Influence of Drying Process Variables on the Wet Tensile Strength of Towel Paper with the Addition of Polyamidoamine-Epichlorohydrin (PAE) Polymer

Mariusz Reczulski,[a,*] Piotr Pospiech,[a] Maria Bieńkowska,[a] and
Joanna Zakrzewska[b]

The tensile strength of paper towels with the addition of polyamidoamine-epichlorohydrin (PAE) polymer was tested. The papers were formed from a pulp consisting of pine and eucalyptus fibres in a 50/50 ratio. PAE was added to the paper pulp in an amount of 3.5 mg/g. The samples were pressed on a conventional press and dried on a drying cylinder. During the drying of the samples, the process parameters were changed, *i.e.*, temperature (100 to 200 °C) and drying time (2 to 15 s). The drying conditions of the papers with the addition of PAE had a significant impact on the wet strength of the paper. The highest ratio of wet tensile index of the papers to dry tensile index in both directions, (MD and CD), was obtained for papers dried at 150 °C for 15 s. The results showed that with the increase in the dose of thermal energy supplied to the paper with the addition of PAE, its wet tensile strength increased. This applies to both the extension of the drying time and the increase in the drying temperature. Dry tensile strength tests of papers with the addition of PAE polymer showed that drying conditions were not of significant importance in that case.

DOI: 10.15376/biores.20.1.1173-1187

Keywords: Wet and dry strength of kitchen paper; Polyamidoamine-epichlorohydrin (PAE); Paper drying; Drying cylinder

*Contact information: a: Centre for Papermaking and Printing, Lodz University of Technology, 93-005 Lodz, Poland; b: Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland; *Corresponding author: mariusz.reczulski@p.lodz.pl*

INTRODUCTION

The paper focuses on tensile strength tests of paper towels made of a mixture of pine and eucalyptus fibers with the addition of polyamidoamine-epichlorohydrin (PAE) polymer. The formed samples were pressed on a conventional press and then dried on a drying cylinder.

Hygiene paper products include many tissue and towel papers for both home and professional use. Such papers should be characterized by appropriate softness, absorbency, and wet and dry strength. Different types of fibers, chemical additives, and appropriate technology in the production line are used to produce these papers (Gigac and Fiserova 2008; De Assis *et al*. 2018). Their selection is extremely difficult for the manufacturer, who, wanting to produce paper with the desired properties, must also ensure the profitability of production. Using conventional solutions in a paper machine, in which wet pressing (mechanical dewatering of the web) is used, paper is produced with higher strength, with lower bulk, softness and absorbency compared to papers produced using other advanced technologies, *e.g.*, through air drying (TAD) (Wang *et al.* 2019, De Assis 2018). However, TAD is a technology characterized by higher energy consumption (Weineisen and Stenström 2005; Ryan *et al*. 2007). Paper tensile strength (dry and wet) is one of the important properties determined for packaging and tissue papers.

The strength of the paper depends strongly on the number and strength (covalent bond, hydrogen bond, van der Waals interactions) of the bonds between the fibres. Fibre-to-fibre surface adhesion is generally believed to be caused by hydrogen bonds (Nissan *et al.* 1985; Tiberg 2001), however, these are not the only impacts. There are various mechanisms of interaction between the surfaces of adjacent fibres (Hubbe 2006; Hirn and Schennach 2017). The first of these is interdiffusion, which involves hydrogen bonds, van der Waals and Coulomb (electrostatic) interactions among functional groups present on polymeric or microfibrillar elements associated with the two bonding surfaces. Diffusion depends on both the type and the length of the polymers and, more importantly, the degree of fibre swelling. It is believed that increased fibre swelling results in a stronger bond (Scallan 1979). The contribution of the individual interactions to this mechanism is still a matter of debate, with many authors considering hydrogen bonds to be the most important (Hubbe 2013), although Coulomb and van der Waals interactions may contribute more (Hirn and Schennach 2017). The reduction in paper strength due to moisture may be due to competition in hydrogen bonding between cellulose OH groups on one side and cellulose OH groups and water molecules on the other side, and to softening of the fibres and the resulting deterioration of the load distribution in the network. Strong Coulomb interactions and increased swelling (increased contact area) will be significant in the presence of carboxyl groups. In turn, van der Waals interactions will be crucial in the crystalline regions of cellulose (Hirn and Schennach 2017).

The second important mechanism of interaction is mechanical interlocking (Schmied 2013). This results from the mechanical entanglement of the fibre surfaces, which translates into an increase in the strength of the bonds between them. In this case, surface of the fibres and hence the degree of fibre refining play a key role. For unrefined fibres, the surfaces are relatively smooth, whereas for refined fibres, there are fibrils on the contact surfaces that become tangled. It is likely that the increase in strength in fibre-to-fibre (refined) junctions is due to the entanglement of the outer filaments rather than increased molecular contact area or diffusion.

To reduce the loss of paper strength in contact with water, reactive, water-soluble polymers are commonly added to the paper pulp, *e.g.*, melamine-formaldehyde resins, polyacrylamide-based polymers, polyethylene glycol (PEG), cationic polymers, modified starch or polyamidoamine-epichlorohydrin (PEA) resins (Linhart 1995). This creates additional chemical bonds of the fiber-polymer and polymer-polymer type, thus increasing the paper's wet strength (Espy 1995; Lindström *et al*. 2005; Francolini *et al*. 2023). The wet strength of paper depends on, among other things, the amount of polymer retained in the paper pulp and the chemical bonds formed in the fibrous structure. Among other, PAE resin is considered to be the most commonly used wet strength agents in the papermaking industry (Espy 1995). After adding the polymer to the pulp, an adsorption phenomenon occurs by electrostatic attraction of anionic carboxylated groups on the surface of the fibre with cationic azetidine groups of the polymer (Obokata and Isogai 2007; Espy 1995, Lindström *et al.* 2005; Wagberg and Bjorklund 1993). This leads to the formation of covalent bonds between the resin and the fibres.

