Wet Tensile Strength Development of PAE Wet-strengthened NBSK Handsheets by AKD Internal Sizing

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Polyamide-epichlorohydrin (PAE) is used in papermaking to increase the paper's wet strength. High levels of PAE can make repulping of paper more difficult. PAE deposits can also impair paper machine performance by plugging the paper machine felts. The results of a preceding study indicated that the wet strength of paper containing a moderate amount of PAE (added amount 0.3 wt%) can be increased by utilizing internal alkylketene dimer (AKD) sizing. In the present study, the effects of an added amount of PAE and AKD on the wet strength of handsheets made from Nordic bleached softwood pulp (NBSK) were examined. The wet strength was measured after soaking the sheets in ion-exchanged water for up to 1 month. The improving effect of AKD sizing on the wet strength was long-lasting and it was apparent especially with a low and moderate added amount of PAE (0.15 and 0.45 wt%) resulting in higher wet strength than the highest added amount of PAE (1.35 wt%) alone. No clear sign of worsened repulpability was observed at low to moderate treatment levels. The results suggest that use of small or moderate amounts of PAE with AKD can be a viable option for paper mills facing problems related to the high usage of PAE.

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INTRODUCTION

Polyamide-epichlorohydrin (PAE) is used in papermaking to increase the strength of wet paper products. PAE is a water-soluble cationic polymer that is retained on negatively charged papermaking fibers via ionic attraction. In papermaking, PAE is typically added to the papermaking furnish. The final curing and attachment of PAE to the fibers take place as the paper is dried and heated in the paper machine drying section (Espy 1995; Scott 1996). According to general understanding, PAE molecules increase the paper wet strength by forming self-cross-linked fiber-bond networks repressing the fiber swelling and thus protecting the fiber-to-fiber bonds when the paper is wetted by water (Häggkvist *et al.* 1998; Ozaki *et al.* 2006; Siqueira 2012). Obokata and Isogai (2007) concluded that the wet strength development of PAE-containing cellulose sheets results primarily from ester bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers. In practice, a large added amount PAE can make the repulping of paper broke and wastepaper more difficult (Siqueira 2012; Su *et al.* 2012). PAE may also contribute to paper machine felt filling and thus impair paper machine runnability and performance (Ringold and Fuhrman 2019).

Alkyl ketene dimer (AKD) is used in papermaking to slow down the absorption of liquid water into the paper. AKD is a waxy organic compound composed of two hydrophobic aliphatic chains and a reactive ketene group (Seppänen 2007; Lindström and Larson 2008). AKD is typically delivered to paper mills as water dispersions stabilized by a cationic polymer such as cationic starch (Scott 1996; Hubbe 2006). In so called "internal sizing," AKD water dispersion is added to the pulp furnish before paper web formation. In the furnish, the adsorption of the AKD droplets onto the papermaking fibers takes place via ionic interaction. AKD droplets and molecules spread onto the fibers during the drying of the paper by surface diffusion and to some extent by vapor phase diffusion (Seppänen 2007; Lindström and Larson 2008). AKD molecules are attached to the fibers so that the hydrophobic part of the AKD is orientated outwards from the fibers and the reactive more hydrophilic group toward the fibers, thus rendering the fiber surfaces water-repellent. According to common understanding, the reactive ketene group of AKD molecules is capable of forming covalent beta-keto ester bonds with the hydroxyl groups of the papermaking fibers (Strazdins 1989; Cates *et al.* 1989; Scott 1996; Bajpai 2005; Hubbe 2006; Hubbe 2014).

Korpela *et al.* (2021) reported recently that AKD internal sizing is capable of increasing the wet strength of PAE-containing NBSK handsheets soaked in water for up to 1 week. In the present study, the influence of added amounts of both PAE and AKD on the long-term wet strength of NBSK handsheets was examined. The added amounts can be considered "low", "moderate", and "high". The wet strength was measured after soaking of the sheets in water up to 1 month.

