Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 7 (2): 280-284, 2007
ISSN 1812-5654

Refining of Polysulfide Pulps

Yalçın Çöpür
Department of Forest Industrial Engineering, Faculty of Forestry,
Duzce University, 81620 Duzce, Turkey

Abstract: This study compares the modified kraft process, polysulfide pulping, one of the methods to obtain higher pulp yield, with conventional kraft method. More specifically, the study focuses on the refining effects of polysulfide pulp, which is an area with limited literature. Physical, mechanical and chemical properties of kraft and polysulfide pulps (4% elemental sulfur addition to cooking digester) cooked under the same conditions were studied as regards to their behavior under various PFI refining (0, 3000, 6000, 9000 revs.). Polysulfide (PS) pulping, compared to the kraft method, resulted in higher pulp yield and higher pulp kappa number. Polysulfide also gave pulp having higher tensile and burst index. However, the strength of polysulfide pulp, tear index at a constant tensile index, was found to be 15% lower as compared to the kraft pulp. Refining studies showed that moisture holding ability of chemical pulps mostly depends on the chemical nature of the pulp. Refining effects such as fibrillation and fine content did not have a significant effect on the hygroscopic behavior of chemical pulp.

Key words: Hygroscopicity, kraft pulp, PFI refining, polysulfide pulp, sugar contents

INTRODUCTION

Almost 90% of the chemical pulp is produced using kraft pulping method and most of the produced kraft pulp is made into bleached pulps. Therefore, in a conventional kraft pulp, a small amount of lignin found in the pulp, which is called as residual lignin, has to be removed with subsequent bleaching operations. However, bleaching is an expensive operation and results in water pollution in pulp mills. When residual lignin is removed by extending the kraft pulping to lower kappa numbers, a significant yield loss occurs due to the degradation and loss of undesirable wood components, cellulose and hemicellulose.

Increasing the yield of kraft pulp is very desirable because pulp yield is an important economic factor in pulping. The economic benefits with higher pulp yield are increased production, reduced chemical cost and less wood consumption. In kraft pulping, research has focused on minimizing the degradation and loss of carbohydrates for improved yield and better fiber strength by modifying the kraft pulping process.

One of these methods, polysulfide (PS) pulping, which is a modified kraft pulping technology, results in substantial yield gains in both hardwoods and softwoods (Jiang, 1995; Çopur, 2002). In this method, most of the yield increase is brought about as a result of glucomannan stabilization. Also, the yield increase is found to be proportional to the PS added to the cook. The properties of polysulfide pulps are comparable to the kraft pulps. However, polysulfide pulps give higher tensile strength but lower tear strength (Jiang, 1995; Pekkala, 1986) compared to the kraft pulps.

Papermaking fibers should mechanically be refined to make them more suitable for papermaking. But refining effects differ depending on the cooking methods through which the pulps are produced. Emerton (1957) and Kibblewhite (1972) offer detailed information on the theory of refining and factors affecting the refining behavior of pulps. The tensile and burst strengths and folding endurance improve in refined sheet and this improvement is thought to be due to the increased fiber swelling and the applied stress on fibers during refining (Page, 1985). On the other hand, tear strength of a sheet always decreases with refining due to the strength attrition of individual fibers. In addition, during refining, the paper stock becomes more difficult to drain and the produced paper sheets become denser and bulkier while the porosity decreases. Limited research on polysulfide pulps showed that polysulfide pulps are easier to beat because of higher hemicelluloses content (Jameel *et al.*, 1995).

Polysulfide pulping has been practiced widely in many mills all over the world. Research on modified kraft pulping (Polysulfide) is an important endeavor to improve pulp yield while maintaining pulp properties. Therefore, the objective of this research is to study the effects of adding elemental sulfur directly to the cooking digester in kraft cook on pulp yield. More specifically, the study is concerned with the effects of refining on polysulfide pulp properties.

