

Recycling of the Hardwood Kraft Pulp

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1. Introduction

According to „Key Statistics 2009 European Pulp and Paper Industry“ CEPI member countries produce 21,6 % of world fibre production, while North America 37,4 % and Asia 23,8 % (Key Statistics, 2009).

Pulp made by kraft process is the most widely used raw material for paper and board production.

For paper and board production is not using exclusively fresh pulp fibres. The portion of recycled fibres increases gradually.

While the portion of new and recycled fibres used in CEPI countries was equivalent in 2008, the consumption of recycled fibres (as a waste paper) increases 2.6 mil. tonnes (fig. 1).

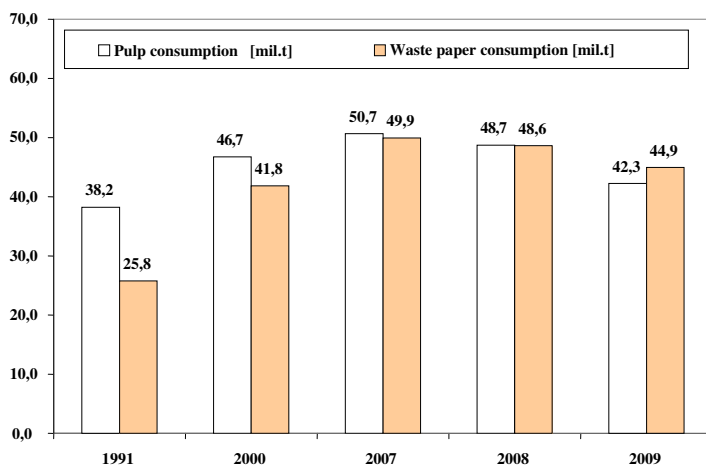


Fig. 1. Evolution of new and recycled fibres.

The year 2009 was the first year when CEPI countries consume more waste paper (44.9 mil. tonnes) than pulp (42.3 mil. tonnes) for production of 88.7 mil. tonnes of paper and board.

The usage level of recycled fibres is evaluated based on predefined parameters - waste paper utilization rate and recycling rate.

The waste paper utilization rate (percentage ratio of waste paper consumption to total paper and board production) in CEPI countries reaches v 50.7 % and recycling rate (percentage ratio of waste paper consumption to paper and board consumption) 72.2 % in 2009. Thereby the obligation of 13 different sectors of paper chain to achieve recycling level 66 % in 2010 was surpassed (www.paperrecovery.eu, 2007).

Figure 2 illustrates the evaluation of waste paper usage rate and recycling level within 1991 and 2009 in CEPI countries (Key Statistics, 2009).

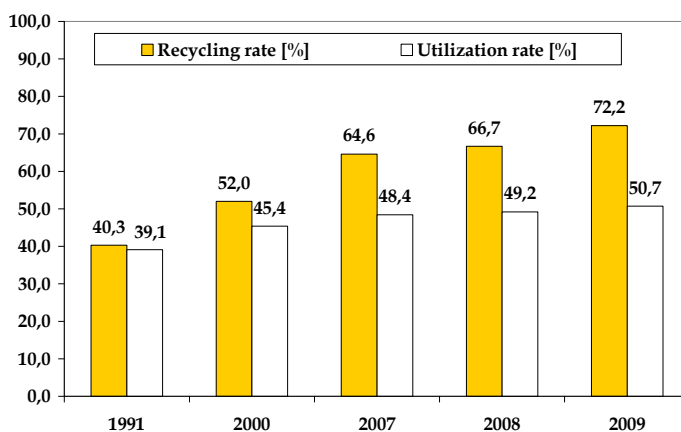


Fig. 2. Evaluation of waste paper usage rate and recycling level in CEPI countries.

Consumption of paper and board per inhabitant is one criteria of industrial and cultural country level. Average world consumption of paper and board was 56.3 kg per inhabitant in 2004. However, paper and board (P&B) consumption of some countries (USA, Finland) was around 300 kg per inhabitant in 2004 (Lešikár, 2006).

Table 1 indicates actual paper and board consumptions of some world countries. (<http://swivel.com/charts/2381-Paper-Consumption-per-capita-by-Country>).

Country	Consumption of P&B [kg/inhabitant]	Country	Consumption of P&B [kg/inhabitant]	Country	Consumption of P&B [kg/inhabitant]
Finland	334	Germany	235	Greece	76,2
USA	312	Switzerland	210	Bulgaria	35,8
Canada	277	Great Britain	208	Russia	34,5
Belgium	264	Luxemburg	198	Romania	25,6
Denmark	257	Italy	195	China	33,6
Japan	250	France	183	Vietnam	6,3
Austria	245	Spain	166	Cuba	4,7
Germany	235	Czech Rep.	116	India	4,4
Nederland	227	Hungary	82	Iran	9,8
Sweden	223	Poland	80	Iraq	1,4

Table 1. Paper and board consumption of some world countries in 2009.

Nowadays adverse price evolution in the area of hygienic paper products is examined. Increased demand for basic raw material leads to the increase in price of pulp (about 40 %) and waste paper (about 80 %) (ŠK, 2010). This evolution was influenced by enormous demand of China for fibres and waste paper. Chinese expansion of paper and board production represents 180 % within the years 1999 and 2009 (MD, 2010). Mentioned negative evolution was influenced by earthquake in Chile; floods in USA and Portugal; transporters strike etc. All these factors conduce to the input increase and the price grow of hygienic paper products at about 10 % at average (ŠK, 2010).

1.1 Paper recycling

Recycling is implemented in paper production for centuries (from 105 A.C.). Initially the paper was made from fibres obtained from old cloth. The usage of wood fibres starts from the half of 19th century (Blažej and Krkoška, 1989).

Europe has long tradition in the effort of the old paper re-usage. First notices are from 1695 (Denmark), chemical processing by decolouration was patented in England in the year 1800. Technical importance of recycling begins to increase in 20th century. Nowadays the development is focussed on old paper processing. Old paper utilization is important for national economy because of:

- Natural fibres and wood material savings,
- Decrease of specific fuel and electricity consumption for paper production,
- Water savings,
- Improvement of production economics, decrease of capital and operating costs,
- Conduce to environment protection (Blažej and Krkoška, 1989; Hnětkovský, 1982 and 1983a, b).

Paper and paper products are the most widely used transmission form of written and printed information and packaging material. Paper and board consumption is authoritative and validated parameter of society economic and cultural level. Therefore used paper is the most widespread waste. So paper occurs everywhere where people are living. Besides of very good useful paper properties, paper provides several advantages contrary to competitive material. Firstly the paper is degraded relatively quickly and without negative effect on environment. Then paper represents valuable secondary raw material mainly because of its regeneration ability after usage, collection and separation.

Waste paper occurrence, its quality and amount vary within time periods, seasons and regional relatives. It depends on paper industry production relatives of country.

European paper industry, companies focussed on paper collection and waste paper vendors are persuaded that it could be achieved more in long-term environment protection and that "paper cycle" could be closed whereas primary and secondary fibres complete each other.

Paper production, processing and utilization create waste paper which is an important source of secondary fibres. If this paper is not used, it represents valueless waste and it contaminates the environment. Nowadays waste paper is not considered as waste but it represents valuable fibre raw material which could be multiply used - recycled. Secondary fibres are routinely recycled for 3- to 5-times (Souček, 2009).

Whereas the majority of mixed grades and OCC grades of recovered paper primarily find use in the production of packaging papers and board (84 %), almost all deinking grades (88 %) go to graphic paper production (Putz, 2000).

Waste paper participates in total paper production (60 %) mostly in Nederland and Great Britain. This limit is almost reached in Germany. Whereas Nordic countries that have sufficient wood raw material source are using only 10 – 15 % of waste paper as a secondary fibres (Milichovský, 1994).

1.2 Recycling influence on pulp fibre quality

Raw material source for paper production including usage of secondary fibres as well as ways of its obtaining varies continually. This fact represents basic and more and more difficult issue in paper production research.

Paper is nonhomogeneous network of pulp fibres. Except of fibres real papers contain also fillers, sizing agents, colours and other auxiliary materials. Paper properties are defined by properties of all used materials and technology of paper process. Describing this wide complex of variables is actually unreal. It is possible to partially describe the properties of laboratory testing sheets prepared under standard conditions or eventually of orthotropic paper made from pulp fibres on paper machine.

Description of fibres properties is based on the dimension characteristic and derived numeric parameters. This description is insufficient and only approximative. Dimensional analysis does not express fibres status and vanish the fine portion which influence significantly paper properties (Blažej and Krkoška, 1989).