With the exception of the manufacture of tissue and absorbent paper products, the new knowledge on the combined effects of PAE and AKD internal sizing on handsheet wet and dry strength properties can find use by paper and board makers seeking solutions to quality or runnability problems related to the high use of PAE in paper and board manufacturing. The shift away from the use of high amounts of PAE may also be motived by opportunities to decrease cost-in-use.

EXPERIMENTAL

Materials

Bleached softwood sulphate pulp (NBSK) sheets were obtained from a Finnish pulp mill. The wet strength agent polyamine-epichlorohydrin (PAE) and cationic alkylketene dimer dispersion (AKD) for this study were technical-grade products used industrially in papermaking. Both PAE and AKD were used as such in the laboratory trials. According to information from the chemical supplier, the AKD formulation contained cationic starch as a dispersing agent (dispersion stabilizer). Ion-exchanged water was used for laboratory sheet making and diluting chemicals.

Preparation of Laboratory Sheets, Application of PAE and AKD, and Testing of Handsheet Properties

Laboratory paper sheets were made using uncirculated ion-exchanged water following ISO 5269-1 (2005). Before sheet making, NBSK-pulp sheets were dispersed in water and refined to a °SR-value of 19.0 using a Voith LR1 laboratory refiner. The °SR-value was measured according to EN ISO 5267-1 (1999). The pH of the pulp was adjusted to 6.5-7.0 using 1 M HCl and 1 M NaOH. Diluted PAE water solution (0.2 wt%) was added to the pulp suspension followed by the addition of the AKD sizing agent. The added amount of PAE and AKD was 0.15 to 1.35 wt% and 0 to 0.6 wt% on dry fiber basis, respectively. The pulp suspension was mixed for 10 seconds after both chemical additions, followed by immediate drainage of the suspension. For curing of the PAE and the AKD, the dried laboratory paper sheets were heated in an oven at 80 °C for 120 min. The targeted handsheet grammage was 80 g/m^2 when the RH was 50%.

The laboratory paper sheets were tested according to ISO and TAPPI standards (Table 1).

Table 1. Utilized Handsheet Test Methods

Grammage (g/m^2)	ISO 5270 (2012)
Bulk (kg/m^3)	ISO 5270 (2012), ISO 534 (2011)
Tensile Index (Nm/g), Strain at break (%), Elastic modulus, N/mm^2	ISO 5270 (2012), EN ISO 1924-2:2008
Z-dir. tensile strength (kPa)	TAPPI T541 om-99 (1999)
Wet tensile strength (kN/m)	ISO 3781 (2011)
Cobb 60 (g/m^2)	ISO-535 (2014)
Repulpability	TAPPI UM 213 (2012) modified

Repulpability testing

The repulpability of the prepared handsheets was compared following a modified TAPPI UM 213 test. In the modified test the handsheets were mixed and tested with readily water dispersing blotting paper. Both the handsheets and blotting paper were cut to 13 mm x 13 mm in size before mixing. In the test mixtures the amounts of the handsheets and the blotting paper were 6.5 g and 8.5 g respectively. Otherwise, the tests followed the standard TAPPI method.

RESULTS AND DISCUSSION

Figure 1 shows the effect of AKD internal sizing on NBSK handsheets wet strengthened by different amounts of PAE. The added amounts of PAE and AKD in the handsheets were 0.15, 0.45, and 1.35 wt%, and 0.15., 0.30 and 0.60 wt%, respectively (reference without AKD). AKD internal sizing increased the wet strength of the handsheets especially with "low" and "moderate" added amounts of PAE (0.15 wt% and 0.45 wt%). The achieved increase of wet strength was also long-lasting. The results show that from the use of AKD-internal sizing with a low or moderate added amount of PAE, a higher wet strength can be achieved than with "high" added amounts of PAE (1.35 wt%) alone.

The reason for the smaller effect of AKD internal sizing on the wet strength of handsheets containing high amounts of PAE (added amount 1.35 wt%) is possibly caused by the low retention of AKD in the handsheets. In the course of sheet making, PAE is added first in the pulp suspension, followed by AKD addition.