There are many studies describing how the presence of PAE resin affects the wet and dry strength of papers (Espy 1995; Charani *et al*. 2020; Liang *et al.* 2020; Korpela *et* *al*. 2022; Francolini *et al*. 2023). PAE primarily has a positive effect on increasing the wet strength of paper due to covalent bonds. Unfortunately, adding resin to the paper pulp also has a negative effect on web formation due to increased flocculation of fibers. The final result depends primarily on the dose of PAE added to the pulp. Too much polymer added to the pulp increases fiber flocculation and limits the increase in wet strength of paper. Additionally, machine clothing becomes contaminated more quickly. Therefore, the appropriate amount of resin added to the paper pulp is important to obtain a well-formed product with high wet strength. Research in this area was conducted by Su *et al*. (2012). The highest wet-to-dry strength ratio of 35% was obtained after adding 10 mg of PAE per gram of absolutely dry cellulose fibers to the pulp. Increasing the PAE dose to the pulp above 10 mg/g caused a decrease and then stabilized the level of wet tensile strength of paper. The main variables influencing the effectiveness of PAE in strengthening paper include, among others, its drying conditions and the type of fibers used (Saito and Isogai 2005).

Various types of cellulose fibers, which are natural polymers derived from plants, are used for the production of tissue paper. The choice of the type of fibers for paper production, which have different morphological characteristics, will affect the final properties of the product (Hubbe *et al*. 2007; De Assis *et al*. 2018). Most tissue paper is made from raw materials based on wood fibers, especially bleached kraft pulp. These are most often bleached hardwood kraft pulp (BHKP) and bleached softwood kraft pulp (BSKP). Paper towels are usually made from a mixture of hardwood and softwood (De Assis *et al*. 2018). Softwood pulp provides paper towels with a strong network of fibers, increasing its strength. Hardwood fibers are used in the production of paper towels to increase their bulk, softness, and smoothness. Most often, hardwood pulp is used for the production of paper towels in the amount of 50 to 80% of the total fiber pulp (Nanko *et al*. 2005; Zou 2017a,b). To obtain paper with high bulk (low apparent density), absorbency and softness, eucalyptus pulp is often used (Hurter and Byrd 2013; Morais *et al*. 2021).

Apart from the type of fibers, the effectiveness of PAE in the reinforcement of fibrous structure, as indicated earlier, depends, among other things, on its drying process. This is an important process activating PAE bonds with fibers. In each paper machine dryer, the drying conditions of the web may be different, regardless of the technology used. Most often, the paper web is dried using steam-heated drying cylinders, which are a simple and very economical solution. In the production of paper towels, a classic system consisting of a Yankee cylinder and a high-performance hood is most often used. In this technology, the web entering the Yankee cylinder area is wet-pressed. The web passes through one or two pressure zones (presses). Drying time and temperature significantly affect the strength of the PAE-added web (Saito and Isogai 2005). This is related to the resin gelation process (Ma *et al*. 2015). Although the effect of PAE resin on the wet and dry strength of papers is relatively well known, knowledge of the effect of methods and drying conditions of papers with PAE on their strength is incomplete. In order to obtain the maximum wet strength that tissue paper will achieve after a period of natural aging in ambient conditions, accelerated aging with heat is often used on test specimens after the sheet has left the paper machine. The strengthening of paper with PAE naturally usually takes place in a few or a dozen days, depending on the resin used. Most often in research work, samples are dried in a dryer at a temperature of 80 to 110 °C for several, a dozen or even 120 min (Obokata and Isogai 2007; Su *et al*. 2012; Francolini *et al*. 2023). Accelerated aging speeds the natural aging process of paper. Unfortunately, paper samples with added resin are most often dried in a dryer immediately after they are formed. This does not reflect the drying process of the web in the paper machine. The question arises as to how the drying conditions of the web used in production with the participation of a drying cylinder affect the final wet tensile strength of the paper after taking into account its ageing.

Paper is most often kept in a "jumbo roll" immediately after being produced on a paper machine. This time can range from a few minutes to a few hours. This causes a slow drop in the high temperature of the paper reached after production. Then the "jumbo roll" is cut into coils and transported to a warehouse, from where it is delivered to the customer after a few/several days. Over time, any paper made from plant fibers ages. This is an irreversible process. It manifests itself in a change in the chemical composition of the paper and its mechanical parameters.

The aim of the study was to determine the effect of drying conditions of very strong kitchen towel without crepe with the addition of PAE resin on its tensile strength when dry and wet. The tests were carried out in conditions reflecting the actual parameters of the paper drying process on the drying cylinder/cylinders in the paper machine. The drying time used was in the range of 2 to 15 seconds and the drying cylinder temperature was 100 to 200 °C. After drying, the paper samples were subjected to natural ageing in ambient conditions for 10 days. The results of the strength tests of the samples with PAE were compared with the results of the tests of the papers without the addition of resin. Wet and dry strength tests of the papers were carried out in both the MD and CD directions. The impulse for conducting the tests was the industrial practice of over-drying the papers to obtain paper with higher wet strength.

EXPERIMENTAL

Materials

The study used PAE resin with the commercial name KYMENE 5715 from Solenis. This product is used in one of the Polish paper mills for the production of kitchen towels. Diluted resin was added to the paper pulp in the form of a solution at a concentration of 0.036%. Paper samples with a grammage of 30 g/m^2 were formed from commercially available bleached softwood kraft pulp (BSKP) and bleached eucalyptus hardwood kraft pulp (BHKP) in a ratio of 50:50. Only the pine pulp was refined to 25°SR in a laboratory Valley beater. The eucalyptus pulp was defibrated in a laboratory centrifugal defibrator. The freeness value of the pulp was 14 °SR. The SR freeness of the pulp was analysed in accordance with the ISO 5267-1 (1999) standard (L&W Schopper–Riegler freeness tester, Sweden).