Pulp fibres dimensions and physic-chemical properties are modified significantly by process of defibering, beating and refining, i.e. via mechanical effect of pulper and beating apparatus in aqueous medium. The interaction between pulp fibres and water is crucial at mentioned operations. The result reached by beating is influenced by fibres parameters (theirs origin, preparation method, drying method and deepness), mill parameters and beating process parameters (e.g. swelling level) (Hnětkovský, 1983a).

The characteristic differences of paper made by secondary fibres and freshly prepared fibres are similar to deviations between properties of paper made by fibres in wet and dry stage. Basic properties of fresh wet fibres change within drying process. Defibering and beating represent regeneration process. However this process is not complete, moreover it introduces additional destructive changes. Similar effect is observed during old paper defibering. Several fibres properties are changed irreversibly. Changes relevancy depends on the cycle count of fibres utilization (regeneration and usage for new paper production) and the way of paper products utilization (ageing destruction). The parameters used for the description of primary fibres paper properties are also suitable for the description of paper properties made by secondary fibres and fibre ageing changes (Blažej and Krkoška, 1989).

The fibres wear irreversibly and change their properties within the count of utilization cycles. Defibering and beating induce water absorption, swelling and partial regeneration of original properties. Repeated beating and drying during several production cycles provoke gradual decrease of swelling ability, which determine fibres bonding ability. Moreover a

fibre shortening is observed within increasing count of utilization cycles. Mentioned modifications reflect in paper properties (Blažej and Krkoška, 1989).

Experiences gained during old paper utilization prove that these fibres show significantly different properties comparing to freshly prepared fibres (Blechsmidt, 1979; Nordman, 1976; Laivins and Scallan, 1993; Hubbe et al., 2007; Howard, 1990, 1994, 1995; Nazhad and Paszner, 1994; Phipps, 1994; Ackermann et al., 2000; Shao and Hu, 2002; Hubbe and Zhang, 2005; Nazhad, 2005). Fibre re-utilization creates extremely non-homogenous mixture of variously old fibres. Old paper is composed by all types of manufactured paper and board. Additional inhomogeneity is caused by the presence of fibres used for several times but unequally (Attwood, 1983).

Pulp fibres are modified within the paper production by beating. Whereas the beating condition optimization is very important because of created fibrillation of fibre surface, release of fine portion and cell wall delamination. Paper rigidity increases during the beating. However recycled fibres repeated beating and drying lead to the decrease of inter-fibre bonding potential (Stürmer and Göttching, 1979; Peng et al., 1994).

Göttching (1976) detected by strength measuring at zero-span of jacks that recycled fibres resistance does not change practically. Decrease of paper resistance made by recycled fibres could be explained as the consequence of inter-fibre bond strength decrease.

Decrease of bonding ability and strength of recycled fibres bring the improvement of several utility characteristics as increased velocity of dewatering and drying, air permeability, blotting paper ability, improvement of light diffusion, opacity, and dimensional stability of paper (Göttching and Stürmer, 1975), which is linked with decreased fibres ability of swelling in contact with water (Ackermann et al., 2000).

Fibres swelling in width orientation and increase of wet fibre flexibility prove inner fibrillation caused by beating. Beating process creates submicroscopic areas in lamellar structure of kraft pulp fibre cell wall. Mentioned areas have tendency to close themselves semi-reversibly during drying (Jayme and Büttel, 1968; Paavilainen, 1993).

2. Experimental

Recycling process of kraft pulp fibres was observed on white kraft pulp sample prepared from hardwood mixture.

Pulp sample was processed into sheets of surface weight 800 – 900 g.m² and brightness 82.7 % MgO.

Original sample after first processing by defibering, milling and drying represents zero recycling. Following pulp fibres processing simulated recycling. Pulp fibres undergo recycling for 8 times. Simulation could be considered as sufficient because usually pulp fibres are re-utilized for 4 to 5 times in practice.

Pulp was returned back into defibering, milling and drying process. The beating value was chosen as 29 °SR because of achieving sufficient strength of paper sheets without redundant fibre weakening and ensuring the possibility of next recycling.

The drying temperature influence on chosen pulp fibre properties was observed at 80 °C, 100 °C and 120 °C. These chosen temperatures cover the action of usually used temperature (100 °C) and extreme temperature values (80 °C and 120 °C) which were chosen for comparison.

Pulp samples taken from each recycling level were used for sheet preparation. Sheets surface weight was determined as relative value needed for calculation of chosen characteristics.

Standardly used procedures were applied for recycled pulp treatment (dry substance determination, wet laboratory defibering, laboratory beating in PFI mill, laboratory sheet preparation for physical tests, determination of dewatering ability according to Schopper-Riegler, determination of surface weight).

Chosen properties were observed on the sheets prepared from original pulp, pulp after first processing (zero recycling) and pulp from particular recycling degrees:

- Fibre dimensional properties (fibre length, fibre width, shape factor, local fibre deformation a. o.)
- Mechanical characteristics (breaking length, tearing index)
- Physical properties (porosity, swelling, polymerization degree)
- Optical characteristics (brightness, colourity)

3. Results

3.1 Dimensional characteristics of recycled fibres

Basic fibre wood information is data of length, width, cell wall thickness, eventually lumen width. Dimensional parameters provide first fibre information and could be used for deduction of fibres utilization suitability for specific paper type.

Hardwood has more complicated structure of cell types comparing to coniferous wood. Tracheids occupy 90 % of total wood volume in coniferous wood. Their length is moving within 2 to 6 mm and it is 100 to 300 times longer than width. Tracheids are at average 2 to 4 times longer than libriform fibres of hardwood typical for Slovak republic. Their length is moving between 0.3 to 2.2 mm. Libriform fibres constitute approximately 50 % of hardwood volume, vessels represent 20 % and parenchymatic fibres 1/3. Vessels dimensions vary depending on wood type, their location in year circle, post and climatic conditions. Their length could be within 0.2 to 0.8 mm and width could reach 0.4 mm (Požgaj, 1993; Blažej et al., 1975).

Changes of dimensional parameters and physico-chemical characteristics created during native fibre isolation decrease primary importance of dimensional parameters. Blažej and Krkoška (1989) claim fibre shortening during wood isolation by comparing of fibre wood length (Chovanec, 1975). Dimensional analysis allows expressing average fibre length and width, as well as cell wall thickness. However it does not describe the fibre stage.

Repeated pulp beating during recycling causes numerous changes of pulp fibre dimensional characteristics. It means fibre shortening (wherever and under random angle across the fibre), inner and outer fibre fibrillation, fibre delamination and fibre downiness.

Dimensional characteristics were observed by microscope until recently. Nowadays modern apparatus which can measure faster and are able to evaluate fibre dimensions are used.

Dimensional characteristics were monitored by Fiber Tester, which allows the evaluation of app. 20 000 fibres in pulp suspension containing 0.1 g of fibres in 100 ml of suspension in one measure (Karlsson, 2006). Double-dimensional view allows fibre length measuring separately and measuring of pulp fibre deformation during the running between two-glass plates.

Following pulp fibre characteristics in recycling process were monitored during dimensional analysis:

- Average fibre length
- Average fibre width
- Fibre shape factor
- Fibre length distribution – in 75 classed divided by 0.1 mm upto 7.5 mm
- Fibre width distribution – in 50 classes divided by 2 μm upto 100 μm
- Fine ratio – fibres up to length 0.2 mm
- Percentual fibre distribution within configured length and width interval
- Local fibre deformation – angle of fibre deviation and fibre length between particular angles of fibre deviation.

Average values of chosen dimensional characteristics - length, width and final fibre shape factor from multiple measures of fibre suspension are stated in tab. 2.

Dimensional characteristics of pulp fibres									
Pulp sample	Average fibre length [mm]			Average fibre width [μm]			Fibre shape factor [%]		
	Drying temperature [$^{\circ}\text{C}$]								
	80	100	120	80	100	120	80	100	120
Original sample	0,824			20,8			90,1		
0 th recycling	0,801	0,792	0,792	20,3	21,0	20,3	89,7	89,9	89,9
1 st recycling	0,774	0,792	0,782	20,2	20,9	20,2	89,9	89,5	90,1
2 nd recycling	0,760	0,784	0,789	20,0	20,6	19,8	90,0	89,2	91,2
3 rd recycling	0,766	0,777	0,771	19,8	20,5	20,0	89,5	89,5	89,6
4 st recycling	0,769	0,770	0,772	20,4	20,4	20,2	87,2	89,6	90,2
5 st recycling	0,767	0,769	0,761	19,8	20,3	19,9	86,7	89,7	89,3
6 st recycling	0,757	0,768	0,761	19,5	20,3	19,9	90,3	89,5	89,4
7 st recycling	0,769	0,762	0,754	19,9	20,2	19,8	89,4	89,5	89,4
8 st recycling	0,771	0,762	0,744	19,8	20,2	19,8	89,8	89,7	89,3

Table 2. Dimensional characteristics of pulp fibres.