As a cationic polymer, PAE may reduce the attraction of cationic charged AKD-droplets on the inherently anionic charged fibers. It is also possible that a high amount of PAE on the fiber surfaces influences the orientation of attached AKD molecules on the fiber surfaces as well as the spread and formation of covalent beta-keto ester bonds with hydroxyl groups of the papermaking fibers. As can be seen in Fig. 2, the reducing effect of AKD internal sizing on the water absorbency of the handsheets (g/m^2) was smallest in the case of handsheets containing the highest amount of PAE (added amount 1.35 wt%).

The wet strength of the handsheets correlated with the dry content of the handsheets after water soaking. The correlation was clear, especially in the case 0.15 and 0.45 wt% added amounts of PAE (Fig. 3). The result is in accordance with the earlier published observations by Korpela *et al.* (2021). The correlation indicates that the improving effect of AKD sizing on the wet strength of the handsheets related to the decreased water absorption of the handsheets. The reducing effect of AKD on water absorption of the PAE containing handsheets was long-lasting.

AKD internal sizing decreased the dry tensile strength and dry z-directional strength of the PAE containing handsheets slightly, with the effect being close to the standard deviation of the results (Fig. 4). There was no significant effect on the handsheet bulk. This means that in practice a shift from the use of high PAE dosages in papermaking to the use of smaller dosages of PAE together with AKD internal sizing will most likely not make dry paper notably weaker.

Although the use of low and moderate amounts of AKD and PAE (added amounts 0.15, 0.3 wt% and 0.15, 0.45 wt% respectively) resulted in high and long-lasting handsheet wet strength, no sign of impaired repulpability was evident in a comparative repulpability test. As shown in Fig. 5, just those handsheets that contained AKD and the highest amount of PAE (added amount 1.35 wt%) showed somewhat worse repulpability. It is worth noting that the results the performed laboratory trials are just indicative. On the basis of the TAPPI UM 213 evaluation criterion, all tested samples can be considered repulpable.

Due to the difficulty of the quantitative analysis of AKD and PAE in paper, the effects of PAE and AKD internal sizing on handsheet properties are considered as a function of the added amounts PAE and AKD in the handsheet furnish. This is the case also in most other related published studies. As quantitative information on the adhered AKD and PAE in paper would help to account for the observed changes in the paper properties it would be very useful if simple and accurate quantitative analysis methods for AKD and PAE were available in the future. Additionally, it would be useful to obtain information about how PAE and AKD interact with each other at the molecular level.

The present study explores the effects of the joint use of PAE and AKD on NBSK handsheet wet strength. It is quite possible that the effects are somewhat different in mill-scale papermaking, where a number of factors such as different dewatering conditions, temperature, pH, and other paper furnish constituents may all effect the retention, functioning, and interaction of PAE and AKD. Pilot-scale verification of the presented effects of PAE and AKD will be a subject of further studies. Pilot scale trials will also enable testing the repulpability of the paper using alternative testing methods.

