Drying Temperature and Hornification of Industrial Never-Dried *Pinus radiata* Pulps. 1. Strength, Optical, and Water Holding Properties

Dante E. Giacomozzi* and Olli Joutsimo

Hornification and changes in properties of bleached *Pinus radiata* pulps were studied for oven-dried pulps and compared to never-dried pulps. Evaluation of unrefined and PFI-refined pulps showed an increase in strength loss with high drying temperature. The tensile index was reduced by 40 to 55%, the tear index was reduced by 14 to 31%, and the degree of hornification, measured as WRV, increased from 25 to 34% when the drying temperature was increased from 25 °C to 130 °C. The tensile stiffness index, Scott bond, and elongation were reduced, whereas the bulk, opacity, air permeability, and light scattering values increased at high drying temperatures. Neither fiber deformations nor damages were observed to justify such reductions in strength properties. In PFI refining, pulps dried at 130 °C required three times more revolutions than never-dried pulps to develop tensile index until 70 Nm/g. Dried pulps were found to have less capability to hold water into the fibers' pore structure, as shown by water retention value. Changes in Scott bond, bulk, and water retention value suggested that besides irreversible pore closure and fibril microfibril aggregation, delamination can contribute to the observed strength loss in dried compared to never-dried pulps.

Keywords: Hornification; Drying; Water holding ability

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INTRODUCTION

The concept of hornification is widely known and has been used extensively since its introduction by Jayme (1944). This term involves the changes observed in fibers and pulps when they are subjected to drying and rewetting cycles. Among the observed changes are the reduction in strength properties and water holding ability, increment in swelling resistance, drainability, bulk and opacity, and flexibility and conformability (Jayme 1944; Lundberg and De Ruvo 1978; Nazhad and Paszner 1994; Weise 1998; Ahrens and Xu 1999; Zhang 2003; Fernandez-Diniz *et al.* 2004; Rebuzzi and Evtuguin 2006). Accordingly, the proposed mechanisms to explain the changes observed in hornification are described below (Brancato 2008):

- Irreversible pore closure: This is the most accepted mechanism for hornification. It is based on the fact that during drying, a fraction of the pores present in the cell wall collapses and closes irreversibly due to formation of internal hydrogen bonds between adjacent surfaces (Stone and Scallan 1965; Maloney and Paulapuro 1999; Maloney 2000).

- Microfibril aggregation or coalescence: Adjacent polysaccharide chains of cellulose are packed tightly when water is removed from the cell wall. This arrangement is only partially reopened after rewetting, leading to an increment in cellulose crystallinity. The aggregation in large units causes a reduction on the accessible surface (Laivins and Scallan 1993; Weise 1997; Pönni *et al.* 2012).
- Authors including Stone and Scallan (1965), De Ruvo and Htun (1983), Rebuzzi and Evtuguin (2006), and Hubbe *et al.* (2007) have explained hornification as a combination of rearrangement of cellulose molecules into fibrils *via* interfibril aggregation and irreversible pore closure due to the formation of internal hydrogen bonds.

Other proposed mechanisms are:

- Crystallization: Rebonding of fibrils to the fiber surface or cross-linking, caused by heating and aging of papers (Klungness and Caulfield 1982).
- Crosslinking: Formation of ester linkages between carboxylic acids of suitable structure and cellulosic hydroxyls during heating and drying of fibers (Back *et al.* 1967; Ahrens *et al.* 1999; Pantze *et al.* 2008). Back *et al.* (1967) postulated that natural ageing or heating of the paper in an acid environment promotes a hemi-acetal type of crosslinking between cellulose and hemicelluloses which restricted the swelling and make fibers brittle.
- Hemicelluloses loss: High hemicelluloses content reduces the hornification effects due to the capacity of them to retain water and reduce the possibility of total collapse of the pores (Oksanen *et al.* 1997; Rebuzzi and Evtuguin. 2006). The hemicellulose content in pulps can be increased by hemicellulose retention in cooking, modifying the cooking conditions or by the addition and adsorption of natural polymers (amylose, xyloglucans) or cellulose derivatives as carboxymethyl cellulose (Genco *et al.* 1990; Dahlman and Sjoberg 2003; Myllytie 2009; Oksanen *et al.* 2014)

The extent of changes upon processing and drying is dependent on multiple variables related to the fiber chemistry, structure, drying method, temperature, and final dryness, among others. It is known that there is a critical solids content to which fibers can be dried without affecting their papermaking properties. Depending on the type of pulp and method applied, pulps can be dried up to 50% to 70% of solids content without losing their swelling capacity (Carlsson and Lindström 1984). As the pulp is further dried, the closer the pulp comes to bone-dried condition, the lower is the swelling capacity of the fibers and higher the changes in strength, optical, and water holding ability properties. Along the same lines, De Ruvo and Htun (1983) found that pulps prepared from sheets dried at high temperatures could not absorb as much water as virgin pulps, even after prolonged refining. It was found that pores closed during room temperature drying could be reopened, but that high temperatures caused irreversible bonding and hornification. Besides drying, hornification phenomena can be observed during wet pressing, as was postulated by Robertson (1964). Studies by Zhang (2003) showed that fiber flexibility is progressively reduced as pulps were dried at temperatures between 25 °C (air-dried) and 175 °C (oven-dried). Flexibility was reduced at high drying temperatures, even after refining. Oven-dried pulps were less flexible than never-dried or air-dried pulps. Welf *et al.* (2005) published a study in agreement with Zhang (2003), concluding that drying intensity influences the extent of WRV loss.

