

SUBSTITUTION OF HIGH-YIELD-PULP FOR HARDWOOD BLEACHED KRAFT PULP IN PAPER PRODUCTION AND ITS EFFECT ON ALKENYL SUCCINIC ANHYDRIDE SIZING

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In recent years there has been an increasing interest in using high-yield pulp (HYP) as a partial replacement for hardwood bleached kraft pulp (HWBKP) in the production of high-quality fine papers as a cost-effective way of improving the product performance. This study investigated the substitution of HYP for HWBKP and its effect on the Alkenyl Succinic Anhydride (ASA) sizing performance. The results showed that the substitution of an aspen HYP for HWBKP can increase the ASA sizing performance at a HYP substitution as high as 15 to 20%. The ASA addition sequence has an influence on the ASA sizing performance and first adding ASA to the HYP followed by mixing with kraft pulps was the preferred method. Using precipitated calcium carbonate (PCC) as a paper filler at a dosage of less than 20% can increase the ASA sizing performance due to the contribution of the calcium soap of the hydrolysed ASA. A PCC dosage greater than 20% resulted in a negative impact on the sizing performance. It was also found that different PCC loading sequences can also affect the ASA sizing performance.

Keywords: ASA sizing; High-yield pulp (HYP); Bleached chemi-thermomechanical pulp (BCTMP); Fine paper; Precipitated calcium carbonate (PCC)

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INTRODUCTION

High-quality fine papers are traditionally produced from a mixed furnish of bleached softwood and hardwood kraft pulps. Generally, the softwood pulp provides strength, thus a good runnability of the paper machine, while the hardwood pulp offers good surface paper properties (Hu et al. 2006). In recent years, however, there has been an increasing interest in using high-brightness hardwood bleached chemi-thermo mechanical pulp (BCTMP), also known as high-yield pulp (HYP), for a partial replacement of the hardwood bleached kraft pulp (HWBKP) in these paper grades as a cost-effective way of improving product performance. It has been reported that the substitution of HYP for HWBKP in wood-free papers showed promising results (Hu et al. 2004). The main advantages of using HYP include a low furnish cost, high bulk, good opacity, and high stiffness (Connell et al. 2000; Zhou 2004; Yuan et al. 2006; Hu et al. 2007; Gao et al. 2008). HYP also has more micro-pores than hardwood kraft fibers (Hui et al. 2009).

Internal sizing during the papermaking process is a chemical treatment to the cellulose fiber surface aimed at decreasing the penetration rate of aqueous liquid into the paper. This is achieved by introducing hydrophobic chemicals onto the cellulosic fibers (Gess et al. 2005). Alkenyl succinic anhydride (ASA), rosin acid, and alkyl ketene dimer (AKD) are the most extensively used internal sizing agents. ASA is a highly reactive sizing agent that can impart good liquid repellence to paper by decreasing the wettability of the cellulose fibers (Hubbe et al. 2006). ASA develops sizing in the paper sheet faster than other sizing agents, such as AKD (Hodgson et al. 1994). In the presence of water, however, particularly if the conditions are not carefully controlled, ASA can undergo hydrolysis. Many studies on ASA sizing have been conducted, for example, in regard to (a) the ASA emulsion stability (Lee et al. 2004; Koskela et al. 2003; Chen et al. 1986; Guan et al. 2002; Hatanaka et al. 1991; Bajpai et al. 2008; Wang and Hu 2005), (b) the ASA sizing mechanism (Wang et al. 2005; Lindfors et al. 2005; Zhang et al. 2007; Sato et al. 2000), (c) the effect of papermaking wet-end variables on its sizing performance (Fernandes and Duarte 2006; Wasser and Brinen 1998; Liden and Tollander 2004; Mccarthy and Stratton 1987; Saolainen 1996), and (d) the ASA content measurement techniques (Sato and Isogai 2003; Yano et al. 1992), all of which were limited to a HYP-free furnish. Several studies, on the other hand, have been carried out on using HYP and its effects on the sizing behaviour in the AKD and rosin acid sizing systems (Li et al. 2001, 2002a,b), but not the ASA system.