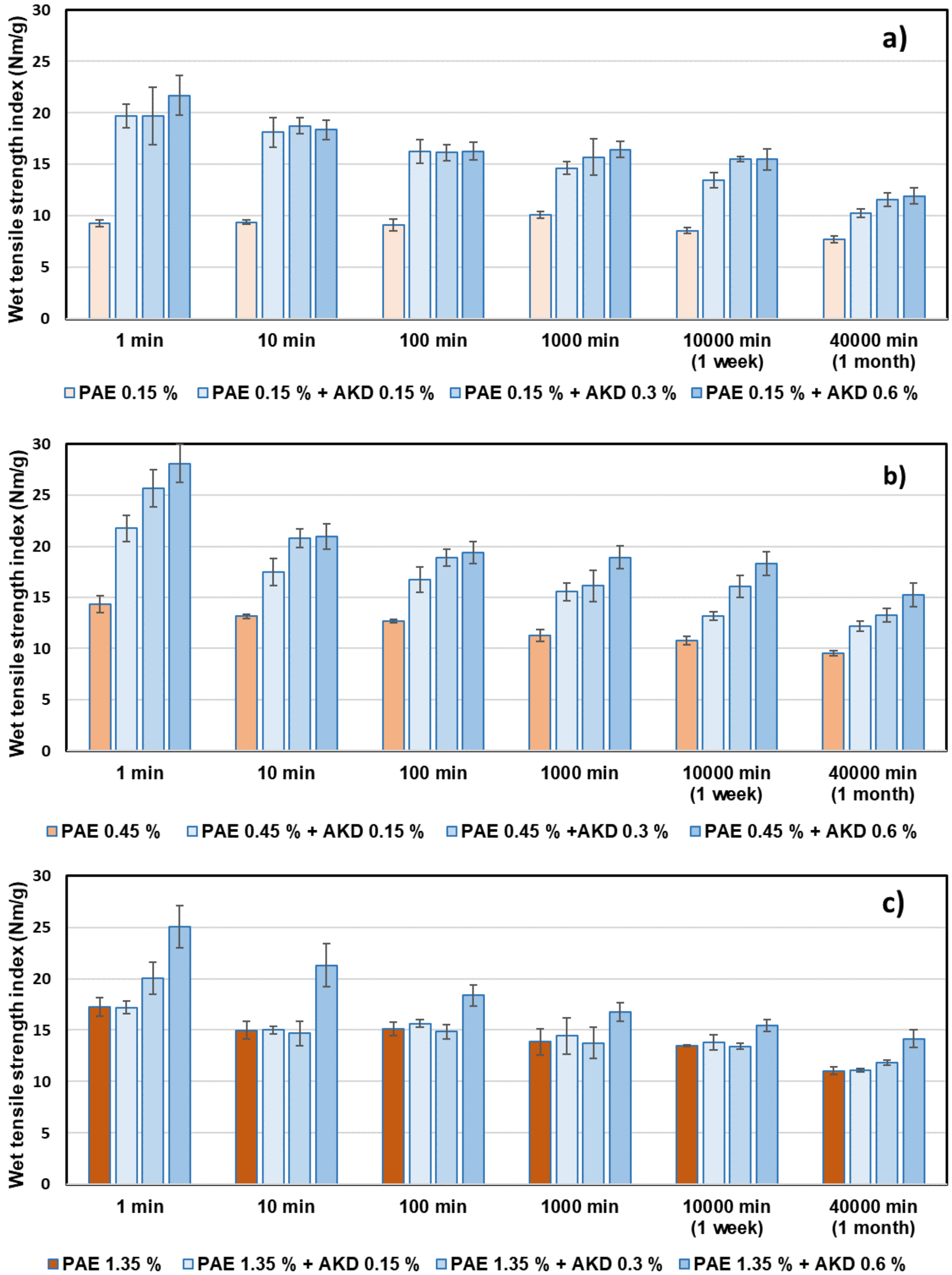

Fig. 1. The effect of AKD internal sizing on the wet tensile strength of NBSK handsheets wet strengthened by PAE: a) PAE 0.15%, b) PAE 0.45%, c) PAE 1.35%. The "%" indicates the amounts of chemical additions in the pulp suspension.