The objective of this study was to analyze changes in *Pinus radiata* fibers during drying and how these variations can be related to changes in the cell wall morphology. The present study is conceptualized as the second of four publications related to changes in chemistry and cell wall structure along the kraft process and how these changes affect the papermaking properties of *Pinus radiata* fibers (Joutsimo and Giacomozzi 2015).

Even though *Pinus radiata* is not used extensively in pulp production in the northern hemisphere, it is indeed widely used in kraft pulp production in the southern hemisphere. It is the main raw material for softwood market pulp in Chile, Brazil, Australia, and New Zealand. Despite the fact that hornification causes have been widely studied, bibliography for *Pinus radiata* fibers is limited compared to other softwood species such as *Pinus sylvestris* and *Picea abies* (Finland, Sweden); *Pinus contorta* and Douglas fir (Canada); or *Pinus elliotti* and *Pinus taeda* (USA). In addition, literature about changes in cell wall structure of *Pinus radiata* during processing and/or drying is of great interest to understand where and how the papermaking properties of these fibers are modified.

EXPERIMENTAL

Industrial, never-dried pulps from *Pinus radiata* were oven-dried in laboratory at different temperatures to the range 92%-93% final dryness. Never-dried and oven-dried pulps were compared based on PFI refinability, strength properties, optical properties, water holding ability, degree of hornification, and morphology. Carbohydrate composition of the never-dried pulp is also presented.

Materials

Never-dried, bleached *Pinus radiata* pulps were obtained from the drying area in a softwood pulp mill in southern Chile.

Methods

Sampling and sample management

Never-dried pulps (60 liters, 3% consistency) were obtained from the feed to the primary cleaners in the drying area in three batches (2 h between each batch, 20 L each). The pulp samples were homogenized, gently dewatered by hand until 20 to 22% solids content was reached, and stored in sealed bags at 4 ºC until drying and testing. These bleached pulps were sampled under normal operation at the mill, based on low-solids cooking (kappa 28±1), double oxygen delignification (Oxytrac, kappa O_2 12±0.5), and ECF bleaching ($DE_{op}DED$ sequence, 89 to 90% ISO brightness).

Carbohydrate composition

Carbohydrate composition of never-dried pulp was determined by HPLC at VTT, Finland, based on SCAN-CM 71:09.

Drying studies for PFI refining

Sixty sheets of 950 g/m^2 basis weight were prepared in TAPPI sheet formers using never-dried pulp sampled from the mill. These sheets were separated in five groups of 12

sheets each. The first group of 12 sheets was chopped, homogenized (180 g o.d. approximately), refined in a PFI mill, and tested according to TAPPI 220 sp-96. The other four groups of sheets were chopped, and oven-dried at 25 ºC, 50 ºC, 90 ºC, and 130 ºC, respectively. After drying (92 to 93% final solids content), sheets were chopped and stored in a cold room (4 ºC) until PFI refining. Pulps were disintegrated (10,000 revolutions in a TAPPI disintegrator) and refined in a Hamjern Maskin AB PFI mill according to ISO standard 5264/2-2003. TAPPI handsheets for testing (T 205 sp-06) were produced from the never-dried and dried pulps. Pulp properties were evaluated at 0, 500, 1,500, 3,000, 6,000, and 10,000 PFI revolutions. Tests included strength properties (TAPPI 220 sp-01), optical properties (ISO 2470-2 2008), morphology (L&W Fibertester Analyzer 912), water retention value (ISO 23714:2007), and intrinsic viscosity (TAPPI 230 0m-08)

RESULTS AND DISCUSSIONS

This section contains the results for optical properties, water-holding ability, degree of hornification and morphology analyses for never-dried, air-dried, and oven-dried *Pinus radiata* pulps. Differences between dried and never-dried pulps are presented including a discussion about the possible causes for those changes.

Carbohydrate Composition

The carbohydrate composition of bleached *Pinus radiata* pulp used as base for the study (never-dried) is presented in Table 1.

Table 1. Carbohydrate Content of the Bleached Pulp Sample (never-dried) and from Bibliography (Uprichard 2002; Syverud *et al.* 2011)

Carbohydrate	Arabinose	Xylose	Mannose	Galactose	Glucose
P. radiata sample	0.6 ± 0.03	8.9 ± 0.4	4.5 ± 0.3	0.3 ± 0.02	85.7 ± 1.7
Syverud *et al.* 2011	1.1	8.6	5.3	0.3	84.9
Uprichard 2002	1.4	8.5	5.8	1.3	82.2

Compared to published data (Uprichard 2002; Syverud *et al.* 2011), carbohydrate content for *Pinus radiata* samples taken from the mill were in the expected range.

Unrefined Properties

Results for unrefined never-dried, air-dried (25 ºC), and oven-dried (50 ºC, 90 ºC, and 130 ºC) pulps are presented in Table 2.

The main results from Table 2 showed that:

- Tensile and tear indices were reduced between 40% and 55% and between 14% and 31%, respectively, when pulps were dried at 25 ºC and 130 ºC, and compared to never-dried pulps (Figs. 1 and 2). Studies by Seth (2001) showed a tensile strength reduction between 55% (at 25 °C) and 90% (130 °C) compared to never-dried pulps. The observed reduction in the tensile index for *P. radiata* pulps was lower than indicated by Seth (2001), due to the different levels of final dryness achieved (Bone-dried in Seth 2001 and 92% to 93% in the present study).