The substitution of HYP for HWBKP in the production of fine paper will change the overall surface area and change the density of the pulp furnish in reference to the bleached kraft pulp (BKP) system (Hu et al. 2004). These characteristics are expected to affect papermaking wet-end conditions, and thus, the sizing behaviour. In the current study, one of the objectives was to determine the ASA sizing behaviour of the HYP-containing furnish. Precipitated calcium carbonate (PCC) as inorganic filler is commonly used in the manufacturing of fine paper; therefore, this study also investigated the effect of adding PCC to the HYP-containing pulp furnish on the ASA sizing performance.

EXPERIMENTAL

Raw Materials

The softwood bleached kraft pulp (SWBKP), HWBKP, and aspen HYP were all market pulps from Eastern Canadian mills. A PCC sample was obtained from Specialty Minerals. Cationic polyacrylamide (CPAM) (Percol® 292) was received from Ciba. The ASA, alum, poly-aluminum chloride (PAC), and cationic potato starch (CS) (Degree of Substitution, DS 0.03) were all commercial products received from a mill.

Preparation of the ASA Emulsions

The ASA aqueous emulsions were freshly prepared using the following procedure. The cationic potato starch slurry at 4% solids was heated to 95°C and held at that temperature for 30 minutes with stirring. The cooked starch was cooled to room temperature, and then ASA was added for emulsification. The amount of liquid ASA in the emulsion was 1%, and the mass ratio of cationic starch to ASA was 4:1. ASA

emulsions were prepared in batches with a variable-speed homogenizer (IKA, T25, Germany). For the emulsification, the rotor speed was set to 20,000 rpm, and the shearing time was 2 minutes. The micrograph results (Fig.1) indicated that the ASA emulsion prepared was uniform and homogeneous.

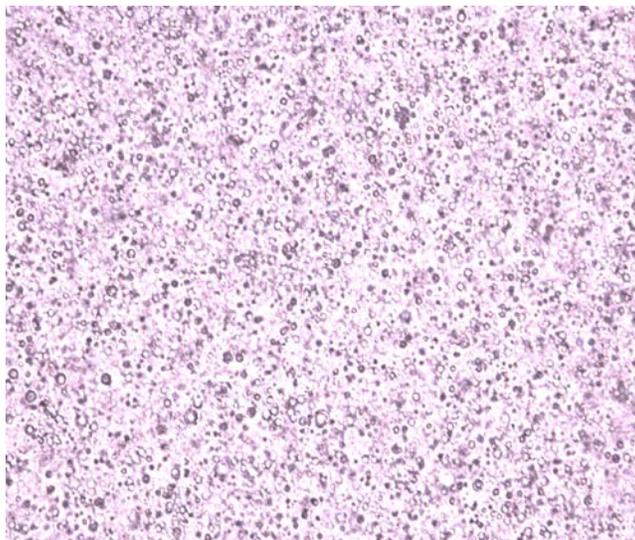


Fig. 1. Micrograph of ASA emulsion (Enlargement:x200)

Fiber Analysis

The surface charge density of fibers was determined based on the polyelectrolyte colloidal back titration method using a Particle Charge Detector, Müttek PCD 03 (Herrsching, Germany) titrator (Tanaka et al. 1990; Lofton et al. 2005). Poly-diallyldimethylammonium chloride (Poly-DADMAC) was used as the cationic polymer, and potassium polyvinyl sulfate (PVSK) was used as the anionic polymer. About 0.2 g of oven-dried pulp (either SWBKP, HWBKP, or HYP) was added to 50 mL of 0.5 mN poly-DADMAC solution, and the pH of the solution was adjusted to 7. The suspensions were immersed in a water bath shaker (Innova 3100, Brunswick Scientific, Edison, New Jersey, USA) and shaken (150 rpm) at 30°C for 2 hours. The suspensions were then filtered and 2 mL of the solutions were taken for the charge density determination using a PVSK solution (0.5 mN). Three repetitions were conducted for each sample, and the average was taken as the charge density.

The pulp characteristics were determined using a Fiber Quality Analyzer (FQA, OpTest Equipment Inc, ON, Canada). Fibers smaller than 200 μm were counted as fines. The pulp freeness was measured using a Canadian Standard Freeness (CSF) tester according to the TAPPI method: TAPPI T 227.

Handsheet Preparation

The SWBKP and HWBKP were refined in a PFI mill to 400 CSF and 500 CSF, respectively. The aspen HYP was used as received without further refining treatment. To prepare ASA-sized handsheets, a pulp slurry of 0.3% consistency was prepared, which consisted of the mixed pulp furnishes. When required, the following was added to the

pulp in the respective order: PAC or alum, ASA emulsion, PCC, and CPAM. The delay time of the chemicals was 45 seconds, and the dosage of CPAM was 0.05%. The pH of the slurry was adjusted before sheet formation.