Preparation of Paper Sheets and their Drying Process

Wet paper samples were formed in an Allimand device. The jet of pulp was injected using a nozzle onto a rotating perforated drum with a synthetic forming wire. This is a device with the ability to adjust the speed of the wire (drum) and the flow velocity of pulp from the outlet nozzle. This allowed the formation of paper samples from pulp with a jet-to-wire ratio of 0.95. Sheets with a basis weight of 30 g/m^2 were formed with a mixture of pulps without resin and with the addition of PAE. The apparent density of the sheets was 0.53 g/cm^3 (average). Before feeding the pulp to the forming device, it was properly prepared. A cationic PAE solution in the dosage amount of 3.5 mg/g (as dry polymer per dry fiber mass, as used in one of the paper mills) at a temperature of 20 °C was added to the paper pulp (consistency of pulp was 0.5%, content of carboxyl group 3.5 meq/100g).

The paper pulp thus prepared was then mixed for 5 min.

After forming a sheet of dimensions 220x880 mm, it was cut into smaller sheets of dimensions 220x260 mm. The dryness of the samples after forming was 23 ± 0.2%. The wet sheets were transferred to a laboratory press under constant air humidity (70%) and temperature (23 °C). All sheets were pressed in a roll press with a pressure of 3 MPa and for 30 ms. The dryness of the sheets after pressing was 38 ± 0.2%. After pressing, the sheets were dried in a cylinder drying device with regulated temperature and cylinder rotation speed. The tensile strength tests of the wet (marked W) and dry (marked D) samples were divided into three series A, B, and C. In the first series (A), the tests were carried out with sheets without the addition of PAE resin. The sheets were dried on a cylinder at a temperature of 100 °C for 8 s. In the second series (B), sheets with PAE addition were dried on a cylinder at 100, 150, or 200 °C. For this series, all sheets were dried for 8 s. For this drying time, the wet tensile index was determined as a function of the cylinder temperature. This choice was dictated by the fact that in 2 s, under-dried samples were obtained and in 15 s, the samples were cockled. The third series (C) consisted of drying sheets with resin for 2 s and 15 s at a constant cylinder temperature of 150 °C. The results from series B, *i.e.*, after drying at 150 °C and in 8 s, were also used to analyse the change in the wet tensile index of paper with PAE as a function of drying time.

The drying time of towel paper was estimated based on three different installations operating at a speed of 400 m/min. The machines used to produce this type of paper include machines with a Yankee cylinder (drying time 2 s), machines with a Yankee cylinder and a set of additional drying cylinders (drying time 8 s) and machines with drying cylinders (drying time 15 s). The tests did not take into account convective drying occurring in the Yankee cylinder area. Additionally, installations with a multi-cylinder dryer do not use the same temperature on each cylinder.

All samples were subjected to natural ageing in ambient conditions for 10 days before strength tests.

Tests of Samples and Geometry Optimization

The tensile strength of the sample in the dry conditioned state was determined based on the PN-EN ISO 12625-4:2023-02 standard. Wet tensile strength tests of samples were conducted in accordance with the PN-EN ISO 12625-5:2017-03 standard.

The measurement results are presented in the form of a tensile index (TI). The tensile index for each sample was calculated as the tensile strength (expressed in Newtons per metre) divided by the grammage.

Samples with a width of 50.0 ± 0.5 mm and a length of 220 ± 0.5 mm were cut from the sheets in the machine direction MD and transverse direction CD. Before testing, the samples were conditioned at a temperature of 23 °C and a relative humidity of 50% for at least 24 h.

The tests were carried out using a standard Zwick Z010 testing machine equipped with a 500N force measuring head and tissue paper testing equipment. All measurements were carried out in a room with the same climatic conditions in which the samples were air-conditioned. An initial force of 1N and a testing speed of (50 ± 2) mm/min were used. The test span for all measurements was (100 ± 0.5) mm. A Finch Cup soaking device was used to test wet tensile strength.

SEM microphotographs were recorded with the JEOL JSM-6010LA (JEOL, Japan) scanning electron microscope operating at an accelerating voltage of 15 kV, equipped with an energy-dispersive X-ray detector. The surfaces of the samples were sputtered with a fine gold layer (20 nm thick) before analysis.

The computational studies were performed using the Gaussian 09 and Hyperchem 8.08 programs (Frisch *et al*. 2010; Hypercube Inc., Gainesville, FL, USA). The starting structures for geometry optimization were obtained from conformational search using the MM+ method with Hyperchem. Geometry optimizations (using Gaussian 09) in the gas phase were carried out using the B3LYP density functional (Becke 1993) and the 6-31G* basis set. All equilibrium structures were identified by frequency calculations. Thermal corrections to the electronic energies for 298K were scaled by 0.96.

RESULTS AND DISCUSSION

The results of the paper tensile strength tests are presented in the form of a tensile index and are illustrated in Figs. 1 and 2 and shown in Tables 1 and 2.

