed PAE is about 3 mg/m² (Ahola et al. 2008). A joint formed from laminating two PAE treated surfaces would have 6 mg/m² PAE. By contrast a randomly deposited monolayer of P41-A12 on each surface puts 37 mg/m² of PAE-loaded microgel in the joint, which corresponds to a PAE coverage of 15 mg/m². In other words, the PAE-loaded microgels put three times more PAE in the joints. However, comparing Figure 4 with the P41-A12 results in Figure 5, shows the PAE-loaded microgels were not much stronger than PAE alone. In other words, the supporting microgels do not contribute to wet-peel delamination; the PAE does the “heavy lifting”. Our PVAm coated microgels, dis-

cussed in the introduction, showed the same behaviors in both wet-peel and handsheet studies. There was no extra benefit to having microgels compared to the same coverage of linear polymers. We believe that microgels are too crosslinked and thus too elastic and not sufficiently viscous to contribute to adhesion (i. e. too much stiff spring, too little dashpot).

From a technology development perspective what are the ideal properties of a degradable PAE supporting particle? The good features of microgels include: they are soft and deformable; microgel structures can be controlled with great precision; and, without modification, microgels are not adhesive. On the negative side, microgels are not commercial, they are not green and they are unlikely to ever be economically viable for commodity paper products. When considering potential microgel replacements, the positive microgels features provide some guidance. The main requirements are the presence of surface groups that graft to PAE and cleavable interior bonds. For example, starch, protein or other biopolymer particles could be degradable with appropriate enzymes.

Conclusions

This report describes a proof of concept, demonstrating what we believe to be a new approach to improving the recycling and composting potential of PAE strengthened paper products. By first loading the PAE onto supporting microgels that have reductant responsive, disulfide crosslinks, the wet strength of cellulose-cellulose joints can be reduced by nearly a factor of two by exposing the joint to a solution of reducing agent. Furthermore, the PAE content of the PAE-loaded microgels can be controlled by the changing the carboxyl content of the supporting microgels.

The supporting microgels degrade in the presence of reducing agent and also carry more PAE into joints compared to treatment with PAE alone. However, the microgels do not directly contribute adhesion because we believe that they are too elastic. Synthetic, degradable microgels are unlikely to appear in commercial applications. However, the microgels do give hints about design criteria for degradable PAE supporting particles.

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References

- Ahola, S., Osterberg, M., Laine, L. (2008) Cellulose nanofibrils – adsorption with poly(amideamine) epichlorohydrin studied by Qcm-D and application as a paper strength additive. *Cellulose* 15(2):303–314.
- Bradley, M., Vincent, B. (2005) Interaction of nonionic surfactants with copolymer microgel particles of nipam and acrylic acid. *Langmuir* 21(19):8630–8634.
- Crisp, M.T., Riehle, R.J. (2018) Regulatory and sustainability initiatives lead to improved polyaminopolyamideepichlorohydrin (PAE) wet-strength resins and paper products. *Tappi J.* 17(9):520–531.
- Devore, D.I., Fischer, S.A. (1993) Wet-strength mechanism of polyaminoamide-epichlorohydrin resins. *Tappi J.* 76(8):121–128.
- Dulany, M.A., Garvey, C.E., Ringold, C.E., Srinivasan, R. (1996) Repulpable wet strength resins for paper and paperboard. Georgia-Pacific Resins, Inc., US 5,567,798.
- Eichenbaum, G.M., Kiser, P.F., Dobrynin, A.V., Simon, S.A., Needham, D. (1999) Investigation of the swelling response and loading of ionic microgels with drugs and proteins: the dependence on cross-link density. *Macromolecules* 32(15):4867–4878.
- Espy, H.H. (1995) The mechanism of wet-strength development in paper: a review. *Tappi J.* 78(4):90–99.
- Fischer, S.A. (1997) Repulping wet-strength paper. *Tappi J.* 80(11):141–147.
- Gaulding, J.C., Smith, M.H., Hyatt, J.S., Fernandez-Nieves, A., Lyon, L.A. (2012) Reversible inter- and intra-microgel cross-linking using disulfides. *Macromolecules* 45(1):39–45.
- Lele, A.K., Hirve, M.M., Badiger, M.V., Mashelkar, R.A. (1997) Predictions of bound water content in poly(N-Isopropylacrylamide) gel. *Macromolecules* 30(1):157–159.
- Lindström, T., Wågberg, L., Larsson, T. (2005) On the nature of joint strength in paper – a review of dry and wet strength of paper during paper manufacturing. In: Symposium on “Advances in Paper Science and Technology”. Transactions of the 13th Fundamental Research Symposium. The Pulp & Paper Fundamental Research Society, Cambridge, UK. pp. 457–462.
- Mclaren, A. D. (1948) Adhesion of High Polymers to Cellulose. Influence of Structure, Polarity, and Tack Temperature. *J. Polym. Sci.* 3(5):652–663.
- Miao, C., Chen, X., Pelton, R. (2007a) Adhesion of poly(vinylamine) microgels to wet cellulose. *Ind. Eng. Chem. Res.* 46(20):6486–6493.
- Miao, C.W., Pelton, R., Chen, X.N., Leduc, M. (2007b) Microgels versus linear polymers for paper wet strength – size does matter. *Appita J.* 60(6):465–468.