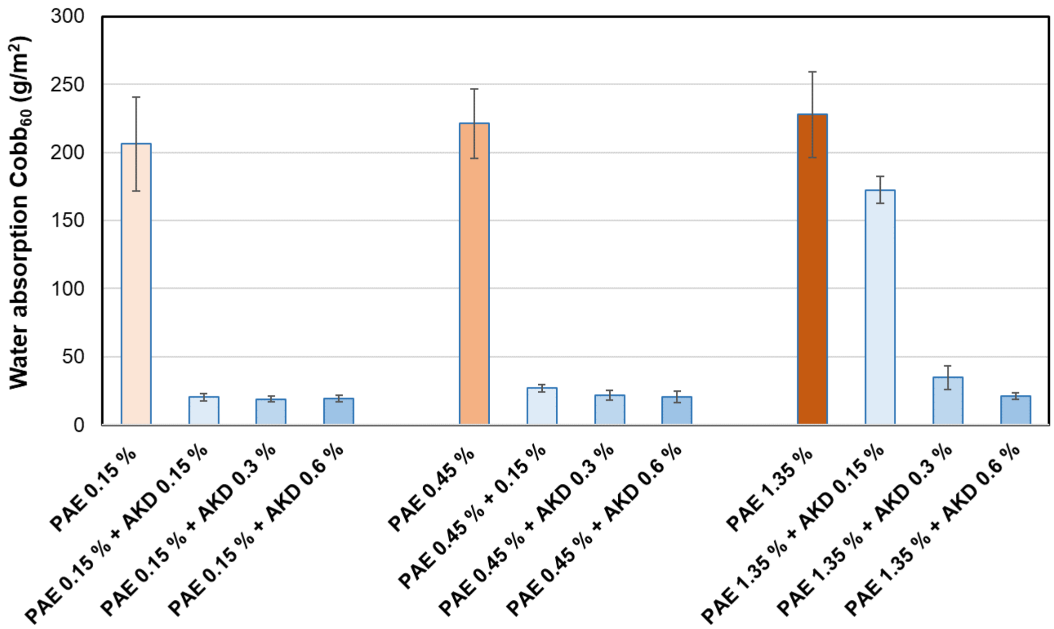

Fig. 2. The effect of AKD internal sizing on the water absorbency ($Cobb_{60}$) of NBSK handsheets wet strengthened by PAE. $Cobb_{60}$ values are averages of top- ja wire sides. The "%" indicates the amounts of chemical additions in the pulp suspension.