Gained results prove that recycling process cause decrease of length, width and fibre shape factor. The most significant modifications were observed during first beating treatment. Although pulp fibres milled only at 29 °SR within repeated recycling, displayed shortening and fibrillation beating effect by decrease of length, width and fibre shape factor values.

Average fibre length of original hardwood pulp mixture was 0.824 mm. The highest decrease of average fibre length within whole monitored recycling range (fig. 3) was observed at drying temperature 120 °C. Average length decrease after 8th recycling represents 9.7 % at drying temperature 120 °C, 7.5 % at 100 °C and 6.4 % at 80 °C comparing to original fibre length.

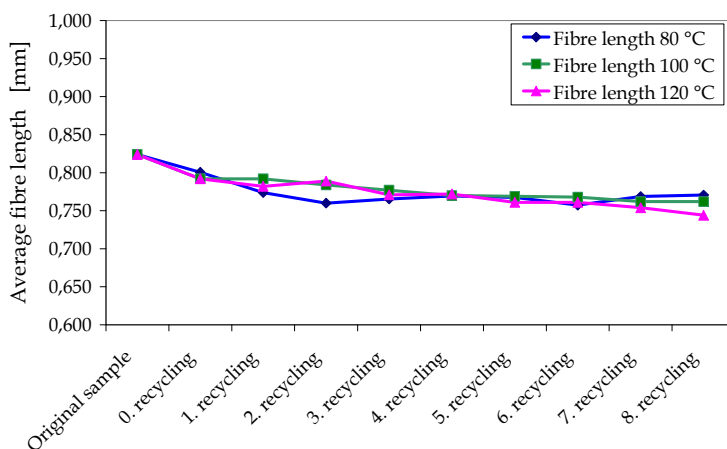


Fig. 3. Average fibre length in recycling process.

Descending trend of average fibre length (tab. 2) during repeated recycling correspond to growing amount of fine ratio (see tab. 3). This effect is clearly visible at drying temperature 100 °C where average fibre length decreases and fine ratio ascend within whole recycling range. The progression was not so explicit at drying temperatures 80 °C and 120 °C. However the correlation between fine ratio content and average fibre length was kept.

Average original pulp fibre width was 20.8 μm and the change of average fibre width after 8th recycling was negligible.

Fibre shape factor is defined as the ratio of join between fibre ends and real fibre length (in %). This factor declines during recycling depending on recycling rate, temperature and fibre beating process (tab. 2).

Relative fibre distribution in length and width interval is more characteristic for pulp than average length and width (fig. 4).

The highest relative distribution of longer fibres was in original pulp sample. Content of longer fibres decreases and of shorter fibres increases because of beating fibre shortening. Although the distribution curve progress at particular temperatures is similar and the

curves are almost overlaid, relative distribution of shorter lengths is the highest at drying temperature 120 °C. This fact gives evidence of higher fibre fragility and hornification caused by the impact of higher temperature.

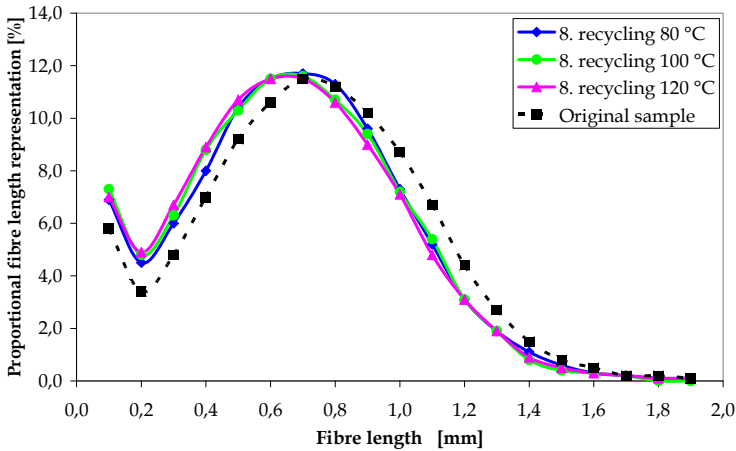


Fig. 4. Relative distribution of pulp fibre length dried at 80, 100 and 120 °C.

Fine ratio content represents in Fiber Tester apparatus record the fibre length from 0 to 0.2 mm. The ratio attained the lowest value in original sample and increased within recycling process even if the fine ratio of mucus and powder was partially eliminated by dewatering.

Table 3 presents average values of fibre fine ratio in original sample and in samples after 8th recycling at monitored temperatures.

Fibre Fine ratio influences negatively the mechanic properties (weak bonding properties) as well as dewatering ability during paper formation in drying machine (Karlsson, 2006).

Fine ratio content [%]						
Drying temperature	80 °C		100 °C		120 °C	
Fraction [mm]	0 - 0,1	0,1 - 0,2	0 - 0,1	0,1 - 0,2	0 - 0,1	0,1 - 0,2
Original sample	5,8	3,3	5,8	3,3	5,8	3,3
8 th recycling	6,9	4,6	7,3	4,8	7,3	5,2

Table 3. Fine ratio content of pulp fibres.

All tested samples of recycled pulp contained lower portion of fraction 0.1 to 0.2 mm. The augment of this fraction increased during recycling. The highest values were observed at drying temperature 120 °C.

Relative fibre width distribution varies within recycling.

Distribution curves (fig. 5) prove that relative pulp fibre distribution of the biggest widths were in original pulp sample. Lower width distribution increased after 8th recycling.

Pulp fibres were suspended in water and repeatedly treated in beating system during 8-times recycling. Fibre beating caused fibre deformation - waving as a result of fibre compression, flattening and distortion beside of shortening and fibrillation effect. Fiber Tester measured and evaluated local fibre deformations beside of basic dimensional characteristics. Local fibre deformations were defined as the modification of main fibre line direction. The deviation was recorded if the achieved angle was higher than 20°.

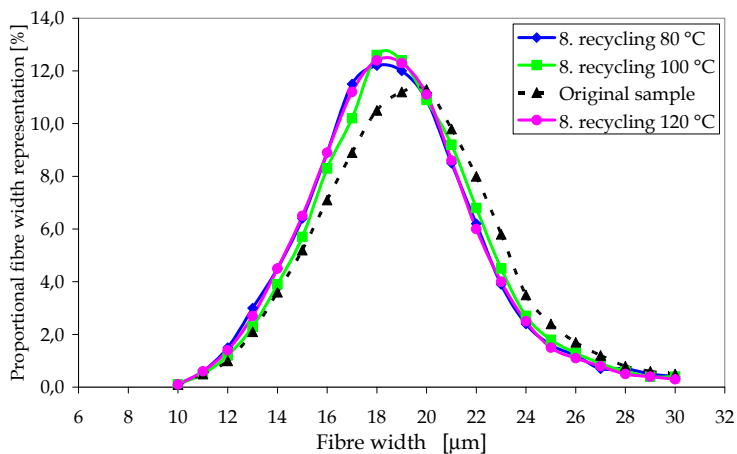


Fig. 5. Relative width distribution of pulp fibres dried 80, 100 and 120 °C.

Number of local fibre deformation informs about fibre weakening which influences strength paper characteristics.

Table 4 shows average values of pulp fibre local deformations in particular recycling levels.

Local deformation of pulp fibres												
Pulp sample	Average angle of fibre deviation			Deformation count per mm			Deformation count per fibre			Medium index of fibre distortion		
	Drying temperature [°C]											
	80	100	120	80	100	120	80	100	120	80	100	120
Original sample	50			0,60			0,50			1,40		
0 th recycling	47	49	48	0,74	0,63	0,67	0,56	0,48	0,51	1,73	1,49	1,58
1 st recycling	48	49	48	0,69	0,69	0,67	0,52	0,53	0,51	1,64	1,65	1,59
2 nd recycling	48	50	47	0,69	0,72	0,55	0,51	0,55	0,42	1,63	1,76	1,29
3 rd recycling	48	50	49	0,76	0,69	0,72	0,56	0,52	0,54	1,79	1,67	1,73
4 st recycling	51	50	47	0,98	0,69	0,66	0,74	0,52	0,50	2,42	1,66	1,55
5 st recycling	52	50	50	1,06	0,70	0,77	0,79	0,52	0,57	2,63	1,68	1,85
6 st recycling	47	46	49	0,69	0,73	0,76	0,51	0,56	0,56	1,63	1,63	1,82
7 st recycling	48	50	49	0,76	0,72	0,76	0,57	0,53	0,56	1,80	1,73	1,83
8 st recycling	48	49	49	0,69	0,72	0,77	0,51	0,53	0,56	1,65	1,72	1,85

Table 4. Local deformations of pulp fibres.