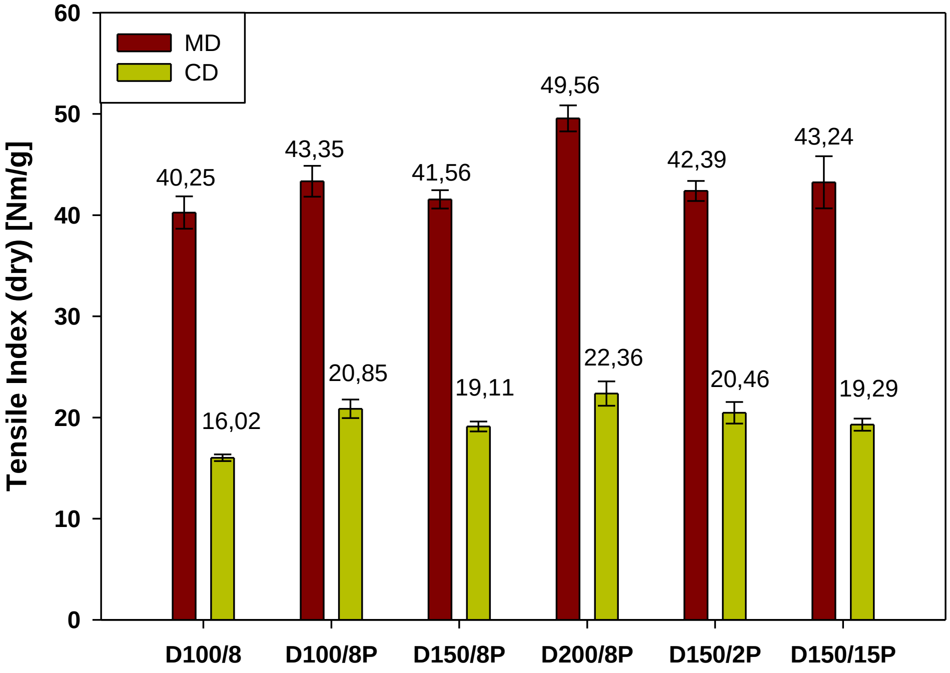


Fig. 1. Dry tensile index (DTI) of paper samples for different drying variants

Paper samples without PAE added that were tested for wet tensile strength had a very low WTI (*Wet Tensile Index*). After adding PAE to the pulp, the ratio of wet tensile index to dry tensile index of all papers increased significantly. These values varied depending on the drying conditions and the direction of cutting the samples.

The greatest increase in this ratio was observed for papers with PAE dried at 150 °C for 15 s. For papers tested in the MD direction, this ratio was 16.2%, while for CD it was 16.9%. The lowest ratio (of wet tensile index of papers to dry tensile index of papers) was obtained for papers dried at 150 °C for 2 s. These values were 10.8% for MD and 9.6% for CD. The values of these ratios were calculated assuming average values of WTI indices. All other papers with added resin tested wet had more than 10% of their dry strength (DTI - *Dry Tensile Index*) in both MD and CD directions.

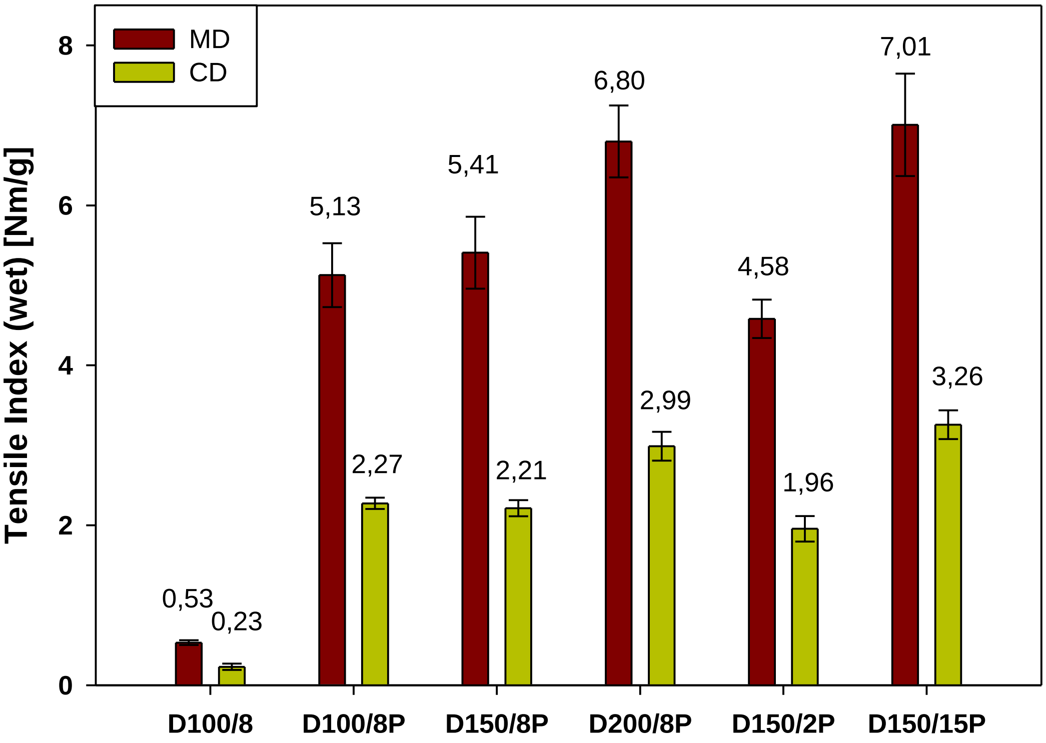


Fig. 2. Wet tensile index (WTI) of paper samples for different drying variants

In the tests of the dry tensile strength of paper, a similar DTI index was obtained for almost all variants tested. In the case of tests of papers in the machine direction (MD), the average DTI values ranged from 41.5 to 43.5 Nm/g and were 3 to 7% higher than those of papers without PAE. The only exception were papers dried at 200 °C, whose average DTI value was 23% higher. The average DTI values for papers with PAE in the cross direction (CD) were 19.5 to 21.0 Nm/g. Compared to papers without PAE (16.0 Nm/g), their strength was higher and more varied by approximately 20 to 40%.

The dry tensile index of the samples with PAE resin addition in the CD direction was almost half lower than in the MD direction (45 to 48%). The CD/MD ratio of the DTI index of the samples without resin was below 40% (assuming average DTI values). By changing the drying parameters, it is possible to influence the strength properties of the papers. It was noticed that papers dried at 200 °C for 8 s (D200/8P) were characterized by a higher dry tensile index than other tested variants. The reason for the increase in dry tensile index of paper with PAE dried at 200 °C for 8 s is attributed, among others, to the increased level of resin cross-linking in the paper structure. Additionally, drying the paper in such conditions (T= 200 °C, t= 8 s) also contributes to the increase in fiber plasticization, which causes an increase in the bonded fiber length and an increase in the fiber-fiber bond strength.