Handsheets with a basis weight of 60 g/m² were prepared according to the TAPPI method T205 om-88. The number of paper sheets prepared for each condition was six. Sizing testing was then carried out after reconditioning the handsheets at 23°C and 50% relative humidity for more than 12 hours in accordance with TAPPI method T530 om-96 (Hercules Size Tester, HST); six HST results were obtained, and the average was reported.

RESULTS AND DISCUSSION

Pulp Characteristics

The characteristics of the SWBKP, HWBKP, and HYP are shown in Table 1. The surface charge density of HYP was significantly higher than that of BKPs, which were in agreement with those reported earlier (Hu et al. 2004). The high charge density of the HYP is attributed to the amounts of carboxylic and unique sulfonic groups present in the HYP (Li et al. 2002a,b). The SWBKP had the highest fiber length, while the HYP had a similar fiber length to the HWBKP (consisting mainly of aspen). The HYP showed the highest fines content, and thus, the highest surface area (Liu et al. 2010).

Table 1. Characteristics of the SWBKP, HWBKP, and HYP Samples

Pulp type	CSF, mL	Surface charge density, µeq/g	Fiber length (LW), mm	Fines content, (wt), %
SWBKP	400	-15.6	2.13	36.2
HWBKP	500	-21.8	0.76	20.4
HYP	460	-110.5	0.78	43.6

Effect of ASA Emulsion Storage Time

The prepared ASA emulsion was added to the mixed pulp furnish of 30% SWBKP, 50% HWBKP, and 20% HYP, and the paper sheets were made. The results in Fig. 2 show that the freshly prepared ASA emulsion had a noticeable sizing effect on the paper sheet.

Figure 2 also shows that the sizing degree decreased as the ASA emulsion storage time increased; however, the decrease in sizing degree was small when the ASA emulsion was stored for less than 2 hours. The sizing degree then decreased significantly, and after 24 hours the ASA emulsion had completely lost its sizing ability. The ASA emulsion underwent hydrolysis in the presence of water, which was responsible for the loss in sizing degree when extending the storage time (Gess and Rende 2005). It is well accepted in the industry that fresh ASA emulsion should be used immediately, or at most should only be stored for a short period of time.

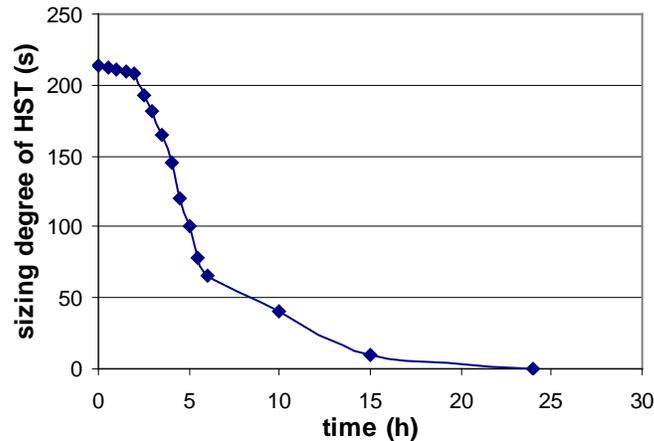


Fig. 2. Effect of the ASA emulsion storage time on its sizing efficiency (PAC: 1.0%, ASA: 0.3%, pH: 8.0)

Effect of HYP Substitution on ASA Sizing

Figure 3 shows the change of ASA sizing degree of handsheets made of 30% SWBKP, 40 to 70% HWBKP, and 0 to 30% HYP (the HYP was substituted for the HWBKP at various ratios). 2% PAC or alum was used due to its ability to anchor the ASA size on the surface of fibers and improve the ASA size retention, thus increasing the size efficiency (Hodgson 1994; Awate et al. 2007).

As shown, the ASA sizing degree was higher with HYP, reaching a maximum at about 20% HYP substitution (an increase of 73.2%) for the PAC system. For the alum system, about 15% HYP substitution showed the best sizing performance, and the sizing degree increased by 35.2%.