Average deviation angle is moving within 46 to 52° during recycling. The highest values of deformations per mm, deformations per fibre and fibre distortion index were measured after 8th recycling at drying temperature 120 °C. This fact proves negative impact of higher temperature on pulp fibre deformation.

3.2 Mechanic characteristics of recycled fibres

3.2.1 Breaking length

Breaking length defining paper strength rate was one of observed mechanic characteristics.

Enlargement of fibre active surface due to the outer pulp fibre fibrillation occurred during beating process (Blažej and Krkoška, 1989). This effect induces the increase of fibre bonding, paper strength and finally the increase of breaking length. The fibres are simultaneously shortened during beating which causes deterioration of mechanic properties. Moreover, the negative impact on dewatering ability and bonding properties is amplified by growing ratio of fine fraction (Hubbe and Heitmann, 2007).

Pulp fibre recycling causes the decrease of fibre wall thickness as well as tension strength. Per contra the ratio of lumen diameter and fibre width increases whereas is the direct proportion between tension strength and fibre wall thickness (Okayama, 2001).

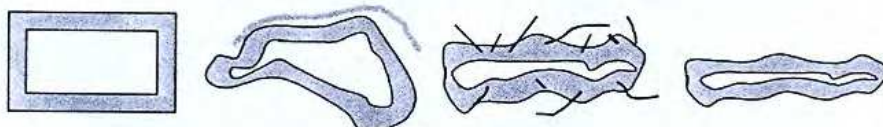


Fig. 6. Different levels of fibre changes (Karlsson, 2006).

Strength properties changes occurred during recycling are closely linked on morphological fibre characteristics (lumen diameter, thinness ratio) (Okayama, 2002).

Tension strength at zero clamping corresponds with fibre strength and increases owing to beating and recycling. Decrease of sheets strength prepared from recycled fibres is caused by the decrease of inter-fibres bonds. Specific strength of inter-fibres bonds is not influenced by recycling fibre treatment. So decreased strength of inter-fibres bonds could be induced only by decrease of inter-fibres bonding surface (Khantayanuwong, 2002).

Figure 7 shows the evolution of pulp sheets breaking length during the process of 8-times recycling.

Intense breaking length increase was caused by the active fibre surface increase after first fibre beating and drying (0th recycling). Whereas the highest value of pulp breaking length was determined at drying temperature 120°C. Consecutive recycling decreases the strength because of pulp fibre shortening and liberation of fibrillated fragments from their surface.

While the values of pulp breaking length dried at 80 °C and 100 °C decrease about 47 %, the breaking length of pulp dried at 120 °C decrease about 68 %.

Based on the evolution of breaking length modification during recycling it could be concluded that the pulp dried at 120 °C reflects the lowest values of breaking length. On the other hand, the highest values of breaking length after 8th recycling were observed on pulp dried at 80 °C. This fact proves the negative impact of higher temperature on strength properties characterized by breaking length.

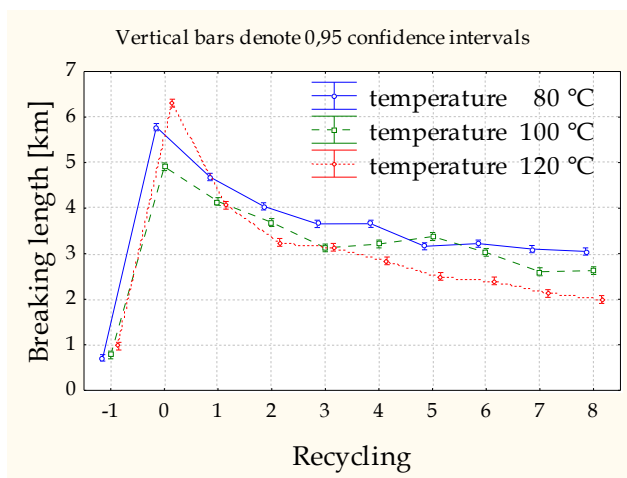


Fig. 7. Pulp breaking length during recycling.

3.2.2 Tearing index

Further monitored parameter characterising strength properties of pulp sheet is tearing index which was established by the method according to Elmendorf.

Tearing strength is characterised by the effort needed for tearing of pre-cut paper sample under established conditions. Tearing strength is then recalculated on square weight and expressed as tearing index.

Tearing strength depends on the character of used fibres and on its treatment level. Higher tearing strengths are observed on kraft pulp and significant decrease of tearing strength is caused by paper bleaching, sizing and intensive drying (Souček, 1977).

Tearing strength is significantly influenced by the fibres amount in tearing area, fibres length, fibres bond density and strength. If the more fibres are longer, the more strength needed for paper tearing divided into bigger surface. Reversely the strength is concentrated on small surface when the fibres are short.

The strength of the paper with small and insufficiently evolved bonding surface is small. It is caused by easy fibre evulsion from the paper structure.

Fibre surface and tearing strength is increasing while fibres beating until the effect of fibres shortening is displayed.

The evolution of tearing index is illustrated by figure 8.

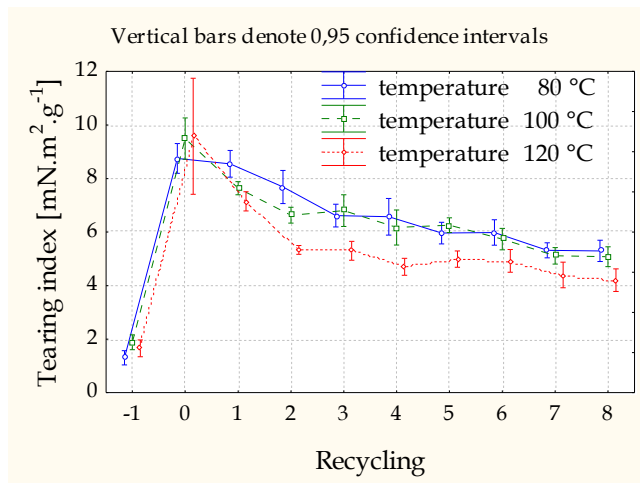


Fig. 8. Tearing index during recycling.

The first beating during 0th recycling shows the highest impact on pulp fibres. Similarly to breaking length the first beating increased significantly tearing index at all observed drying temperatures because of the bonding surface increase. This fact caused by first intensive fibre beating 29 °SR. The highest tearing index value observed on pulp dried at 120 °C, lower at 100 °C and the lowest at drying temperature 80 °C.

Tearing index shows descending character within the whole recycling process. The pulp was beaten at 29 °SR in each recycling level so the fibres were not enormously destroyed.

The pulp dried at 120 °C shows the lowest values of tearing index after 8th recycling. This diminution represents 53 % of maximally achieved value in comparison to 0th recycling. This significant difference is caused by repeated beating and drying at higher temperature. Lower tearing index decrease (46 %) was observed at drying temperature 100 °C and 38 % at 80 °C. Stated tearing index values confirm growing negative impact of increasing drying temperature during whole recycling process.

The negative impact on pulp sheets tearing strength was amplified by growing fine ratio content. The highest fine ratio (0-0.2 mm) content was measured by Fiber Tester after 8th recycling at drying temperature 120 °C and represented 12.5 %, 12.1 % at 100 °C and 11.5 % at 80 °C.

Repeated pulp beating and drying caused fibres surface changes (fig. 6). Enlarged fibre surface (increase of contact surface due to the fibrillation) caused by beating ensures the increase of mechanical characteristics values due to the higher inter-fibres hydrogen bond amount which provides the improvement of fibrils and fibres enlacement during dewatering (Hubbe, 2006 b).

Klofta and Miller (1993) present in their article the importance of liberated fibrils capillary strength and fine ratio on fibre surface during the creation of bleached kraft fibres network.

According to Ackermanna et al. (2000) the fibres shortening influence on fibres mechanic characteristics is not critical since these characteristics are influenced by presence or absence of fine ratio (Ackermann et al., 2000). Moreover, the fibre after repeated recycling is fragile and inclinable to destruction during beating (de Ruvo and Htun, 1983).

The results prove negative impact of drying on mechanic characteristics of recycled fibres. While the evolution of mechanic characteristics changes (fig. 7 and 8) at drying temperatures 80 °C and 100 °C was almost the same, the evolution at drying temperature 120 °C was significantly lower. Fibre hornification and fragility is demonstrated significantly at 120 °C which is proved by increase of fine ratio within recycling process. Matsuda et al. (1994) introduced that typical temperature interval of hornification is 80-120 °C.