- Burst index was reduced between 48% (at 25 °C) and 69% (at 130 °C) when it was compared to never-dried pulps. Higher reductions in tensile and burst indices were observed in the present study compared to previous reports by Dang *et al.* 2007. Dang reported a 12% reduction in tensile index and 19% in burst index when bleached softwood pulps were dried at 25 ºC and compared to pulps dried at 105ºC in a hot plate.
- Tensile energy absorption was reduced between 60% and 75%. Reduction in TEA values shows that papers made from dried fibers are less capable of absorbing and transferring energy, thus reducing the measured strength of the paper web.
- The strength reduction (in tensile, tear, burst, TEA) could be related to diminished bonding ability of the fibers, reduced individual fiber strength (longitudinal) or a combination of both mechanisms.

Table 2. Unrefined Properties of Never-Dried, Air-Dried, and Oven-Dried *Pinus radiata* Pulps Including Confidence Interval at 95% (C.I.)

Property	Unit	**Never-Dried**		**Air-Dried**		**Oven-Dried**					
				25ºC		**50ºC**		**90ºC**		**130ºC**	
		Value	*C.I.*	***Value***	*C.I.*	***Value***	*C.I.*	***Value***	*C.I.*	***Value***	*C.I.*
Schopper Drain.	ºSR	***12.5***	*0.20*	**12.0**	0.19	**12.0**	0.19	**11.5**	0.18	**12.0**	0.19
Water Ret. Value	g/g	***1.58***	*0.01*	**1.18**	0.01	**1.13**	0.01	**1.10**	0.01	**1.05**	0.01
Tensile Index	Nm/g	***35.9***	*1.89*	**21.5**	1.13	**17.2**	0.90	**17.3**	0.91	**16.3**	0.86
Tens. Stiff. Index	kNm/g	***4.75***	*0.24*	**3.48**	0.17	**2.69**	0.13	**2.73**	0.14	**2.58**	0.13
Elongation	%	***2.86***	*0.14*	**1.87**	0.09	**1.83**	0.09	**1.86**	0.09	**1.63**	0.08
Tens. En. Abs.	mJ/g	***0.76***	*0.04*	**0.30**	0.02	**0.23**	0.01	**0.24**	0.01	**0.19**	0.01
Tear Index	mNm^2/g	***18.0***	*0.34*	**15.5**	0.29	**13.7**	0.26	**13.2**	0.25	**12.4**	0.23
Burst index	$kPam^2/g$	***2.90***	*0.15*	**1.50**	0.08	**1.20**	0.06	**1.00**	0.05	**0.90**	0.05
Bulk	cm^3/g	***1.64***	*0.04*	**2.00**	0.05	**1.95**	0.05	**1.96**	0.05	**2.08**	0.06
Gurley Porosity	s/100 ml air	***1.60***	*0.12*	**1.30**	0.10	**1.30**	0.10	**1.30**	0.10	**1.30**	0.10
Scott Bond	J/m^2	***75.0***	*1.08*	**55.0**	0.80	**54.0**	0.78	**52.0**	0.75	**46.0**	0.67
Light Scattering	m^2/kg	***28.1***	*0.72*	**34.2**	0.88	**35.8**	0.92	**35.6**	0.92	**37.0**	0.95
Absorption Coeff.	m^2/kg	***0.17***	*0.005*	**0.15**	0.004	**0.15**	0.004	**0.14**	0.004	**0.16**	0.004
Opacity	%	***71.5***	*1.23*	**75.4**	1.30	**76.0**	1.31	**76.1**	1.31	**76.6**	1.32
Zero Span	N/cm	***89.0***	*0.60*	**88.1**	0.60	**88.5**	0.60	**88.1**	0.60	**88.1**	0.60

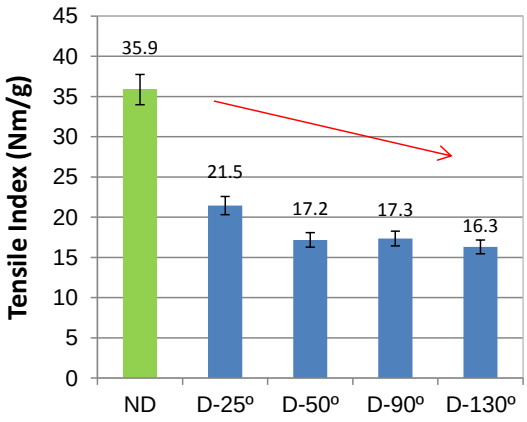

Fig. 1. Tensile index at different drying temperatures for *Pinus radiata* pulps

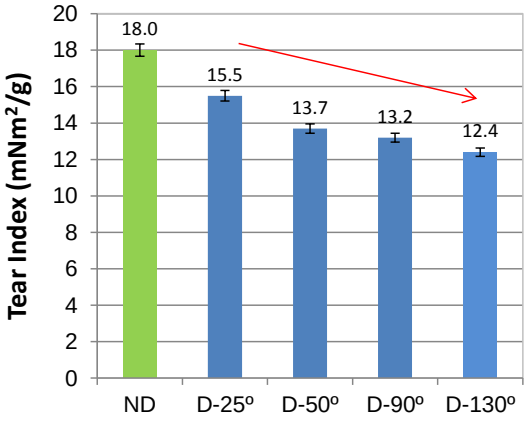

Fig. 2. Tear index at different drying temperatures for *Pinus radiata* pulps

- Scott Bond values were lower for oven-dried (50 ºC→130 ºC) compared to never-dried and air-dried pulps at 25 ºC (Fig. 3). Scott Bond measures the internal bond strength and resistance to delamination in papers and boards (Isaksson e*t al.* 2010).