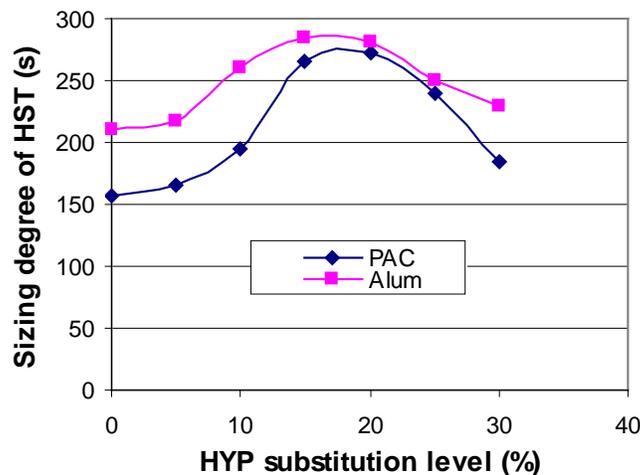


Fig. 3. Effect of HYP substitution on ASA sizing (2.0% PAC or 2.0% alum, 0.3% ASA,)

The sizing degree was lower at higher HYP substitutions, although it was still higher than that of the HYP-free furnish. These results can be explained by the fact that HYP contains more anionic groups (carboxylic and sulfonic groups), which helps retain the ASA size and increase the sizing degree (Li et al. 2001, 2002a,b). Similar results were reported for AKD and rosin sizing of HYP systems (Li et al. 2001).

HYP also contains large amounts of lignin and fines, which have negative effects on ASA sizing; this explains why a very high HYP substitution leads to a low ASA sizing degree. These results are in agreement with those of an earlier study that investigated the HYP substitution on AKD sizing behavior (Hu et al. 2004).

Effect of pH on ASA Sizing

The effect of pH on ASA sizing of sheets made of 30% SWBKP, 50% HWBKP, and 20% HYP is shown in Fig. 4. The pH was adjusted with either diluted hydrochloric acid or sodium hydroxide. The ASA sizing was effective within a wide pH range of 6.5 to 9.0, as indicated by the sizing degree greater than 270 seconds. At a pH of 6, the sizing degree was about 250 seconds. These results suggest that under industrial conditions a good sizing degree can be obtained from ASA sizing when the HYP-containing furnish is used. For AKD sizing of the HYP system, it was reported that the sizing effect at a pH lower than 7 was limited (Hu et al. 2004). These results confirm the conclusion that ASA sizing has a wider pH range than AKD sizing.

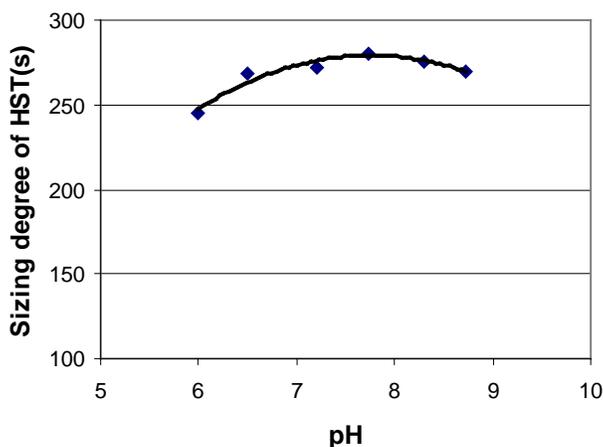


Fig. 4. Effect of pH on ASA sizing (2.0% PAC, 0.3% ASA, pH of 8.0)

ASA Addition Sequence

Figure 5 shows the results from three different ASA adding sequences: i) adding PAC (alum) and ASA to the HYP first, then mixing with BKP; ii) adding PAC (alum) and ASA to the mixture of HYP and BKP; and iii) adding PAC (alum) and ASA to the BKP first, then mixing with HYP. The furnish components were 30%SWBKP, 50% HWBKP, and 20% HYP. It is evident that for both the PAC and alum systems, the sizing degree was the highest for the sequence that added the ASA to the HYP, subsequently mixing with BKP. The results can be explained by the presence of a higher amount of carboxyl groups and unique sulfonic groups in HYP, which, as mentioned earlier, is beneficial for ASA sizing. Liu et al. (2010) reported that when using C-PVA as a

strengthening aid, the addition of C-PVA to the HYP first, subsequently mixing with the blend of SWBKP/HWBKP improved the paper properties more significantly than the addition of C-PVA directly to the mixed furnish of SWBKP/HWBKP/HYP.