MATERIALS AND METHODS

Freshly cut logs from a Scots pine (*Pinus sylvestris*) were utilized as wood raw material. 4.7 L. M/K-digester was used to make kraft and polysulfide cooks. Pulping conditions are given in Table 1. The targeted H-factor was 2020. Polysulfide cook was made by adding 4% elemental sulfur based on oven dry chip weight to the digester along with the chips (added sulfur is not included in the sulfidity calculation).

After cooking, the pulps were disintegrated, washed with hot tap water (40°C) and then screened using a laboratory flat screen with a slot width of 0.006 (0.15 mm). The yield contents of the pulps and rejects were measured according to Tappi (T 210) by gravimetric measurements in the laboratory environment. The screened/unscreened yields were measured through duplicate analyses. The carbohydrate composition of the pulps was determined using the new NMR technique (Copur *et al*., 2003). Klason lignin was determined according to Tappi T 222.

Refining was accomplished using PFI mill in accordance with Tappi T 248 in which pulps were refined for 0, 3000, 6000 and 9000 revolutions. The freeness values of the pulps were determined according to Tappi T 227. Handsheets were prepared in accordance with relevant Tappi T 205 instead of 200 mesh screen to diminish the fine loss. In addition, applying high pressure (85 psi), set of handsheets were prepared using a standard press. Physical properties of handsheets were tested in accordance with the appropriate Tappi test method: tensile strength (T 494), burst strength (T 403), tear resistance (T 414), porosity (T 547)and folding endurance (T 511). The hygroscopic behaviors of fluffy pulps and handsheets (standard and high pressure) were monitored in a controlled humidity chamber. The weight of the samples were recorded when samples reached to constant weight which took 4 days.

Table 1: Pulping conditions

Method	Polysulfide	Kraft
Wood charge (g)	500	500
Active alkali, % Na_2O/weight of o.d. wood	22	22
Sulfidity, %	30	30
Polysulfide sulfur, % of o.d. wood	4	-
Liquor to wood	4/1	4/1
Time to 170°C	90	90
Time at 170°C	90	90

RESULTS AND DISCUSSION

Conventional kraft and polysulfide pulps cooked under the same conditions resulted in variations in kappa number and pulp yield (Table 2). The variations could be due to the 4% elemental sulfur addition directly to the cooking digester in polysulfide pulping. On the other hand, the use of polysulfide lowered the kappa number while stabilizing the carbohydrates by oxidizing reducing end groups (Jiang, 1992). But contrary to the finding of Dillen and Noreus (1967), in this study, polysulfide was found to give a higher kappa number than that of corresponding kraft pulp (Table 2) consistent with what Jameel *et al*. (1995) observed. The possible reasons for this observation could be that the hydroxide that is used for delignification decreases quickly since the polysulfide sulfur reacts with hydroxide and oxidizes organic material. Moreover, it is known that higher sulphidity accelerates the delignification rate more when the alkali charge is low (Paavilainen, 1989). In other words, high sulphidity at high alkali charge may lower the delignificaiton for polysulfide pulp resulting in higher kappa number as observed in this study. As a result, if low kappa numbers are desired with polysulfide pulping, the active alkali must be increased or sulphidity must be decreased in cooks.

In terms of pulping yield, in this study, the yield of polysulfide pulp was found to be 3.8% higher compared to kraft method. Yield increase in polysulfide pulping depends on two main factors: the amount of added sulfur and the resultant pulp kappa number. In literature, yield increases of 1.5% (Jiang, 1995), 4.5% and 11% (Dillen and Noreus, 1967) were reported when 2%, 3%and 12% sulfur was added in polysulfide pulping, respectively. The percentage of yield increase in this study was lower than that of 4.5% reported by Dillen and Noreus (Dillen and Noreus, 1967). This result could be explained by higher delignification rate due to the higher alkali charge and sulphidity in this study. Another possible factor for the lower pulping yield in this study could be the secondary peeling reactions taking place during polysulfide pulping which render yield loss prevention ineffective. The carbohydrate analysis on the other hand showed that yield increase by sulfur addition is brought about by the stabilization of glucomannan and xylan in polysulfide pulping (Table 2) as also observed earlier by Jiang (1995).