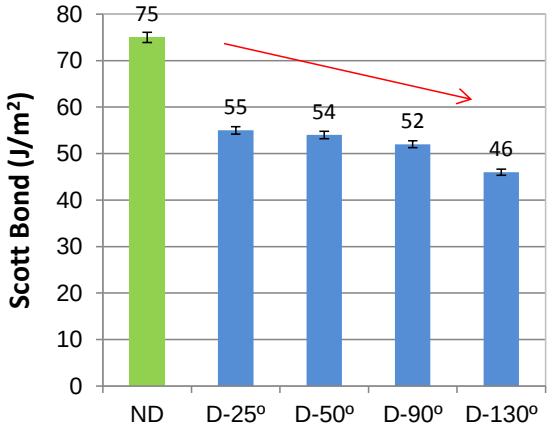

Fig. 3. Scott Bond at different drying temperatures for *Pinus radiata* pulps

- The reduction in Scott Bond could indicate that:
  - ✓ The dried fibers are less bonded and have less segment activation compared to never-dried fibers. Damages and dislocations in fibers can affect the shape and structure of the fibers, thus affecting the conformability and bonding ability of the fibers.
  - ✓ The dried fibers are in some way damaged in the z-direction, reducing the strength of the individual fibers to forces as that produced in the Scott Bond test.
  - ✓ A combination of both mechanisms.
- Zero Span was almost unchanged upon drying, which indicates that the structure of individual fibers remained more or less intact after drying (Fig. 4). According to Seth (2001), this is because zero span is more dependent on individual fiber strength to axial forces than to bonding ability of the fibers.

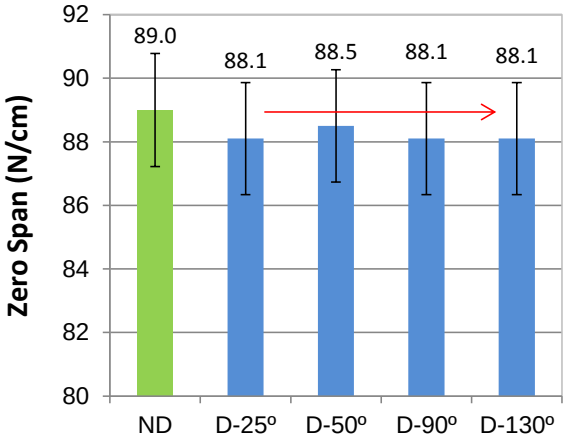

Fig. 4. Zero Span at different drying temperatures for *Pinus radiata* pulps

- Reduced Gurley porosity and higher bulk and opacity, confirmed a more open structure of sheets made from dried fibers compared to never-dried ones (Table 2).
- Water retention values were lower for dried pulps compared to never-dried pulps. These results agree with information regarding hornification and change in water holding ability of the pulps after drying (Jayme 1944; Stone and Scallan 1965; De Ruvo and Htun 1983; Nazhad and Paszner 1994; Weise 1998; Ahrens *et al.* 1999; Maloney and Paulapuro 1999; Zhang 2003; Fernandez-Diniz *et al.* 2004; Rebuzzi and Evtuguin 2006; Hubbe *et al.* 2007; Brancato 2008; and others).
- According to Jayme (1944), the degree of hornification can be determined based on water retention value before and after drying (Eq. 1), where the water retention value of the never-dried sample is WRV_0 and that of the hornified sample is WRV_1.

$$\text{Degree of hornification (\%)} = \frac{(WRV_0 - WRV_1)}{WRV_0} \quad (1)$$

Using this definition and data from never-dried and dried pulps, the degrees of hornification of pulps dried at different temperatures are shown in Fig. 5.

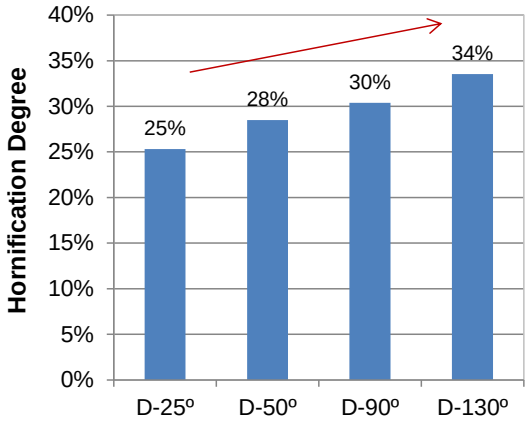

Fig. 5. Degree of hornification of bleached pulps dried at different temperatures

The increase in drying temperature in the range of 25 °C to 130 °C had a negative effect on the degree of hornification of bleached *Pinus radiata* pulps (final dryness 92% to 93%). Values obtained agree with previous studies:

- Brancato (2008) obtained values of 15% and 30% for air-dried and hot plate-dried (105 °C) softwood pulps.
- Claramunt *et al.* (2010) obtained a degree of hornification of 25% for fully bleached softwood pulps (*Pinus radiata*, Spain) after one drying-wetting cycle.
- Results from Brancato (2008) are similar to those obtained in the present study, which is consistent with the fact that both studies were based on industrial bleached pulps dried at similar temperatures and more or less the same final dryness (92% to 93% solids). The only difference was that pulps were dried under restraint in the Brancato study (Emerson Speed Dryer and Emerson microwave), and on the contrary, pulps were freely dried (oven) in the present study. In the case of Claramunt *et al.* (2010), a degree of hornification of 25% was obtained based on industrial unbleached pulps delignified and bleached in laboratory and dried at 60 °C. Under these considerations, results obtained in the present study are similar to those obtained by Brancato (2008) and Claramunt *et al.* (2010).