3.3 Physical characteristics of pulp fibres

Pulp fibre recycling caused beside of dimensional and mechanic changes, also physical characteristics modifications.

3.3.1 Porosity

Porosity is defined as ability of paper, cartoon or board to permeate the air under established conditions.

Air permeability is given by permeable pores which connect both paper sites and allows air circulation in the direction of hydraulic gradient. Air permeability depends on paper porosity and decrease with increasing beating level, content of fillers and sizes (Souček, 1977).

Pulp sheet samples porosity was observed after particular recycling levels based on ISO 5636/3 according to SCAN P 26:78.

Figure 9 illustrates evolution of porosity changes measured after recycling levels at monitored drying temperatures.

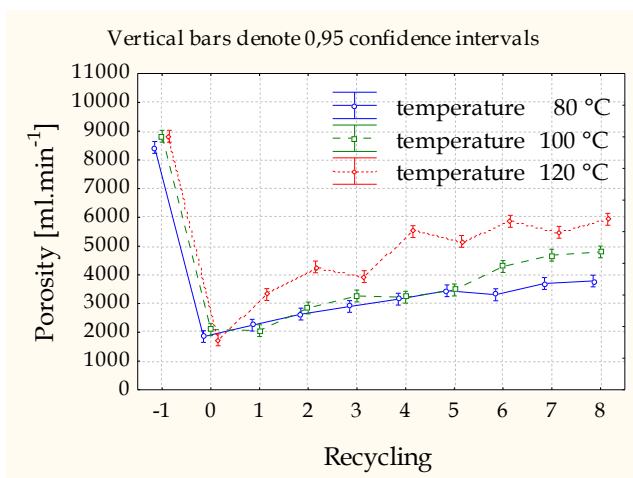


Fig. 9. Evolution of porosity during recycling.

The evolution of porosity values was opposite to the evolution of monitored mechanic characteristics. The highest porosity was observed in original pulp sample where pulp fibres were not affected by beating and air permeability between pulp fibres was high.

First intensive treatment of original fibres by beating increased bonding surface, strength properties (breaking length, tearing index), and the sheet created more consistent fibres network, decreased inter-fibres areas and the porosity plummets.

Beating at 29 °SR in following recycling levels caused fibre shortening, fibrillation and consequent unstuck of cell wall outer primary part and elimination of fine ratio. This fact caused decrease of mechanic characteristics and porosity increase.

The porosity values of pulp sheets dried at 80 °C and 100 °C were much closed until 5th recycling level. The negative impact of higher temperature was demonstrated from next recycling levels. The porosity of sheets dried at 120 °C was higher within all range of repeated recycling.

The increase of sheets porosity between 8th and 0th recycling was 2-times at drying temperature 80 °C, 2.3-times at 100 °C and 3.4-times at 120 °C.

The influence of higher drying temperature was manifested by fibre hornification, theirs shrinkage due to the pore closing in cell wall (Alinec, 1997, 2002; Stone and Scallan, 1968), which leads to consequent increase of pulp sheets air permeability (porosity). Electron microscope photos (fig. 10 and 11) shows the surface of recycled kraft fibres and proves this shrinkage.

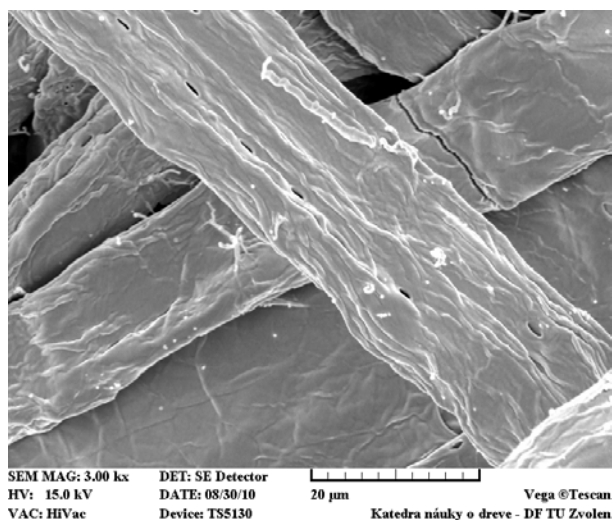


Fig. 10. Surface of dried non-beated pulp fibres.

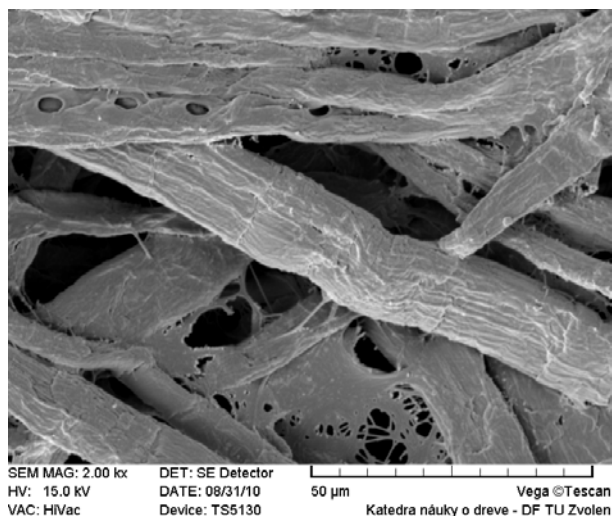


Fig. 11. Surface of pulp fibres after 8th recycling and drying at 120 °C.

3.3.2 Swelling

Swelling is defined as wood ability to increase its linear dimensions, surface or volume via bonded water absorption in range from 0 to the point of fibres saturation. The water comes into the amorphous areas of cellulosic fibrils and enlarges cell wall of particular elements and whole wood. The wood swells during water and water steam absorption until the point of fibres saturation. Swelling does not caused additional increase of water content because the water fill in only lumens or eventually inter-cells cavities (Požgaj et al., 1997).

Swelling ability is given mainly by free -OH groups which are able to bond water via hydrogen bonds. The wood content of free -OH groups is markedly limited because of lignin-saccharide bond blocks. Bleached pulp fibres with almost complete lignin removal contents higher amount of free -OH groups. Swelling is more intensive with regard to speed as well as maximal values.

Figure 6 shows different levels of fibres changes which they pass during recycling process because of repeated beating and drying. Original pulp fibre cell structure is devoid of outer layer parts by beating (P, S1). Moreover the fibres are fibrillated and swell in water medium. Consecutive drying causes fibres collapse which induces decrease of swelling ability.

Kraft pulp with significantly decreased strength during recycling swells less and has lower bonding potential. Recycled fibres are markedly less hydrophilic than original fibres. Water contact angle increases extremely which is related to fibre surface inactivation during recycling known as “irreversible hornification” (Takayuki, 2002).

Plenty of scientists (Stone and Scallan, 1966; De Ruvo and Htun, 1983) concluded that the loss of repeated pulp fibres swelling abilities is caused by the pores closure in pulp walls and pore disability to re-open when watered.

Beating is one of the most important operations for obtaining paper potential of recycled fibres and it could partially reverse recycled pulp fibres hornification. Beating increases fibres flexibility and their swelling ability which improve bonding and strength (Woodward, 1996).

Fibre crystallinity index varies within recycling process. This effect is caused by negligible crystallinity increase of specific amorphous fibre area during recycling. The insufficient lumen re-opening of moist recycled fibres causes that water content bonded in fibre wall influences considerably re-swelling of recycled fibres. The decrease of recycled fibres re-swelling ability is parallel with the decrease of cell wall bonded water content. This event is caused by the diminution of amorphous areas known as sub-morphological changes of fibre wall (Khantayanuwong, 2002).

Modified method of swelling kinetics determination (Solár et al., 2006) was used for experimental monitoring of pulp fibres swelling. The method is based on dimensional changes recording of test pulp sheets swelled in water via sensors and their transfer into electric signals. Swelling is defined as the difference between immediate and initial sample dimensions (in %).

The experimental results of recycled pulp fibres swelling changes depending on the time allow concluding that:

- maximal pulp fibres swelling speed is achieved during first seconds of contact between pulp sheet and used medium – water. Swelling speed descends consequently till zero value
- swelling ability of pulp fibres decreases with recycling
- maximal swelling of pulp fibres was achieved always during 0th recycling (after first beating).

Figure 12 indicates the swelling evolution of pulp fibres dried at 80 °C.