Table 1. Summary of Results for the Dry Tensile Index for the Studied Papers

Paper samples	**Series of tests**	**Variant**	**Drying temperature (°C)**	**Drying time (s)**	**DTI (Nm/g) MD**	**Standard deviation; MD**	**DTI (Nm/g); CD**	**Standard deviation; CD**
Without PAE	A	D100/8	100	8	40.25	1.17	16.02	0.24
With added PAE	B	D100/8P	100	8	43.35	1.14	20.85	0.67
		D150/8P	150	8	41.56	0.67	19.11	0.36
		D200/8P	200	8	49.56	0.94	22.36	0.87
With added PAE	C	D150/2P	150	2	42.39	0.76	20.46	0.77
		D150/15P	150	15	43.24	1.88	19.29	0.44

Table 2. Summary of Results for the Wet Tensile Index for the Studied Papers

Paper samples	Series of tests	Variant	Drying temperature (°C)	Drying time (s)	WTI (Nm/g) MD	Standard deviation; MD	WTI (Nm/g); CD	Standard deviation; CD	Dryness of paper after drying (%)
Without PAE	A	W100/8	100	8	0.53	0.03	0.23	0.04	93-94
With added PAE	B	W100/8P	100	8	5.13	0.40	2.27	0.07	93-94
		W150/8P	150	8	5.41	0.45	2.21	0.10	93-95
		W200/8P	200	8	6.80	0.45	2.99	0.18	97-98
With added PAE	C	W150/2P	150	2	4.58	0.24	1.96	0.16	88-90
		W150/15P	150	15	7.01	0.64	3.26	0.18	97-98

The WTI index of the tested paper samples varied depending on their drying conditions. The lowest index value was obtained for paper samples without PAE resin. For samples tested for MD, the average value of the index was 0.53 Nm/g, while for CD – 0.23 Nm/g. After adding resin to the pulp, the wet tensile index increased in some variants more than 10 times (*e.g.* W150/8P, W200/8P, W150/15P). The highest WTI values for paper samples tested for both MD and CD were obtained after drying at 150 °C for 15 s (W150/15P). These were average values of 7.01 Nm/g and 3.26 Nm/g, respectively. It should be noted that the paper samples had high wet tensile index values when dried at 200 °C for 8 s (W200/8P). In this case, the WTI decreased by only 3.1% in the MD direction and 9.0% in the CD direction compared to the test with paper drying at 150 °C for 15 s. In these two cases, the heat transfer to the paper was the highest compared to other variants tested. Paper samples dried at 100 and 150 °C for 8 s showed similar WTI values depending on the direction tested. The differences in WTI values were small, close to the measurement error. These values were significantly lower than the values obtained in the W150/15P variant by 36.6% in the MD direction and 47.5% in the CD direction. The lowest strength value was obtained for paper samples dried at 150 °C for 2 s (W150/2P). The WTI value of 4.58 Nm/g was obtained in the MD direction and 1.96 Nm/g in the CD direction. In relation to papers dried according to the W150/15P variant, reducing the drying time to 2 s caused a decrease in the WTI by 53.1% in the MD direction and 66.3% in the CD direction. The CD/MD ratio of the WTI index of the samples with resin was 40 to 46%, with the lowest value obtained for samples W150-8P and the highest for W150-15P.

Micrographs of the obtained sheets were obtained, and molecular modelling was performed using density functional theory (DFT) methods. The fibrous structure of paper with and without polymer for selected cases (100/8, 150/2P, 150/15P) is shown in Fig. 3.

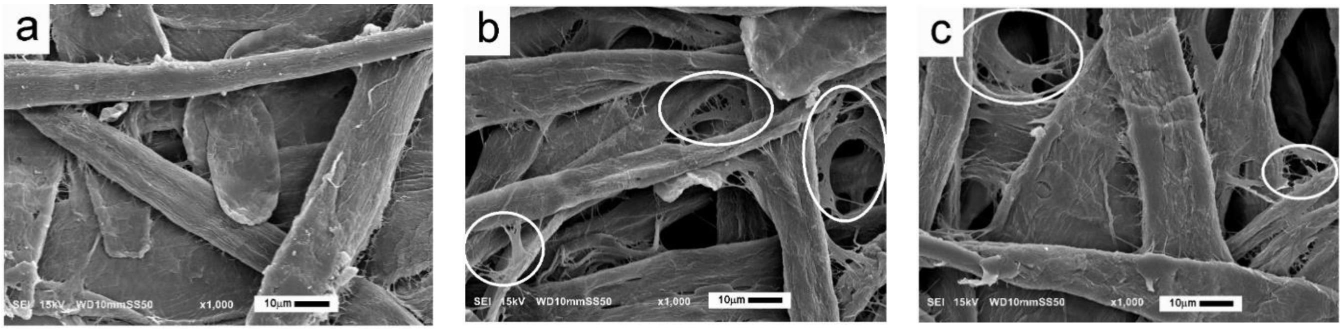


Fig. 3. Fibrous structure, a) without polymer (100/8), b) with polymer (150/2P), c) with polymer (150/15P)

In SEM micrographs of PAE-added papers, interfibers connections can be observed. The thin, thread-like connections between fibers (average thickness 0.18 µm), can be regarded as cellulosic fibrils resulting from partial fibrillation of the fiber surfaces. In addition to single threads, there are also spiderweb forms in the interfiber spaces. These small but numerous forms contribute to the reinforcement of the fiber network structure. Because these forms are less in paper without PEA it can suggest that polymer presence strengthens these structures.