Fiber Morphology

Changes in fiber morphology were evaluated based on fiber length (length-weighted average), coarseness, curl, and kinks, among others. The results are presented in Table 3.

Table 3. Morphology of Pulps Dried at Different Temperatures

Sample	Length mm	Width µm	Shape %	Curl	Fines %	Coarseness µg/m	Kinks per fiber	Fiber Pop. Nº/g
ND	2.370	34.50	85.5	0.170	3.10	249.5	0.987	2.439
D-25 ºC	2.369	34.05	86.1	0.162	2.80	235.8	0.948	2.573
D-50 ºC	2.361	34.70	85.2	0.174	3.05	236.2	1.062	2.582
D-90 ºC	2.345	34.60	85.8	0.166	2.95	234.0	0.935	2.615
D-130 ºC	2.338	34.95	85.4	0.172	2.70	234.4	1.023	2.596

ND: Never-dried; D-25 °C: Air-dried at 25 °C; D-130 ºC: Oven-dried at 130ºC.

Fiber length and coarseness decreased slightly when increasing drying temperature (Figs. 6 and 7). The most likely cause is the shrinking and collapse of the fiber structure during drying, but without compromise of the strength of individual fibers. This observation agrees with zero-span tensile testing values for unrefined fibers.

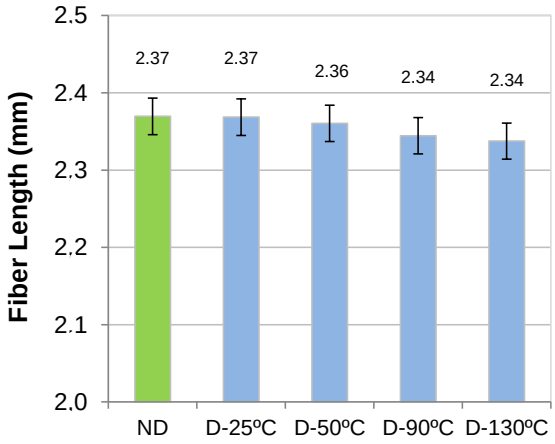

Fig. 6. Fiber length of *Pinus radiata* pulps dried at different temperatures

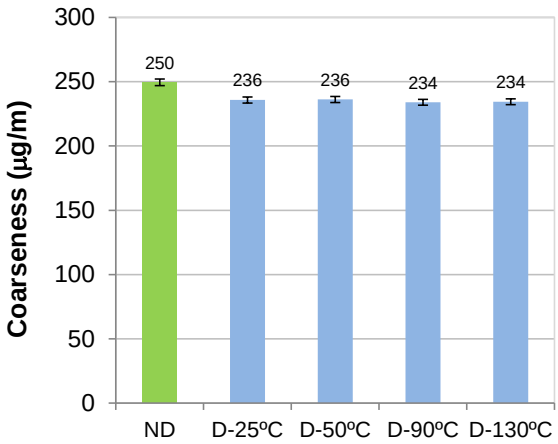

Fig. 7. Coarseness of *Pinus radiata* pulps dried at different temperatures

The following authors, MacLeod (1990, 1995, 2010), Hakanen and Hartler (1995), Hartler (1995), Nyholm *et al*. (2001), and Seth (2006) addressed the importance of the damaged and/or deformed fibers in the reduced ability of the fibers to carry and distribute load, thus reducing the strength properties of the fibers. Properties such as zero span, curls, and kinks count are important in determining the existence of such dislocations, twists, or damaged points that can affect the papermaking properties of the pulps.

According to fiber morphology results, the observed strength loss in the dried pulps cannot be attributed to fiber deformations or damages. Even if some deformations are observed, studies made by Joutsimo *et al*. (2005) showed that some kinds of deformations were introduced into fibers without significantly affecting fiber strength.

PFI Refining

PFI refining was done to evaluate the strength development in dried pulps and determine how much energy is necessary to obtain similar properties from dried fibers compared to never-dried ones. Results from PFI refining showed a 308% increase (3,700 vs 1,200 PFI revs) in required revolutions to achieve 70 Nm/g of tensile index for pulps oven-dried at 130 °C compared never-dried pulps (Fig. 8).

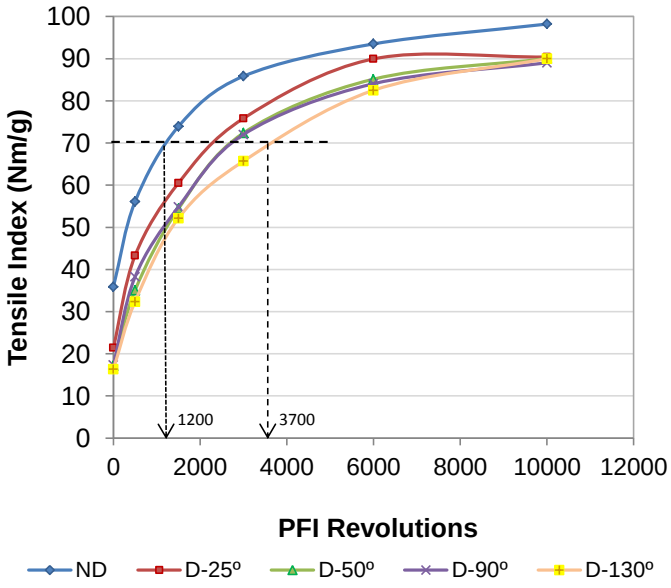

Fig. 8. PFI Revolutions to achieve tensile indices of 70 Nm/g for never-dried and oven-dried pulps