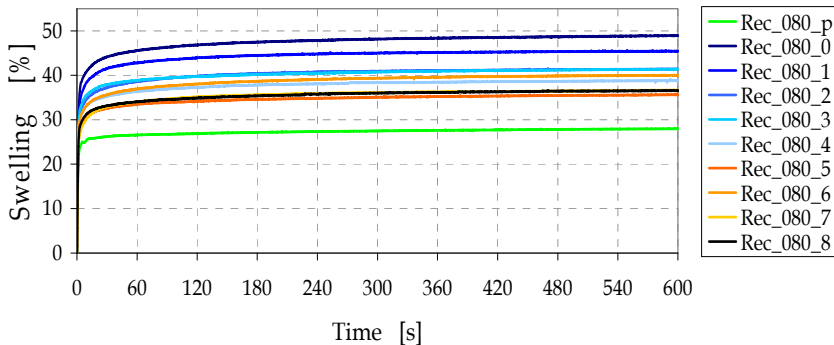


Fig. 12. Swelling evolution of pulp fibres dried at 80 °C.

Swelling of recycled pulp fibres dried at different temperatures after one-second contact with water shown on figure 13.

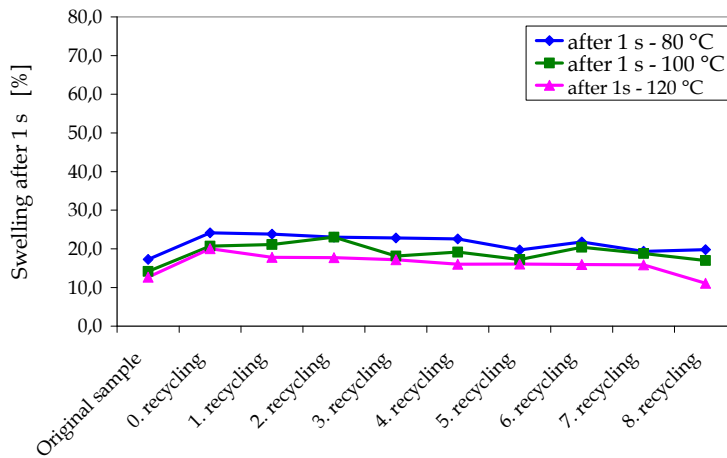


Fig. 13. Swelling of pulp fibres after one second contact with water.

Pulp fibres dried at 80 °C shown the highest swelling value after one second contact with water within whole recycling range.

Figure 14 illustrates swelling values of pulp fibres after 600 seconds contact with water.

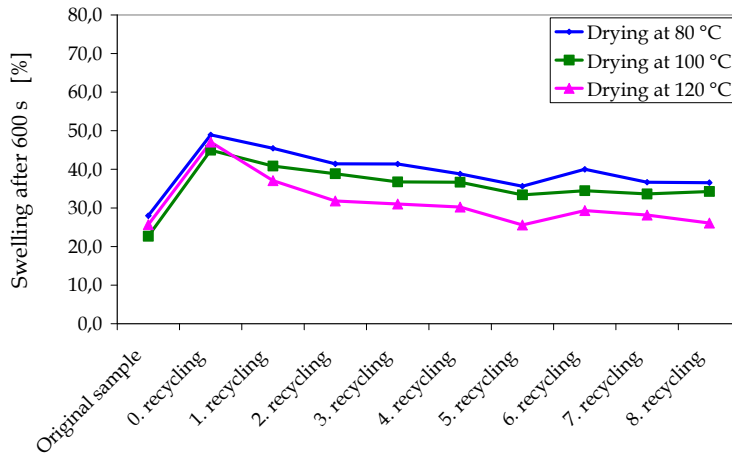


Fig. 14. Swelling of pulp fibres after 600 seconds contact with water.

Swelling ability of pulp fibres decreases with increasing recycling level. Maximal swelling of pulp fibres was achieved during 0th recycling (after first beating).

Difference of swelling abilities at different drying temperatures increases after 600 seconds of pulp fibres swelling.

The fibres swelling decreases because of repeated recycling which covers water plucking, refining and re-drying at monitored temperatures. It is caused by pulp fibres hornification as a result of irreversible pore closing in cell walls. Whereas significant negative influence of higher temperature on swelling values was observed.

3.3.3 Degree of polymerization

Cellulose is natural polymer with variably long chains. Several authors indicate higher degree of polymerization (DP) as 6000-8000 (Albersheim, 1965), 14000-15000 (Hon, 1994, Rowell, 2005), 14000 Marx et al. (1966) for native cellulose form. Wood delignification and cellulose chains degradation occur during kraft cooking and consecutive pulp bleaching. This process continues during recycling and drying process. DP depends on wood species, technological treatment process and cellulose determination (isolation) method. The values are moving within 500-1500 (Kačík and Kačíková, 2007) and 100-10000 Solár (2001). Zugenmaier (2008) mentions the interval of DP within 950-1300 for kraft pulp.

DP of cellulose constituting cell wall skeleton influences several paper characteristics, mainly strength that is given by fibres strength and inter-fibres bond amount.

Humidity and temperature action causes beside of fibres fragility and hornification, also degradation of cellulose chains (Kato and Cameron, 1999; Ackermann et al., 2000; Hubbe et al., 2003; Dupont, 1996) which is manifested by DP decrease. This DP decrease is more significant during the action of higher temperatures on wet pulp fibres than on dry fibres.

Viscosity measure in solvent FeTNa (ISO 5351/2-1981 (E) where the cellulose is relatively stable, is suitable method for monitoring of cellulose degradation. This method allows to establish limit viscosity number (LVN) which is used for DP calculation based on Staudinger equation $DP = [LVN]/8,14 \cdot 10^{-4}$.

Figure 15 shows DP changes of hardwood pulp in recycling levels.

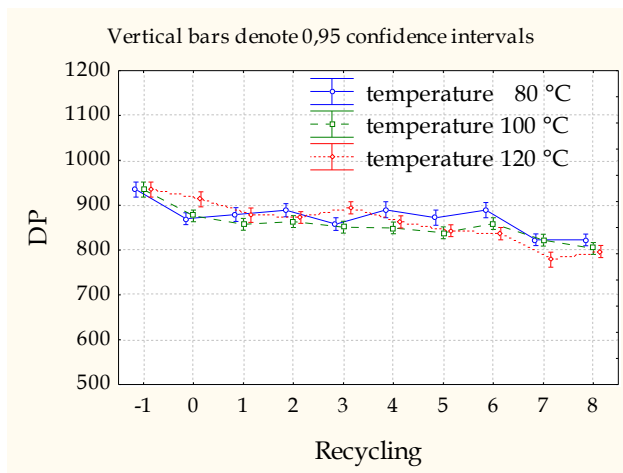


Fig. 15. DP of hardwood pulp during recycling (Čabalová and Geffert, 2009).

Cellulose samples contain cellulose chains of different length. Viscometric determination of DP represents the value characterising average chain length. Gained DP results allow concluding that cellulose chains shorten during recycling because of glucosidic bond fission whereas DP decrease was the slightest at drying temperature 80°C.

The disadvantage of viscomeric measure is that it provides only the information about average values of DP. Therefore, it is better to characterise recycled pulp by gel permeability chromatography (GPC) which allows detecting the distribution of molar weights too (Dupont and Mortha, 2004).

The cellulose in pulp samples was derivatized on tricarbonylates according to Kačička et al. (2007) for GPC needs. The samples were analysed and evaluated based on the conditions stated by Kačička et al. (2009). The main advantage of this method is that derivatization process of complete cellulose tri-substitution runs in one reaction step and without degradation impact on cellulose. GPC method for the analysis of cellulose tricarbonylates was used by several authors (Daňhelka et al., 1976; Kačička et al., 2007; Kučerová and Halajová, 2009; Čabalová et al., 2009).

Measured results (Kučerová and Halajová, 2009) of distribution - log (M) upon taking into account complete tri-substitution ($DP = M/519$) were used for the evaluation of relative distribution of cellulose DP in pulp dried at monitored temperatures (80 °C, 100 °C a 120 °C) within recycling levels.

Figure 16 illustrates the relative distribution of cellulose DP in pulp after 8th recycling at drying temperatures 80 °C, 100 °C and 120 °C.