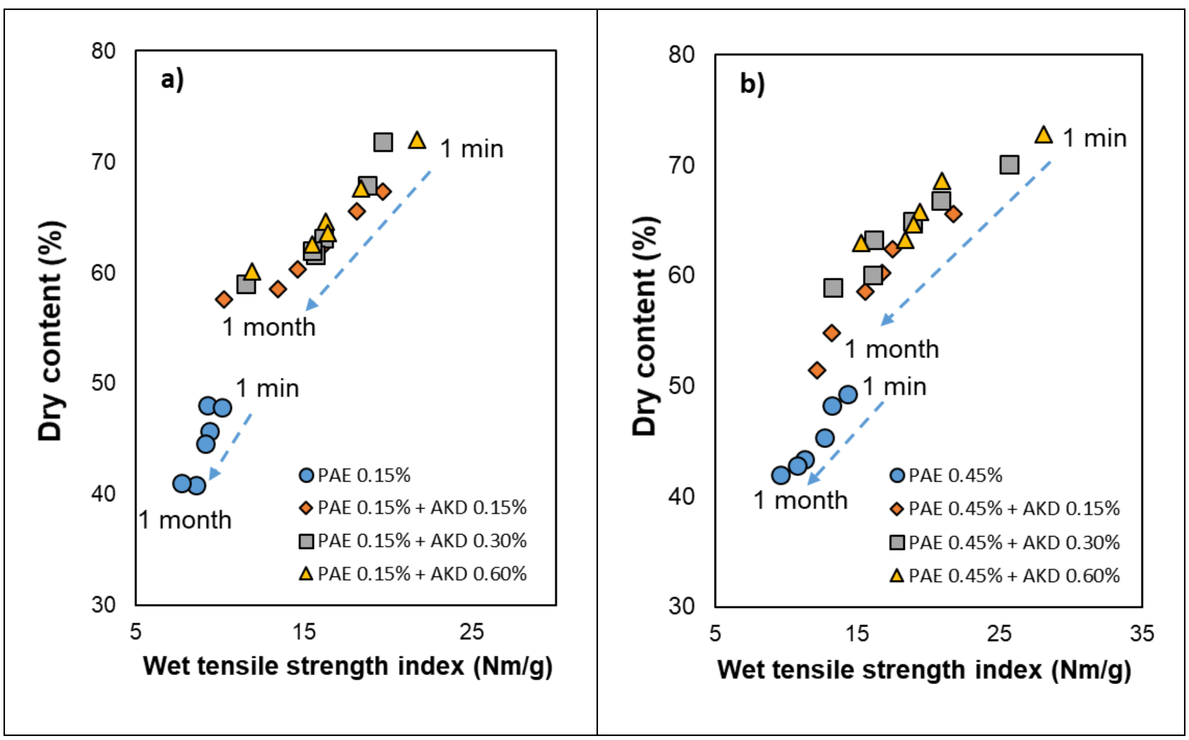

Fig. 3. The relationship of the wet tensile strength index (Nm/g) and dry content (%) of AKD internally sized NBSK handsheets wet strengthened by PAE. The "%" indicates the amounts of chemical additions in the pulp suspension. a) PAE 0.15%, b) PAE 0.45%.