Mechanical treatments, such as refining, increase internal and external fibrillation, making fibers more conformable, but in the case of dried pulps, the initial difference in tensile strength between oven-dried and never-dried pulps was not surmountable, even with refining. In studies done by Garg and Singh (2006), the authors showed that at 10,000 revolutions, more than 10% of the maximum tensile strength was lost due to reduced bonding ability and less conformability of the dried fibers.

Compared at a standard 70 Nm/g tensile index, the tear index decreased when the samples were dried. Dried pulps presented a shift in tear-tensile refining curve to lower tear values at the same tensile, when compared to never-dried tear-tensile curve. The temperature produced pulps with lower tear indices at the same tensile index (70 Nm/g), as presented in Fig. 9.

Despite the final dryness, it is important to note that fibers dried at higher temperatures produced pulps with lower tensile strength, higher drainability, and higher refining energy requirements to reach 70 Nm/g tensile index. Dried pulps required more PFI revolutions to achieve the same Schopper-Riegler drainability, *i.e.* 25°SR (Fig. 10) compared to never-dried pulps.

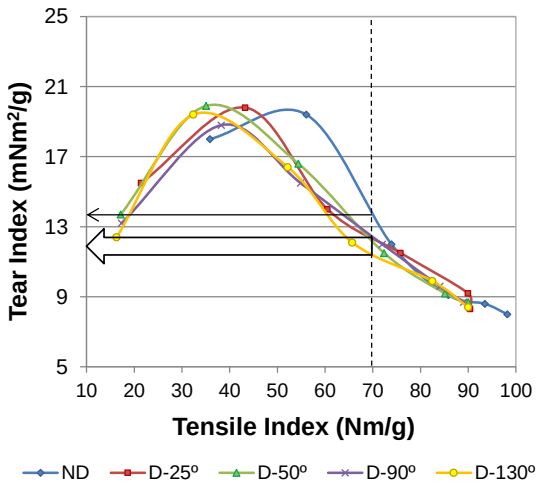

Fig. 9. Tear *vs*. Tensile index for never-dried and oven-dried pulps

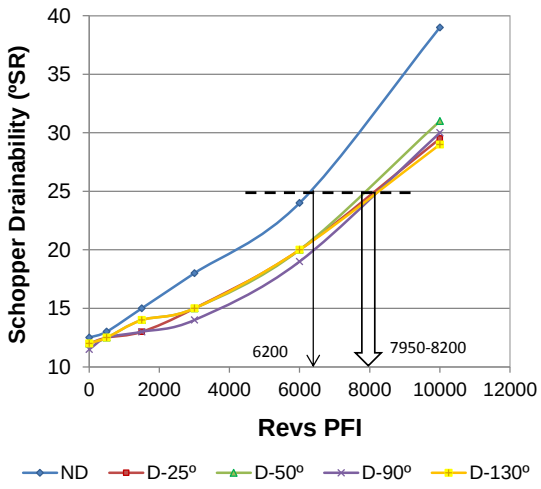

Fig. 10. Drainability *vs*. PFI Revs for never-dried and oven-dried pulp

Compared at the same drainability (25ºSR), optical properties as opacity, light scattering, and bulk increased when compared to those of never-dried pulps (Figs. 11 and 12). This result shows that even after refining, dried pulps generate bulkier sheets with high opacity and light scattering properties in both PFI-refined and unrefined pulps.

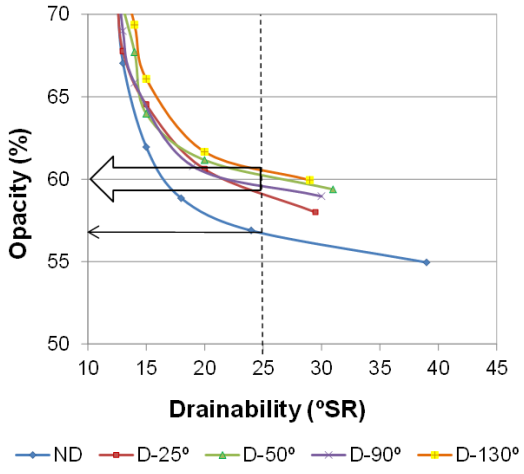

Fig. 11. Opacity *vs*. drainability for never-dried and oven dried *P. radiata* pulps

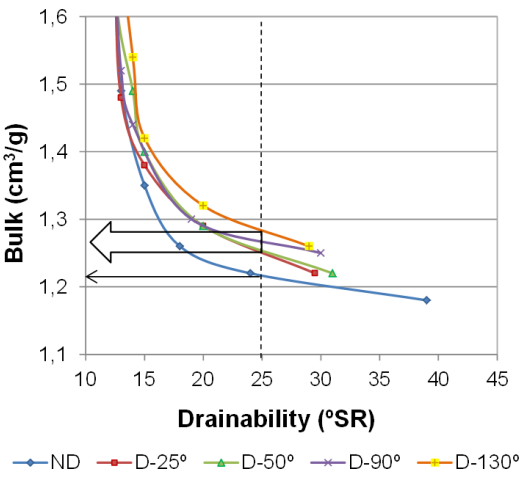

Fig. 12. Bulk *vs*. drainability for never-dried and oven dried *P. radiata* pulps

The more opened structure of the papers dried at high temperatures is maintained after refining, which was confirmed also by lower Gurley values of the dried pulps (Fig.13).