- Obokata, T., Isogai, A. (2005) Deterioration of polyamideamine-epichlorohydrin (PAE) in aqueous solutions during storage: structural changes of PAE. *J. Polym. Environ.* 13(1):1–6.
- Obokata, T., Yanagisawa, M., Isogai, A. (2005) Characterization of polyamideamine-epichlorohydrin (PAE) resin: roles of azetidinium groups and molecular mass of PAE in wet strength development of paper prepared with PAE. *J. Appl. Polym. Sci.* 97(6):2249–2255.
- Pelton, R. (2000) Temperature-sensitive aqueous microgels. *Adv. Colloid Interface Sci.* 85(1):1–33.
- Saito, T., Isogai, A. (2006) Introduction of aldehyde groups on surfaces of native cellulose fibers by TEMPO-mediated oxidation. *Colloids Surf. A* 289(1–3):219–225.
- Sharma, S., Deng, Y. (2016) Dual mechanism of dry strength improvement of cellulose nanofibril films by polyamide-epichlorohydrin resin cross-linking. *Ind. Eng. Chem. Res.* 55(44):11467–11474.
- Sierra-Martin, B., Retama, J.R., Laurenti, M., Fernández Barbero, A., López Cabarcos, E. (2014) Structure and polymer dynamics within pnipam-based microgel particles. *Adv. Colloid Interface Sci.* 205:113–123.
- Siqueira, E., Naoui, W., Marlin, N., Schott, S., Mauret, E. (2013) Effect of chemical additives on the degradation of polyamideamine-epichlorohydrin (PAE) films and paebased papers made from bleached kraft pulps. *Nord. Pulp Pap. Res. J.* 28:529–540.
- Staib, R.R. (2002) Repulpable wet strength paper. Hercules Incorporated, US 6,355,137 B1.
- Su, J., Mosse, W.K., Sharman, S., Batchelor, W., Garnier, G. (2012) Paper strength development and recyclability with polyamideamine-epichlorohydrin (PAE). *BioResources* 7(1):0913–0924.
- Wagberg, L., Bjorklund, M. (1993) On the mechanism behind wet strength development in papers containing wet strength resins. *Nord. Pulp Pap. Res. J.* 8:53–58.
- Wen, Q., Pelton, R. (2012) Microgel adhesives for wet cellulose – measurements and modeling. *Langmuir* 28(12):5450–5457.
- Yang, D., Diflavio, J.-L., Gustafsson, E., Pelton, R. (2018) Wet-peel: a tool for comparing wet-strength resins. *Nord. Pulp Pap. Res. J.* 33(4):632–646.
- Yang, D., Pelton, R.H. (2017) Degradable microgel wet-strength adhesives – a route to enhanced paper recycling. *ACS Sustain. Chem. Eng.* 5(11):10544–10550.

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