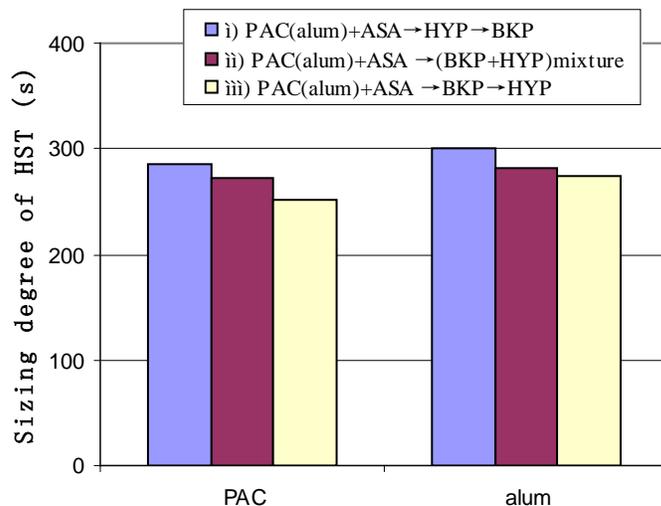


Fig. 5. Effect of different ASA addition sequences on ASA sizing (2.0% PAC or 2.0% alum, 0.3% ASA, pH of 8.0)

PCC Loading

Figure 6 shows the effect of PCC loading on ASA sizing of the paper sheets made of 30% SWBKP, 50% HWBKP, and 20% HYP. The PAC and ASA were first sequentially added to the mixed pulp, followed by the addition of PCC and CPAM. The results show that the sizing degree increased by about 27% at a PCC loading between 10% and 20%. A further increase in the PCC loading resulted in a decrease in the sizing degree; at a PCC loading of 40% the sizing degree decreased by about 84%.

The observed results are somewhat different from the results reported by Fernandes and Duarte (2006), who found that: 1) less than 20% PCC loading had negligible effect on the ASA sizing efficiency in the fine papers produced from *Eucalyptus globulus* kraft pulp, and 2) more than 20% PCC loading decreased the ASA sizing efficiency. For AKD sizing, the sizing degree was found to decrease drastically in the presence of PCC in a mixed furnish containing aspen HYP (Hu et al. 2004). PCC fillers usually have a negative impact on the sizing performance because: 1) fillers have a higher specific surface area than fibers and as a result, sizing molecules preferably stay with fillers rather than fibers and ASA size attached to fillers does not contribute significantly to the sizing degree; and 2) not all fillers are retained in the paper sheet, which means that ASA size may be lost with the fillers during the papermaking process, further decreasing the sizing efficiency (Hu et al. 2004).

On the other hand, for ASA sizing, the calcium salt of hydrolyzed ASA is hydrophobic, which can impact the sizing degree (Wasser and Brinen 1998; Liu et al. 2008). This hypothesis is supported by the results shown in Fig. 7.

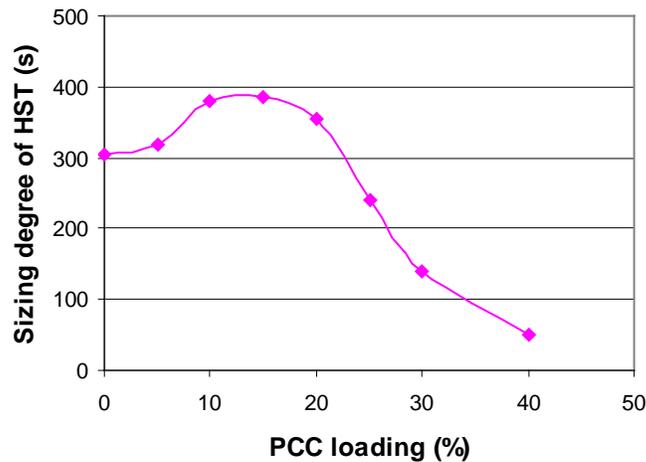


Fig. 6. Effect of PCC loading on ASA sizing (2.0% PAC, 0.3% ASA, 0.05% CPAM, pH of 8.0)

It can be found that the dissolved calcium ion has a positive effect on ASA sizing. It should be noted that in the present system with 20% PCC, the dissolved calcium ion concentration was about 1000 ppm. The sizing degree increases with an increase in calcium ion concentration. During the process, some of the ASA emulsion was hydrolyzed; the hydrolyzed ASA can form calcium salt, which is beneficial to its water resistance, thus improving the sizing degree. This hypothesis was well supported by Wasser and Brinen (1998).