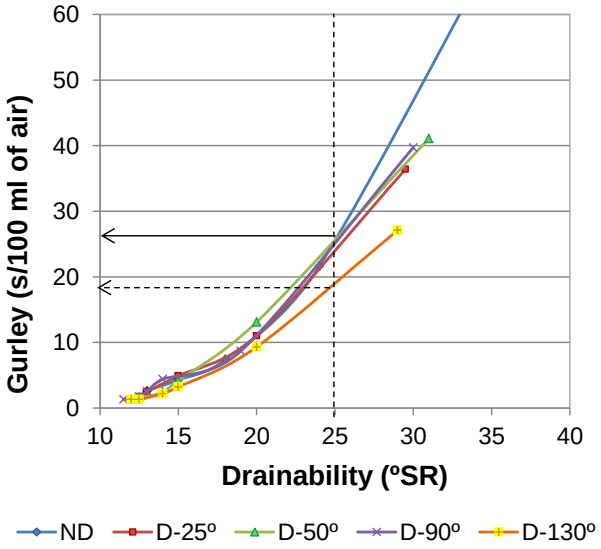

Fig. 13. Gurley air resistance *vs*. drainability SR for never-dried and oven-dried pulps

After PFI refining, there was still a clear difference in water holding ability between dried and never-dried pulps, as it is presented in Fig. 14. At 25 °SR of drainability, the loss in water retention value was 6% at 25 °C and 11% at 130 °C when compared to never-dried pulps.

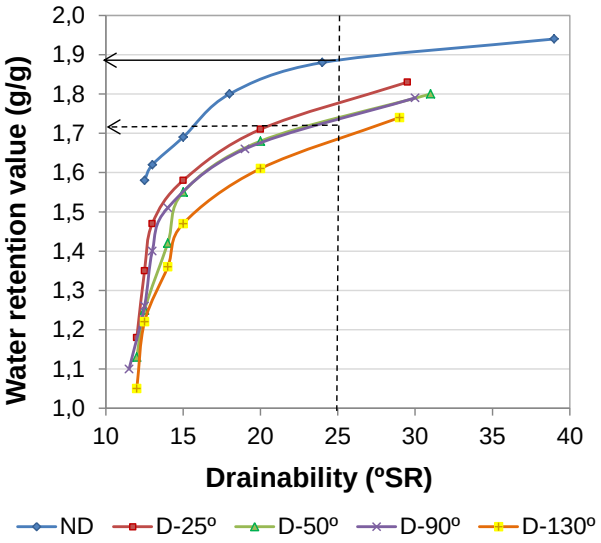

Fig. 14. Water retention value *vs*. Schopper-Riegler drainability for never-dried and oven-dried pulps

The water retention results confirmed that, even after refining, pulps showed changes in their capability to hold water molecules inside their pores.

When pulp properties are compared as a function of bulk (*i.e.* 1.40 cm^3/g), from Fig. 15 it can be observed that tensile index values were slightly higher for oven-dried compared to never-dried pulps. The result seems to be contradictory with the fact that dried pulps produce paper with lower strength properties, but it is important to remember that the

amount of refining energy required to get the same bulk is 3 to 4 times higher in the dried pulps. After drying, unrefined pulps are 19% to 27% bulkier than when they are in a never-dried condition, as was presented in Table 2. Refining generates internal and external fibrillation and reduces the specific volume of the sheets, thus increasing the contact area and strength properties such as tensile. Even though refining increases the tensile strength of the pulps, from Fig. 15 it is clear that the maximum tensile achievable was higher in never-dried than in the air-dried or oven-dried pulps. Also in the never-dried pulps, the minimum achievable bulk after refining was lower compared to dried pulps. As it is presented in Fig. 15, changes in bulk and strength after drying can be partially reversed by refining, but at 10,000 revs PFI, it is clear that sheets made of never-dried pulps were more compact and have a higher bonding degree than in their dried state.

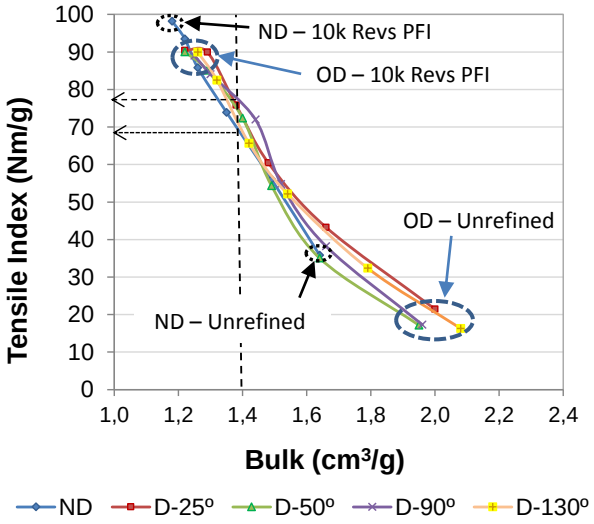

Fig. 15. Tensile index *vs.* bulk for never-dried and oven-dried pulps

Based on the PFI–refined properties, unrefined properties, and morphology it was possible to confirm most of the expected results for hornified fibers. Dried *Pinus radiata* fibers produced papers with less water holding capacity, higher bulk and opacity, and lower strength properties compared to never-dried pulps.