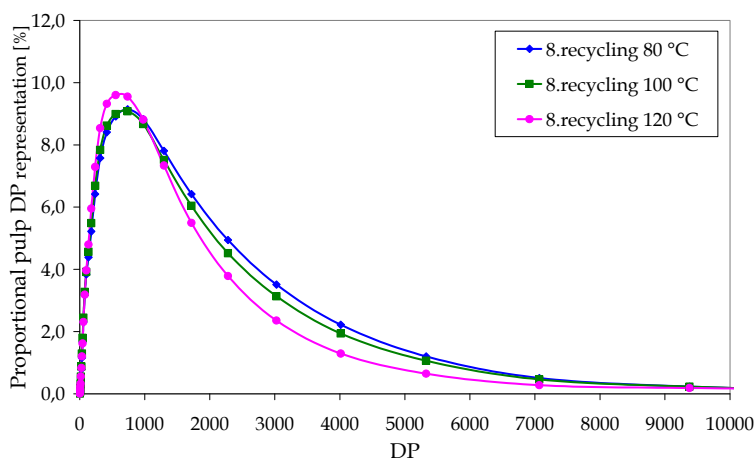


Fig. 16. Relative DP of pulp dried at 80 °C, 100 °C and 120 °C

The comparison of relative cellulose DP distribution after 8th recycling at all monitored temperatures shows that relative distribution of shorter cellulose chains increases with increasing drying temperature.

Maximal DP value of pulp dried at 80 °C and 100 °C was 736, while the maximum DP of pulp dried at 120 °C was 645. Particular deviations of DP decrease were observed during recycling since this process is relatively complicated and influenced by many factors acting positively as well as negatively.

Some authors (Khantayanuwong, 2003; Chen, Wang, Wan and Ma, 2009) realized beside of DP decrease, also crystallinity increase in recycling process. This increase could be relative since shorter hemicellulose chains and amorphous cellulose portion is degraded as first during repeated recycling and drying.

3.4 Optical characteristics of recycled fibres

Many various optical events perceived as diffusion surface reflection appears during light fall on paper. One light part is reflected from paper as emitted light and the other part is absorbed by fibres and pigments. Four optical phenomena are observed - reflection, refraction, absorption and diffraction of light.

Reflection, refraction and diffraction are merged in one term - light diffusion which represents important property in paper technology domain (Pauler, 2002). Fibrillar paper, cartoon and boar structure with fibres and filler particles divided by pores filled by air creates suitable conditions for diffused reflection. Each interface between solid matter and air creates light rays reflection and refraction (Souček, 1977).

3.4.1 Brightness

Brightness is defined as material ability to diffuse light flow upon minimal absorption or penetration in the way that spectral composition of reflected light in visible domain remains the same as falling light. Brightness is expressed in reflectivity percentage of basic brightness standard (MgO) measured at wave $\lambda = 457 \pm 5$ nm (Souček, 1977).

Hardwood pulp sheets were prepared after each recycling level. Experimental sheets were used for measurement and statistics evaluation of brightness. Optical changes depending on drying temperature occur during the process of repeated recycling and drying. Figure 17 shows brightness variation of pulp sheets surface at monitored drying temperatures (80 °C, 100 °C and 120 °C).

Pulp brightness decreases in 0th recycling at all temperatures because of fibres surface changes due to intensive beating (in average from 15 °SR to 29 °SR). First beating caused the increase of fibre surface due to the liberation of primary fibre wall and the significant increase of light diffusion. Brightness increase observed during next recycling when pulp fibres were slightly refined at 29 °SR. This increase was the most significant at 80 °C. This effect could be explained firstly as successive leafing of small fibre primary wall particles and theirs removal from suspension during dewatering and then as decrease of total fibres surface. Deviations of brightness values during recycling are probably linked to other fibres surface changes due to the refining (shortening, fibrillation, delamination).

Statistic evaluation of achieved results reflects significant influence of recycling, temperature and the interaction of both factors on brightness values.

Negative influence of higher sheets drying temperature on pulp brightness is illustrated on graphic dependence of figure 17. Lower brightness of pulp sheets surface due to the higher drying temperature (120 °C) was examined during whole 8-times recycling process. This is the consequence of cellulose and hemicellulose oxidation reaction at higher temperature in the presence of air oxygen. Reactions are running on primary and secondary hydroxyl groups of pyranose circle and create carbonyl and carboxyl groups. This fact causes paper yellowing since arising substances are chromophores and have the ability of visible radiation absorption (Solár, 2001; Margutti et al., 2001).

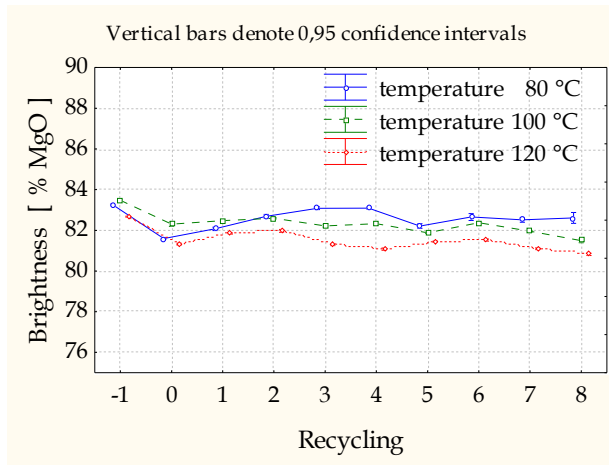


Fig. 17. Brightness of sheets surface during recycling at different drying temperatures.

3.4.2 Colourity

Paper industry has noted important changes of paper optical properties measurement in 70th and 80th years. Due to this development the brightness was not sufficient to paper quality characterization. Spectrophotometers allow to measure and define paper lightness and colour.

World widely used colour system CIE L*, a*, b* which consists of grey scale axis L*, yellow-blue axis a* and green-red axis b* in three-dimensional colour system based on 4basic colours (Pauler, 2002).

The colour of sheets surface was measured by spectrophotometer Minolta CM 2600d and the process of measure and evaluation was realized by software „Spektra Magic“.

Sheets surface reflection was measured in whole range of visible spectrum from 360 nm to 740 nm with resolution of 10 nm. Whereas difference spectrum was evaluated from the difference of average sheets reflection values after particular recycling levels at monitored drying temperatures.

Negative influence of higher drying temperature manifests already on sheets surface reflection of original pulp sample (fig. 18). While the reflection within whole measured spectrum at drying temperatures 80 °C and 100 °C was almost overlaid, the reflection values mainly in lower wave lengths were lower at drying temperature 120 °C.

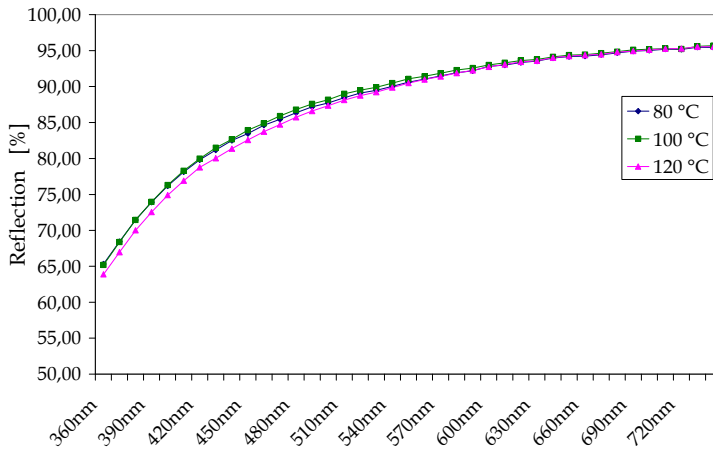


Fig. 18. Reflection of original pulp sample.

The reflection difference of pulp dried at monitored temperatures was the most significant after 8th recycling (fig. 19). The highest reflection in whole measured spectrum was kept only for pulp fibres dried at 80 °C. The lowest reflection was measured for pulp dried at 120 °C. The reflection of pulp dried at 100 °C was moving between the reflection values of 80 °C and 120 °C, at higher wave length it approximates to the reflection values of pulp dried at 80 °C.

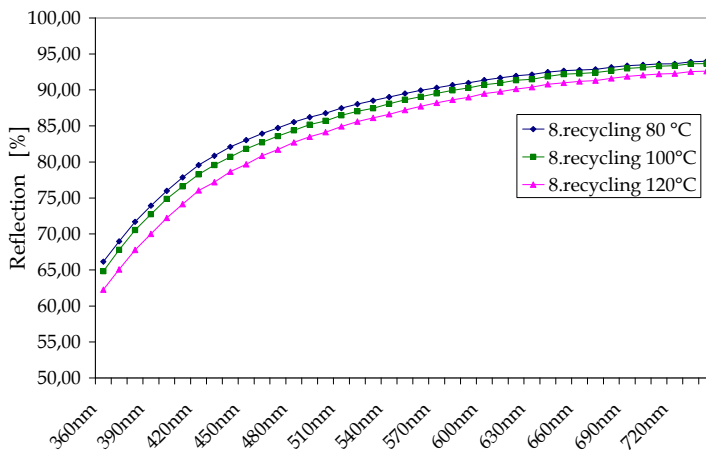


Fig. 19. Pulp reflection after 8th recycling.