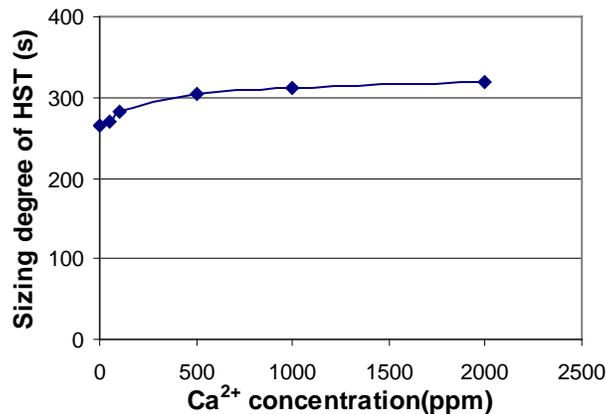


Fig. 7. Effect of Calcium ion on ASA Sizing (2.0% PAC, 0.3% ASA, pH of 8.0)

When the PCC loading was less than 20%, the increased sizing degree from the hydrolyzed ASA calcium salt was dominant, resulting in an overall positive effect of PCC on the ASA sizing degree. On the other hand, when the PCC loading was greater than 20%, the decreased sizing degree from the filler effect became dominant, and was responsible for an overall negative effect from the PCC, as shown in Fig. 6.

PCC Addition Sequence

The effect of the PCC addition sequence on ASA sizing (30% SWBKP, 50% HWBKP, and 20% HYP) was determined, and the results are shown in Fig. 8. It was found that when PCC was added before the ASA emulsion, the ASA sizing performance was not as good as the opposite sequence, i.e., adding ASA prior to the addition of PCC. This is because when PCC is added before ASA, the PCC absorbs more ASA size. With more PCC present, more ASA size will be absorbed onto PCC, leaving less ASA available for pulp fibers, resulting in inferior ASA sizing performance. Sequence 1) showed a better sizing efficiency than Sequence 2), due to the fact that the former had a higher PCC and fines retention (Wang et al. 2001).

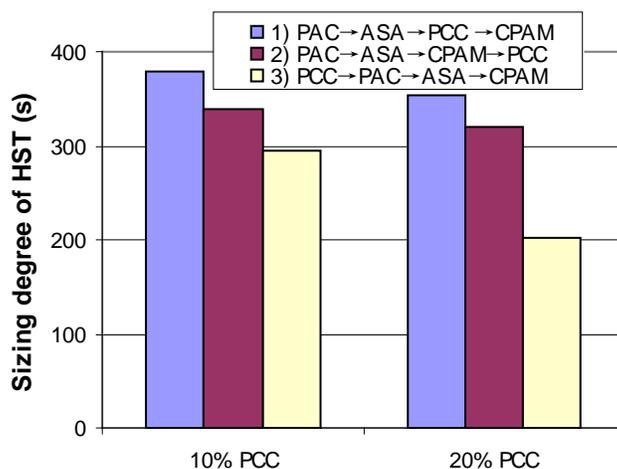


Fig. 8. Effect of different PCC adding sequences on ASA sizing (2.0% PAC, 0.3% ASA, 0.05% CPAM, pH of 8.0)

CONCLUSIONS

1. The substitution of an aspen high-yield pulp (HYP) for hardwood bleached kraft pulp (HWBKP) at a level up to 20% can increase the ASA sizing performance. The sequence of adding ASA to the HYP first, then mixing with kraft pulp, is the preferred method to yield the highest sizing degree under otherwise the same conditions, and the results can be attributed to the presence of a higher amount of carboxyl groups and unique sulfonic groups in the HYP fibers. ASA sizing was effective in the pH range of 6.0 to 9.0.
2. At a PCC load of less than 20% in the HYP-containing furnish, the addition of PCC enhances the ASA sizing performance, which can be explained by the formation of the calcium salt of hydrolyzed ASA, which is hydrophobic and contributes to the overall sizing degree. A PCC load of higher than 20% led to a decrease in the sizing performance. The best PCC loading sequence was determined to be the following in the respective order: PAC, ASA emulsion, PCC, and CPAM.

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