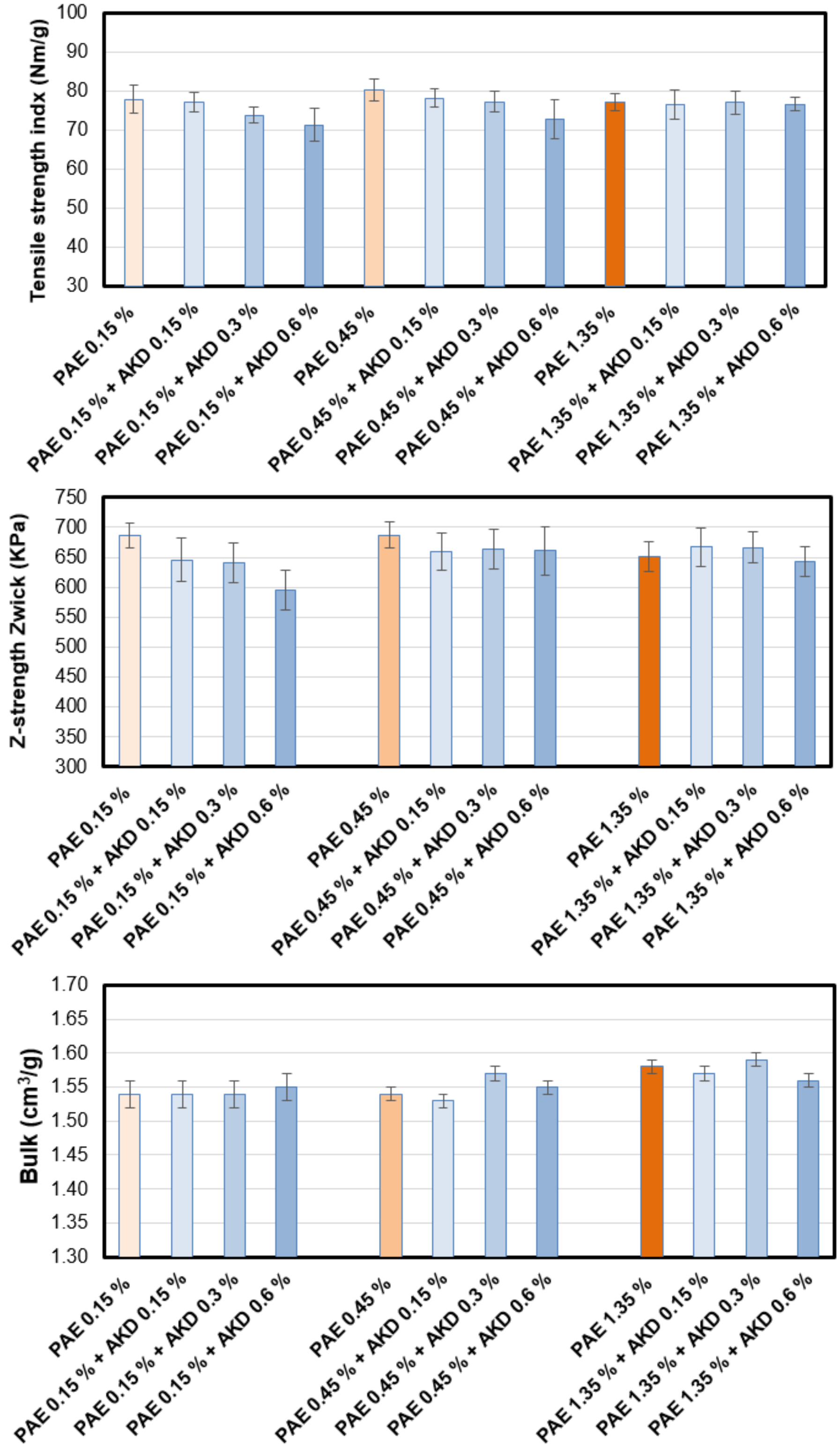

Fig. 4. The effect of AKD internal sizing on the tensile strength index (Nm/g), Z-directional tensile index (kPa) and bulk (cm^3/g) of NBSK handsheets wet strengthened by PAE. The "%" indicates the amounts of chemical additions in the pulp suspension.

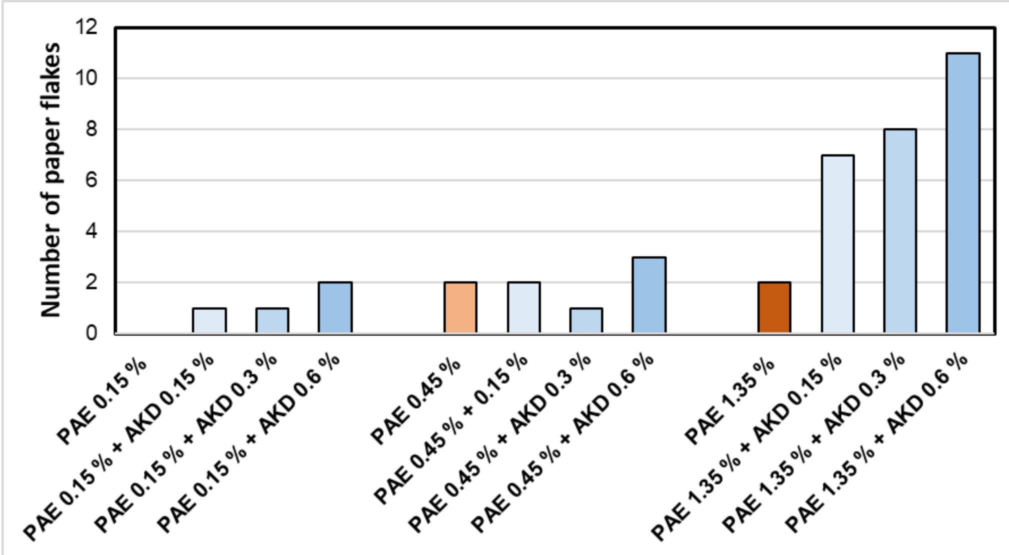

Fig. 5. The number of undispersed paper flakes (diameter > 0.15 mm) in repulped pulp

CONCLUSIONS

1. The results show that by using alkylketene dimer (AKD)-internal sizing with low or moderate added amounts of polyamidoamine-epichlorohydrin (PAE), a higher wet strength can be achieved than with a "high" added amount of PAE (1.35 wt%) alone.
2. The improving effect of AKD sizing on the wet strength of the handsheets resulted from the reduced water absorption of the handsheets. The decreasing effect of AKD on the water absorption of the PAE containing handsheets was long-lasting.
3. In papermaking, a shift from the use of high PAE dosages to the use of smaller dosages of PAE together with AKD internal sizing will likely not make dry paper notably weaker.
4. Although the use of low and moderate amounts of AKD and PAE (added amounts 0.15, 0.3 wt% and 0.15, 0.45 wt%, respectively) resulted in high and long-lasting handsheet wet strength, no sign of impaired repulpability was revealed by the repulpability test.
5. The results suggest that apart from tissue and absorbent papers, the use of small or moderate amounts of PAE and AKD in papermaking can be a viable option for paper mills facing paper quality or paper machine runnability problems related to the high dosing of PAE. The shift to lower chemical usage may be motivated also on cost-in-use basis.

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