Results of physical and mechanical properties are summarized in Table 3. The beatability of the pulps was evaluated based on the development of the tensile index after a given number of revolutions in a PFI mill (Table 3). The results showed that kraft pulp required higher number of PFI revolutions and thus required higher refining energy to reach certain freeness. The ease of polysulfide

Table 2: Data on pulps kraft and polysulfide

Method		Polysulfide	Kraft
Kappa (mL g^{-1})		32.6	28.1
Yield (% of o.d. wood)	Total	47.7	43.9
	Reject	1.4	1.5
Sugars (% of total carbohydrates)	Arabinose	0.20	0.31
	Galactose	0.59	0.40
	Glucose	83.6	87.1
	Mannose	12.1	9.29
	Xylose	3.49	2.88
Hemicullulose**	(% o.d. pulp)	19.4	15.3

** Arabinose+galactose+mannose+xylose+/3 mannose (glucomannan)

Table 3: Handsheet properties of pulps at three refining levels

Method	Polysulfide				Kraft			
Refining degree (rev.)	0	3000	6000	9000	0	3000	6000	9000
Freeness (mL)*	783	641	477	337	795	688	615	447
Porosity**	2524	1007	172	48	3522	1717	1092	335
Tear Index, (mN m^2/g)	24	23	23	22	28.3	25.5	25.0	23.3
Folding endurance (count)	350	874	1336	1388	140	745	896	765
Tensile index (N-M/Gm)	56.0	90.3	100.6	103.1	49.1	70.0	78.3	82.0
Burst Index (kPa m^2/g)	3.89	7.42	7.66	8.02	3.23	5.25	5.99	6.32

* Corrected based on consistency (0.2%) and temperature (20°C), ** Sheffield porosity tester with orifice # 1. Values are averages of wire and top sides

pulp refining is ascribed to higher hemicellulose retention in pulp, however; this might be a disadvantage due to the higher moisture holding capacity of polysulfide pulps especially at higher humidity conditions (Table 3). Polysulfide pulp showed higher tensile (Table 1) and burst index compared to the kraft pulp. The higher tensile index could be explained by higher fiber flexibility leading to improved inter-fiber bonding as a result of higher hemicellulose content (Table 2). On the other hand, higher burst index of polysulfide pulp could be explained by the higher kappa number of the initial brownstock as also observed by Parthsarathy *et al.* (1995).

On the other hand, polysulfide pulp had lower tear strength than the kraft pulp. For polysulfide pulp, a constant tear value was observed but the tear value of kraft pulp decreased through refining as it was refined to higher tensile index (Table 2). It is well known that refining decreases the tear strength of pulps after reaching an initial maximum. Lower tear strength could be explained by the fact that polylsulfide pulps carry higher hemicellulose content which makes fibers more flexible. Also, polysulfide pulp, having higher pulp yield, produces fewer load-bearing fibers at certain sample weight. In addition, it is suggested that (Hakanen and Teder, 1997) higher glucomannan and lower cellulose contents may be the reason for lower tear strength of polysulfide pulp, because cellulose is the main contributor to tear strength. However, it should be noted that in this study, polysulfide pulp had higher (0.8% relative difference) cellulose content than it was reported in the literature (Hakanen and Teder, 1997). This shows that earlier explanations, such as hemicellulose content have premier effect on pulp tear strength.

In this study, the addition of 4% sulfur resulted in a higher tensile and lower tear strengths. Consequently, the strength of polysulfide pulp, which is described as tear

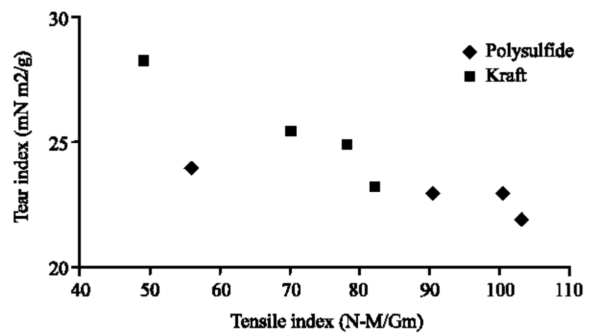

Fig. 1: Tear vs. tensile strength of kraft and polysulfide pulps at different numbers of refining in PFI mill