However, if one considers the result that dried fibers were as straight as never-dried ones, at least a couple of questions remain open:

- What is the reason for bulk and opacity increase?
- Why Scott bond values decreased after drying?
- Why after extensive refining, sheets made from never-dried pulps are more compact and have a higher tensile ceiling compared to dried pulps?

An accepted explanation is based on the hornification concept and in the aggregation of concentric lamellae in the cell wall upon drying. According to Stone and Scallan (1965), during drying at high temperatures (*i.e.* 105 ºC), and as the drying proceeds, the lamellae draw together into thicker aggregates and the total pore volume decreases. After a drying and rewetting cycle, the first pores to close do not reopen, whereas the pores closed during the later stages of the drying do so. On the contrary, low temperature drying (*i.e.* 25 ºC) does not affect the distance between lamellae. According to Stone and Scallan

(1965), drying temperature has a strong effect on lamellae separation and, as the drying temperature increased, it is more difficult to reopen pores, swell fibers, and make them more conformable, thus affecting the bonding ability of the fibers.

Another hypothesis, that can be complementary to hornification, is that during drying there is a change in the porous structure of the fibers, caused by dislocations and/or partial delamination of the cell wall. The extent of this delamination may be related to the previous processes applied to the fibers (pulping, delignification, and bleaching), and the combination of mechanical forces, chemical environment and temperature in the different stages of the process. This delamination phenomenon was previously postulated by Joutsimo (2004) as one of the possible causes for strength loss of fibers when they are subjected to mechanical treatment, as it happens in a fiberline process. Studies by Billosta (2007) using Transmission Electron Microscopy (TEM) confirmed that aggregation between individual cellulose microfibrils resulted in local retractions that create free spaces between aggregated microfibrils. Additionally, Billosta reported an increased fragility caused by the apparition of large dislocation areas in the secondary wall of the dried and rewetted fibers. Another study by Brändström *et al.* (2005) using TEM, showed different levels of delamination in recovered fibers. According to the author, concentric delamination was observed during refining, which most likely occurs in the weak areas under consecutive lamellae.

The effect of dislocations in pulp properties has been studied by Page *et al.* (1985), Hartler (1995), Nyholm *et al.* (2001), Terziev *et al.* (2005), Seth (2006), Wathén (2006), and Salmen and Hornatowska (2014). According to Salmén and Hornatowska (2014), there are at least three types of effects based on the changes in fiber structure:

- Changes in transverse fiber shape, which causes the observed differences between industrial and laboratory pulps. Main differences can be observed in higher solids content and drainability, and lower density and strength properties for industrial pulps when they are compared to laboratory pulps.
- Changes in the longitudinal direction, which affects the measured length but without compromising the individual strength of the fibers i.e. fiber curl. Such changes can be partially reversed with pressing and/or beating.
- Creation of damaged zones along the fibers, *i.e.* kinks and dislocations, affecting the structure and thus the strength of individual fibers. These changes are related to a loss in tearing resistance and lower zero span values.

Considering the presented results: loss in strength properties and water holding ability, increase in bulk and opacity, the observed changes after drying of *Pinus radiata* pulps are similar to those described as changes in the transverse fiber shape by Salmén and Hornatowska (2014). Based on this definition, is it possible to hypothesize that, besides the pore closure and microfibril aggregation, delamination of the cell wall with creation of new pores is another mechanism that contributes to strength loss of bleached pulps, as it was presented by Joutsimo (2004), Chevalier-Billosta *et al.* (2007), and Joutsimo *et al.* (2015). According to these findings, the change in process conditions both in fiberline and drying machine can contribute to reduce the observed effects in cell wall structure and thus reduce the strength loss during the kraft processing and drying of softwood fibers.

CONCLUSIONS

1. For *Pinus radiata* pulps, strength loss was higher when the drying temperature was increased. The tensile index was reduced around 40 and 55%, and the tear index was reduced around 14 and 31% when the drying temperature was shifted from 25 to 105 °C.
2. The tensile stiffness index, air resistance, and elongation were reduced at higher drying temperatures. Bulk, opacity, and light scattering increased with drying temperature.
3. The degree of hornification, measured as water retention value, was increased from 25 to 34% when the drying temperature was increased from 25 to 130 °C.
4. The Scott bond was reduced by 39% at higher drying temperatures, indicating lesser bonding between fibers, potentially caused by partial delamination of the fiber wall.
5. The observed strength losses are not related to fiber damage. Neither fiber deformation nor damage was observed following drying, as measured by fiber length, curls, and kinks.
6. The revolutions required to achieve a tensile index 70 Nm/g increased by 308% in pulps oven-dried at 130 °C as compared to never-dried pulps.
7. After drying, fiber had lesser capability to retain water into its pore structure, as determined by measuring the water retention value.
8. Results agreed with the conventional explanation for hornification based on irreversible pore closure and fibril aggregation or coalescence.
9. However, changes in Scott bond, bulk and water retention value suggests that besides irreversible pore closure and fibril microfibril aggregation, delamination can contribute to the observed strength loss in dried compared to never-dried pulps.
10. Further methods to study pores between 300 and 10,000 nm in size are required to better understand the change in pore structure during pulp processing and drying.

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