Previous reports (Obokata and Isogai 2007; Siqueira 2012) indicate that the dominant cause of the strength enhancement is the PAE binding reaction with cellulose. The azetidine ring opens and is attached to carboxyl groups on cellulose chains. However, it should be remembered that the reactivity of the ring allows for a number of reactions with other groups, *e.g.* hydroxyl or amino groups (Goethals *et al*. 1980; Masson *et al*. 2021). This leads to self-crosslinking of the polymer and the formation of a gel structure. The different reactivity of the available functional groups with the azetidine ring means that the conditions of the process will significantly affect the final structure of the polymer. The increase in strength depends on the number and type of connections formed.

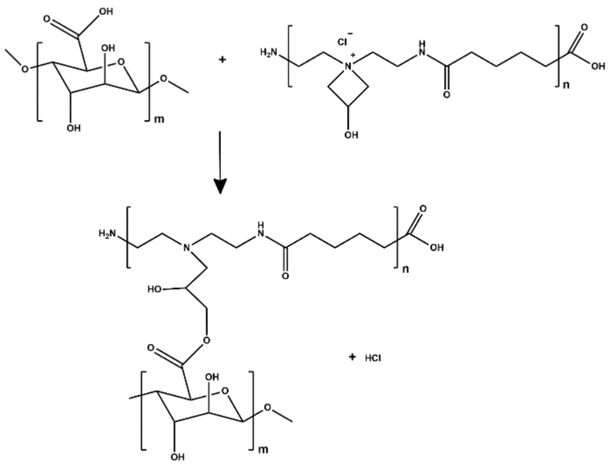
Most authors indicate the main reaction – the binding of the open azetidine ring with carboxyl groups present in the cellulose chain. The possibility of binding with hydroxyl groups, which occur in large amount and in greater density on the cellulose chain, is omitted. Such a potential path would increase the probability of rapid and permanent attachment of PAE to the cellulose chain. Analysis by molecular modeling using density functional methods (DFT) indicates that the enthalpy of the binding reaction with -OH groups directly attached to the glucopyranose ring (Fig. 4, Scheme 2, paths b and c) is even four times lower than the enthalpy of binding with the carboxyl group (Fig. 4, Scheme 1). On the other hand, the difference between the enthalpy of binding with the carboxyl group and the enthalpy of binding with the -OH group at the C-6 carbon atom is ~1 kcal/mol (Table 3). This increases the probability of PAE binding to cellulose.

Table 3. Enthalpy of Formation Cellulose-PAE and PAE-PAE Structures (PAE – Linking by Open Azetidine Ring)

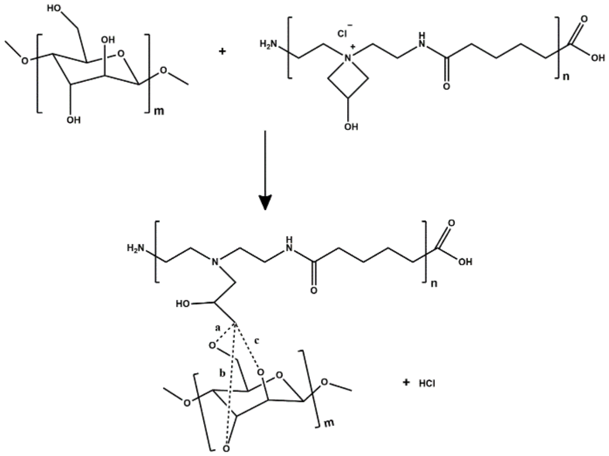
Structure	ΔH (kcal/mol)
Cellulose-COOH – PAE (scheme 1)	-17.82
Cellulose-OH – PAE [terminal] (Scheme 2 path b and [c])	- 4.08 [-12.34]
Cellulose-CH_2-OH – PAE (Scheme 2 path a)	- 19.16
PAE – terminal COOH in PAE	- 9.42
PAE – terminal NH_2 in PAE	- 11.85
PAE – PAE (scheme 3)	- 31.27

In the case of the PAE cross-linking reaction of the open azetidine ring with PAE end groups (COOH, NH_2), the enthalpies are lower than the enthalpies of the bonds with cellulose. On the other hand, the enthalpy of the most frequently postulated cross-linking reaction between the open azetidine ring and the nitrogen to which the ring is attached turns out to be significantly higher than the enthalpy of the cellulose-PAE bonds (Fig. 4, Scheme 3). The obtained results suggest that the dominant reaction will be the cross-linking of PAE and then the bonding to the cellulose chains. The obtained results of the strength analyses confirm this thesis to some extent. Drying the paper at a lower temperature or a short drying time would cause intensive cross-linking of PAE, but the bonding of the polymer to the fibers would be insignificant. In turn, increasing the temperature or extending the heating time would lead to a strong bonding of the polymer with the fibers, and thus an increase in mechanical strength.

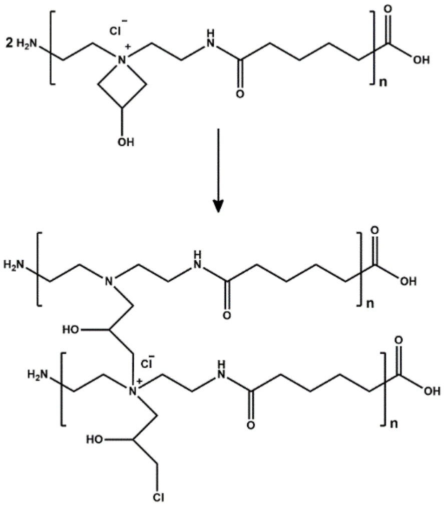
The obtained results also indicate that increased temperature and extended heating of papers contribute to their increased wet strength. This indicates a reinforced structure of the cellulose-hydrogel composite by creating a large number of intermolecular bonds. However, it should be noted that extending the time is more effective, because the formation of new bonds is limited by the kinetics of the reaction.