index at a constant tensile index, was found to be ~ 15% lower than kraft pulp, which is inconsistent with the earlier observation (Kleppe, 1975). It seems that refining has a positive effect on polysulfide pulp strength after 3000 (revolutions) in PFI mill (Fig. 1). The inherent fiber strength, as found earlier (Jameel *et al.*, 1995), is better in polysulfide pulp; therefore, through optimized refining, it might be possible to correct the lower strength of polysulfide pulp. In addition, similar to earlier finding (Parthsarathy *et al.*, 1995), in this study too, the PS pulp had lower double fold than the kraft pulp.

The hygroscopic behavior of pulps was studied for fluffy pulps and standard handsheets. Moisture holding ability of fluffy pulps and handsheets showed variations. Fluffy pulps hold an average of 1.75% (relative difference) more moisture at 80% RH for both polysulfide and kraft pulps (Table 4). This could be explained by the consolidation during the forming of handsheets which results in less free OH groups available for moisture as a result of more hydrogen bonds in/between fibers. The variation, on the other hand, was higher for polysulfide

Table 4: Moisture of the pulps at different relative humidity

	Moisture (% of o.d. pulp)					
	Pulps (fluffy)			*Handsheets*		
	Relative humidity (%)					
Methods-refining degree (rpm)	↓80	↓50	↓20	↓80	↓50	↓20
Polysulfide	18.3	11.7	5.84	16.2	11.4	5.01
PS-3000	18.5	12.0	5.94	16.5	11.9	5.56
PS-6000	18.1	11.7	5.59	16.8	11.3	4.55
PS-9000	18.7	11.8	5.79	16.5	11.8	5.26
Kraft	17.4	11.6	5.82	15.7	11.4	5.09
Kraft-3000	17.2	12.0	5.86	15.9	10.9	5.66
Kraft-6000	17.0	11.8	5.45	15.5	11.6	5.31
Kraft-9000	17.8	12.0	5.64	15.9	11.7	5.44

(1.9% relative differences) compared to kraft (1.5% relative differences). This might be due to the flexibility of the polysulfide fibers caused by higher hemicellulose content which leads to better consolidation and less free OH groups in handsheets.

The results observed for the fluffy pulps and standard handsheets were similar for both polysulfide and kraft methods (Table 2). At 80% RH, polysulfide, which has more hemicellulose, held higher moisture (0.9% relative difference) compared to kraft pulp. This could be because hemicelluloses are the most hygroscopic cell wall constituents which have low degree of polymerization, include freer hydroxyl groups and are more amorphous. Along with the content of hemicellulose, the composition of the hemicellulose is likely to affect the sorption behavior too (Copur, 2002). Of hemicellulose components, Xylose was found to be the most hygroscopic (Copur, 2002; Salmen and Olsson, 1998)and since polysulfide contains higher amount of xylose, it should be expected that it hold more moisture content (Table 2).

When examining the effect of refining on moisture holding ability of fibers at various RH, the results unexpectedly showed that refining does not have any significant effect on moisture holding ability of pulps. It would be expected that as a result of refining, with increased available surface area, higher fibrillation, shorter fiber and higher fines, the moisture holding ability of fibers would increase. It seems that in chemical pulps the proportions of amorphous cellulose and hemicellulose are important factors affecting the moisture content of pulps. Refining effects, fibrillation, increasing fine contents etc., do not contribute much to moisture holding ability of chemical pulps. However, the fine content of mechanical pulps contributes the moisture holding ability considerably (Nanri and Uesaka, 1993). Stronger refining increases the sensitivity of the fibers and the resultant paper to moisture. Higher hemicellulose retention in polysulfide pulps seems to be a disadvantage due to the increased moisture holding capacity.

CONCLUSIONS

In this study, kraft and polysulfide pulps cooked under the same conditions showed variations in kappa number and pulp yield. Although sulfur addition in polysulfide pulping is expected to lower the kappa number and increase the yield, this study showed that polysulfide pulp gave higher kappa number that can be explained by higher sulfur content in cooking chemical that may lower the hydroxide concentration at the beginning of the cook. On the other hand, the yield increase with sulfur addition in polysulfide pulping could be due to the glucomannan and xylan retention resulting in 4% higher hemicellulose content.