Scheme 1



Scheme 2



Scheme 3

Fig. 4. Potential reaction pathways of polyamideamine-epichlorohydrin (PAE) resin in a paper sheet forming environment

CONCLUSIONS

1. The increase in wet strength of poly(amidoamine epichlorohydrin) (PAE)-containing samples is attributed to the formation of ester bonds between the azetidine groups of PAE and the carboxyl groups of cellulose fibers, *i.e.*, the formation of covalent bonds. In addition, a series of PAE self-crosslinking reactions occur. A significant effect on the increase in the number of bonds in PAE samples is their heat treatment, *i.e.*, the drying process.
2. Analysing the effect of drying temperature on the results of wet tensile strength tests of papers, it was noted that for the same drying time of 8 s, with the increase of drying temperature (from 100 °C to 200 °C), the wet tensile index (WTI) value increased in both tested directions (MD and CD). The effect of drying time on the wet tensile strength of samples was also noted. The longer drying time (2 to 15 s) led to a higher WTI index value. The tests were carried out at a drying temperature of 150 °C. Therefore, the higher the dose of thermal energy supplied to the fibrous structure of PAE paper, the higher the wet tensile strength of the paper. The highest strength was characterized by papers dried under the conditions of T=150 °C and t=15s and T=200 °C and t=8s. Unfortunately, these papers were characterized by high final dryness of 97 to 98% and the occurrence of cockling. Such results are unacceptable for paper mill, because it increases the consumption of thermal energy in production and reduces the final quality of the paper. Papers dried at T=150 °C and t=2s were, however, under-dried. Their final dryness was 88 to 90%.
3. Paper samples dried at 100 and 150 °C for 8 s had a final dryness of 93 to 95%, which corresponds to the actual values obtained on the paper machine. By increasing the final dryness of the papers by approx. 3% to 97 to 98%, their wet tensile index increased by 26 to 37% in the MD direction and 32 to 48% in the CD direction. Unfortunately, the energy efficiency of the dryer in this case will deteriorate. After adding PAE to the fibrous pulp, the wet tensile strength of all papers increased significantly.
4. The WTI index for papers with PAE added, was 8 to 14 times higher than for papers without resin for both directions (MD and CD), depending on the drying conditions. The largest increase in the WTI to DTI ratio was seen for papers with PAE dried at 150 °C for 15 s, amounting (for MD and CD) to over 16%. Papers dried at temperatures of 100 to 150 °C and for 2 to 15 s did not show any changes in dry tensile strength. Therefore, drying conditions were not of significant importance in this case.
5. Image analysis indicates the formation of connections between the fibers and the cross-linked PAE structure. Strengthening the fiber network by connecting to the hydrogel network improves the strength parameters of the entire product.
6. Analysis using molecular modeling methods indicates the priority of the PAE cross-linking reaction, followed by reactions with cellulose, both to COOH and COH groups at the C-6 carbon atom in the glucopyranose ring.
7. Increasing the temperature and extending the heating time allows for the efficient course of the above reactions.

ACKNOWLEDGMENTS

This research was supported in part by the PL-Grid infrastructure.

REFERENCES CITED

Becke, A. D. (1993). "Density-functional thermochemistry. III. The role of exact exchange," *The Journal of Chemical Physics* 98(7), 5648-5652. DOI: 10.1063/1.464913.

Charani, P. R., Moradian, M. H., and Mousavi, S. F. (2020). "Strengthening tensile strength of wet and dry layer of paper from chemical-mechanical pulp by cellulose nanofibers and PAE," *Journal of Environmental Sciences Studies* 5(2), 2458-2465.

De Assis, T. Reisinger, L., Dasmohapatra, S., Pawlak, J., Jameel, H., Pal, L., Kavalew, D., and Gonzalez, R. (2018). "Performance and sustainability vs. the shelf price of tissue paper kitchen towels," *BioResources* 13(3), 6868-6892. DOI: 10.15376/biores.13.3.6868-6892

De Assis, T., Reisinger, L. W., Pal, L., Pawlak, J., Jameel, H., and Gonzalez, R. W. (2018). "Understanding the effect of machine technology and cellulosic fibers on tissue properties – A review," *BioResources* 13(2), 4593-4629. DOI: 10.15376/biores.13.2.DeAssis

Espy, H. H. (1995). "The mechanism of wet-strength development in paper: A review," *Tappi Journal* 78(4), 90-99.

Francolini, I., Galantini, L., Rea, F., Di Cosimo, C., and Di Cosimo, P. (2023). "Polymeric wet-strength agents in the paper industry: An overview of mechanisms and current challenges," *International Journal of Molecular Sciences* 24(11), 9268. DOI: 10.3390/ijms24119268

Frisch, M. J. *et al*. 2010. "Gaussian 09, Revision C.01," ed. Inc. Gaussian Wallingford CT, 2010.

Gigac, J., and Fiserova, M. (2008). "Influence of pulp refining on tissue paper properties," *Tappi Journal* 7, 27-32.

Goethals, E. J. Schacht, E. H., Bogaert, Y. E., Ali, S. I., and Tezuka, Y. (1980). "The polymerization of azetidines and azetidine derivatives," *Polymer Journal* 12(9), 571-581. DOI: 10.1295/polymj.12.571

Hirn, U., and Schennach, R. (2017). "Fiber-Fiber Bond Formation and Failure: Mechanisms and Analytical Techniques," in: *Advances in Pulp and Paper Research*, Oxford 2017, Trans. of the XVIth Fund. Res. Symp. Oxford, 2017, W. Batchelor and D. Söderberg (eds.), pp. 839-863, FRC, Manchester, 2018. DOI; 10.15376/frc.2017.2.839

Hubbe, M. A. (2006). "Bonding between cellulosic fibers in the absence and presence of dry-strength agents - A review," *BioResources* 1(2), 281-318. DOI: 10.15376/biores.1.2.281-318

Hubbe, M. (2013). "Prospects for maintaining strength of paper and paperboard products while using less forest resources: A review," *BioResources* 9(1), 1634-1763. DOI: 10.15376/biores.9.1.1634-1763

Hubbe, M., Venditti, R., and Rojas, O. (2007). "What happens to cellulosic fibers during papermaking and recycling? A review," *BioResources* 2(4), 739-788. DOI: 10.15376/biores.2.4.739-788

Hurter, R., and Byrd, M. (2013). “Considerations for the use of nonwood raw materials for tissue manufacture,” in: *TAPPI PaperCon*,.