Higher refining requirement with kraft pulp is due to the lower hemicellulose retention which shows the importance of pulp swelling in refining. In this study, polysulfide pulp resulted in higher tensile and burst index. Higher tensile index may be explained by higher hemicellulose retention resulting in better interfiber bonding. On the other hand, higher burst index may be due to the higher kappa number of the polysulfide pulp. Though tear index was lower for polysulfide pulp, it was constant through the refining which indicates the importance of hemicellulose. On the other hand, kraft pulp refined to higher tensile index showed lower tear index. The strength, tear index at a constant tensile index, was found to be 15% lower for polysulfide pulp compared to the kraft pulp.

Having contained higher hemicellulose content polysulfide pulp held higher moisture indicating that moisture holding ability of pulps depends on the available OH groups in the pulp. Refining surprisingly did not have any significant effect on the moisture holding ability of pulps indicating that the chemical properties, rather than the physical properties, are the main factors affecting moisture holding ability of chemical pulps.

REFERENCES

Çöpür, Y., 2002. Fiber properties as an indication of yield in chemical pulping of pine and maple. (Ph.D. SUNY-ESF, Syracuse NY).

Çöpür, Y., D. Kiemle, A. Stipanovic, J. Koskinen and H. Makkonen, 2003. ^{1}H NMR spectroscopic determination of carbohydrates and yield in pine and maple pulps. Paperi Puu., 85: 158-162.

Dillen, S. and S. Noreus, 1967. On the influence of sulphidity and alkali charge in Kraft and Polysulfide pulping of Scots Pine. Svensk Papperstidn, 70: 122-134.

Emerton, H.W., 1957. Fundamentals of beating process: The theory and the development in pulps of papermaking characteristics by mechanical treatment. Kenley, in British Paper and Board Industry Research Association.

Hakanen, A. and A. Teder, 1997. Modified kraft cooking with polysulfide: yield, viscosityand physical properties. Tappi J., 80: 189-196.

Jameel, H., J. Gratzl, D.Y. Prasad and S. Chivukula, 1995. Extended delignification with AQ/polysulfide. Tappi J., 78: 151-160.

Jiang, J.E., B.F. Greenwood and J.R. Phillips, 1992. Combining modified continuous cooking with two stage oxygen bleaching for optimal extended delignification. SPCI, Bologna, Italy, pp: 89-99.

Jiang, J.E., 1995. Extended delignification of southern pine with anthraquinone and polysulfide. Tappi J., 78: 126-132.

Kibblewhite, R.P., 1972. Effect of beating on fiber morphology and fiber surface structure. Appita, 26: 196-202.

Kleppe, P.J., 1975. Polysulfide pulping in a dual-vessel Kamyr digester. Tappi, 58: 172-176.

Nanri, T. and T. Uesaka, 1993. Dimensional stability of mechanical pulps-drying shrinkage and hygroexpansivity. Tappi J., 76: 62-66.

Paavilainen, L., 1989. Effect of sulphate cooking parameters on the papermaking potential of pulp fibres. Paperi ja Puu., 71: 356-363.

Page, D.H., 1985. The mechanism of strength development of dried pulps by beating. Svensk Papp, 88: R30-R35.

Parthsarathy, V.R., C. Glen, S. Glen, F. Rudie, A.E. Detty and J.J. Steffy, 1995. Application of anthraquinone in extending the delignification of kraft and polysulfide pulps. Part 1. Pulping and bleaching of mixed hardwoods. Tappi J., 78: 113-125.

Pekkala, O., 1986. Prolonged kraft cooking modified by anthraquinone and polysulphide. Paperi Ja Puu., 68: 385-400.

Salmen, L. and A.M. Olsson, 1998. Interactions between hemicelluloses, lignin and cellulose; Structure property relationships. J. Pulp Paper Sci., 24: 99-103.