Hypercube Inc., (year). HyperChem(TM) Professional 8.0.

Korpela, A., Jaiswal, A. K., Tanaka, A., and Asikainen, J. (2022). “Wet tensile strength development of PAE wet-strengthened NBSK handsheets by AKD internal sizing,” *BioResources* 17(2), 3345-3354. DOI: 10.15376/biores.17.2.3345-3354

Liang, S.-B., Ning, X., Fu, Q.-J., Liu, Q., and Yao, C.-L. (2020). "The use of a PAE /bentonite binary system to improve the wet strength of paper," *BioResources* 15(4), 8449-8458. DOI: 10.15376/biores.15.4.8449-8458

Lindström, T., Wågberg, L, and Larsson, T. (2005). “On the nature of joint strength in paper - A review of dry and wet strength resins in paper manufacturing,” in: *Advances in Paper Science and Technology*, Trans. of the XIIIth Fund. Res. Symp. Cambridge, 2005, (S.J. I’Anson, ed.), pp. 457-562, FRC, Manchester, 2018. DOI: 10.15376/frc.2005.1.457.

Linhart, F. (1995). “The practical application of wet-strength resins,” in: *Applications of Wet-End Paper Chemistry*, C. O. Au and I. Thorn (eds.), Springer, Dordrecht, Netherlands, pp. 102-119. DOI: 10.1007/978-94-017-0756-5_7

Ma, S. D., Liu, C., Xu, Q., and Lv, G. P. (2015). “Investigation on the synthesis of self-crosslinking polyamideamine–Epichlorohydrin as in-depth profile control agent and its properties,” *Materials Research Innovations* 19, S9-282. DOI: 10.1179/1432891715Z.0000000001987

Masson, G., Pardo, D. G., and Cossy, J. (2021). “Ring-opening of azetidiniums by nucleophiles. Synthesis of polysubstituted linear amines,” *Chirality* 33(1), 5-21. DOI: 10.1002/chir.23280

Morais, F. P., Carta, A. M. M. S., Amaral, M. E., and Curto, J. M. R. (2021). “Micro/nano-fibrillated cellulose (MFC/NFC) fibers as an additive to maximize eucalyptus fibers on tissue paper production,” *Cellulose* 28, 6587-6605. DOI: 10.1007/s10570-021-03912-9

Nanko, H., Button, A. L., Hillman, D., and Swann, C. E. (2005). *The World of Market Pulp*, TAPPI Press, Atlanta, GA, USA.

Nissan, A. H., Byrd, V. L., Batten, G. L., and Ogden, R. W. (1985). “Paper as an H-bond dominated solid in the elastic and plastic regimes,” *TAPPI Journal* 68, 118-124.

Obokata, T., and Isogai, A. (2007). “The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin,” *Colloids and Surfaces A* 302, 525-531. DOI: 10.1016/j.colsurfa.2007.03.025

Ryan, M., Zhang, J., and Ramaswamy, S. (2007). “Experimental investigation of through air drying of tissue and towel under commercial conditions,” *Drying Technology* 25(1), 195-204. DOI: 10.1080/07373930601161088

Saito, T., and Isogai, A. (2005). “A novel method to improve wet strength of paper,” *Tappi Journal* 4, 3-8.

Scallan, A. M., and Grignon, J., (1979). “The effect of cations on pulp and paper properties,” *Svensk Papperstidning* 82(2), 40-47.

Schmied, F., Teichert, C., Kappel, L. *et al*. (2013). “What holds paper together: Nanometre scale exploration of bonding between paper fibres,” *Sci. Rep*. 3, article 2432. DOI: 10.1038/srep02432

Siqueira, É. (2012). *Polyamidoamine Epichlorohydrin-Based Papers : Mechanisms of Wet Strength Development and Paper Repulping*, Ph.D. Dissertation, Université de Grenoble, France.

Su, J., Mosse, W. K. J., Sharman, S., Batchelor, W., and Garnier, G. (2012). "Paper strength development and recyclability with polyamideamine-epichlorohydrin (PAE)," *BioResources* 7(1), 913-924. DOI: 10.15376/biores.7.1.913-924

Tiberg, F., Daicic, J., and Froberg, J. (2001). "Surface chemistry in paper," in: *Handbook of Applied Colloid and Surface Chemistry*, K. Homberg (ed.), Wiley, New York Ch. 7, pp. 123-173

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. DOI: 10.3183/npprj-1993-08-01-p053-058

Wang, Y., Zambrano, F., Venditti, R., Dasmohapatra, S., De Assis, T., Reisinger, L., Pawlak, J., and Gonzalez, R. (2019). "Effect of pulp properties, drying technology, and sustainability on bath tissue performance and shelf price," *BioResources* 14(4), 9410-9428. DOI: 10.15376/biores.14.4.9410-9428

Weineisen, H., and Stenström, S. (2005). "Modeling through drying of tissue—Effect of pore size distribution on drying characteristics," *Drying Technology* 23(9–11), 1909-1923. DOI: 10.1080/07373930500210317

Zou, X. (2017a). "Overview of tissue grades and their pulp furnish selection," in: *PaperCon 2017*, Minneapolis, MN, pp. 1-28.

Zou, X. 2017b. "Refining of HW and SW kraft for tissue making," in: *PaperCon 2017*, Minneapolis, MN.

Article submitted: September 20, 2024; Peer review completed: November 9, 2024; Revised version received and accepted: November 20, 2024; Published: December 6, 2024.
DOI: 10.15376/biores.20.1.1173-1187