Graph of differential spectrum indicates the change of average reflection measured on pulp sheets surface within the wave length range 360 nm to 740 nm after 8th recycling with the regard to average reflection of original sample at monitored temperatures (fig. 20).

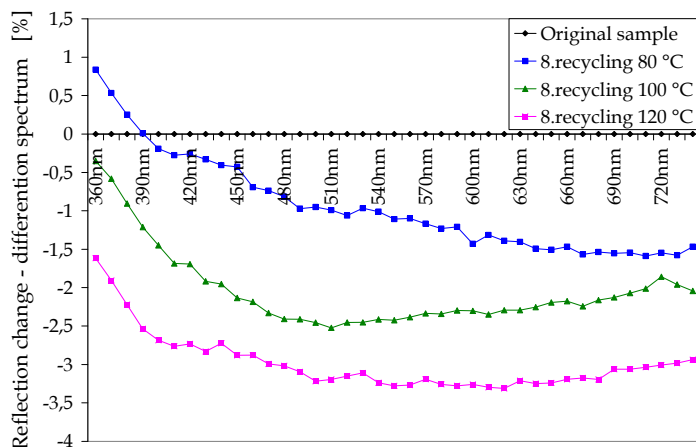


Fig. 20. Differential spectrum at monitored temperatures.

The smallest difference between the sheets surface reflection after 8th recycling and reflection of original pulp was determine at 80 °C and the biggest one at 120 °C.

The evolution of sheets surface differential spectrum dependence after 8th recycling is similar at all monitored drying temperatures. The decrease from 360 nm to 410 nm was linear, the differential spectrum of pulp dried at 80 °C slightly descends in whole wave length range, while for drying temperature 100 °C it was observed slight difference decrease 520 to 740 nm and the decrease was moved to the end of monitored spectrum within 680 to 740 nm for drying temperature 120 °C.

Achieved results indicate that higher drying temperature causes chromophores creation absorbing at whole monitored spectrum range.

Light reflection decrease of sheets surface made by repeatedly recycled and dried pulp fibres indicates the creation of secondary chromophores.

Absorption maximum at 350-368 nm is given by resting lignin chromophores. This effect is caused by $C\alpha-C\beta$ π bonds conjugated system with aromatic nucleus, phenolic and methoxyl structures which results to increased light absorption. Moreover kraft pulp contains chalcones chromophores with absorption maximum at 368 nm and extremely high absorption maximum at 478 nm is given by p, p'-stilbenchinones present in lignin (Solár, 2009). Absorption spectrum of cellulose materials below 420 nm is influenced mainly by lignin and the absorption of other components is relatively low (Blažej et al., 1975). In addition α -karbonyl conjugated with aromatic nucleus is intensive chromophore in UV spectrum (358-365 nm). In the case of extended system conjugation with phenolate anion in p-position of aromatic nucleus the absorption maximum is moved into the zone of 400 nm. Insaturated γ -karbonyl structures with resting lignin macromolecule are important chromophores that cause the absorption of visible radiation within 340-440 nm (Solár, 2001). Absorption maximum of thermic oxidated cellulose is set at wave length 360 nm (Bos, 1972).

The reason of pulp colouration in visible spectrum could be also the presence of microelements, iron and heavy metals that create colour complex with phenolic structures (Falkehag and Marton, 1961; Blažej and Šutý, 1973).

Colour changes of paper surface was evaluated in colour space CIE L*, a*, b* depending on colour shade shift along axis a* (from green to red) and along axis b* (from blue to yellow). The change of lightness colour component was characterized by the value of specific lightness L*.

Sheets surface colour after particular recycling levels was evaluated based on measured reflection values in visible spectrum area (360 nm to 740 nm), coordinates values in colour CIE L*, a* a b*.

Specific lightness evolution (L*) of monitored sample surface dried at three different temperatures is shown on figure 21 and in colour space moves from black to white colour.

Recycling caused slight decrease of sheets surface specific lightness at all three drying temperatures. Specific lightness values at 80 °C and 100 °C were very closed in whole recycling range.

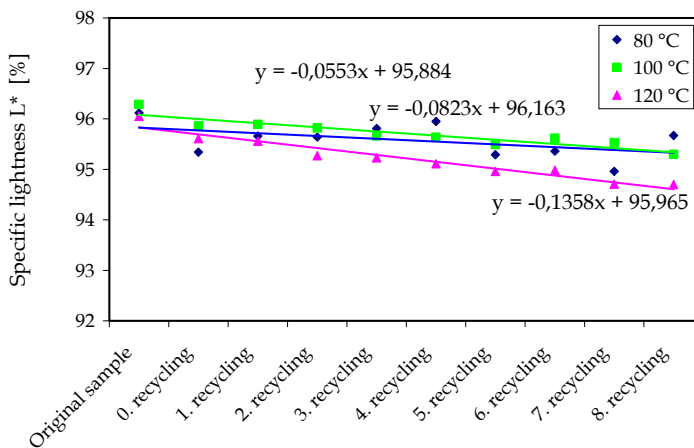


Fig. 21. Specific lightness change L*.

Evolution of values b* in particular recycling levels that characterized the coordinate in colour space from blue to yellow is shown on figure 22 at all three temperatures.

Sheets dried at 120 °C display the highest values of coordinate b* (shift into yellow shape) and the lowest values were determined at 80 °C (closer to blue shape). The values b* of sheets dried at 100 °C are situated between them.

Figure 23 illustrates the shift in plane L* b* of colour space CIE L*a*b* of original pulp sample and pulp after 8th recycling at all three monitored temperatures.

Introduced figure indicates that the colour of pulp sheets moves into dark and yellow shapes with increasing drying temperature.

Variation of coordinate a^* during recycling was negligible.

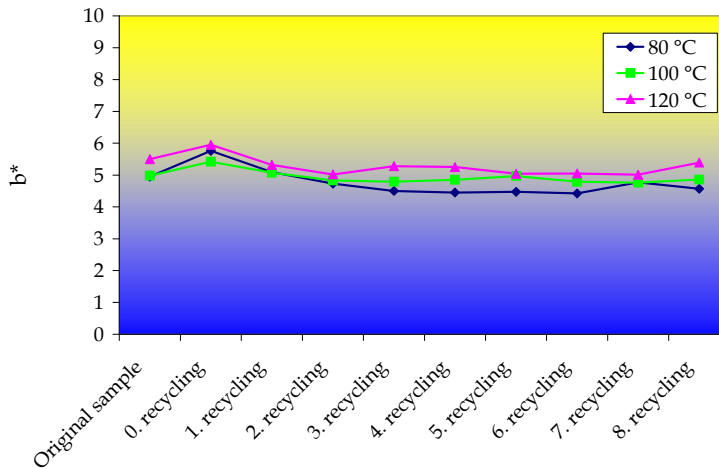


Fig. 22. Change of colour shape coordinate b^* .

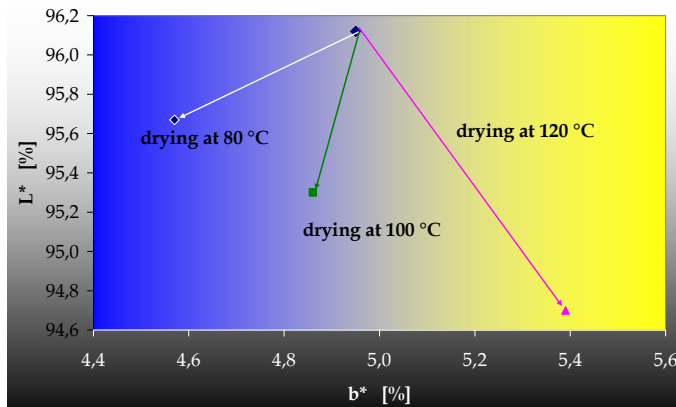


Fig. 23. Shift in plane L^*b^* of colour space in the beginning and in the end of recycling.

3.5 Additional beating influence on changes of recycled pulp fibres properties

Pulp fibres were refined at 29 °SR within each 8-times recycling level. Monitored chosen characteristics deteriorate depending on recycling level and drying temperature. The biggest variations of qualitative parameters were observed on the fibres of bleached hardwood pulp dried at 120 °C. The aim of 9th recycling – additional beating at 49 °SR and drying at 120 °C was deeper investigation of 8-times recycled fibres influenced by higher loading at beating.

Characteristics	Original sample	After 8 th recycling	After refining at 49 °SR
Fibre length [mm]	0,824	0,744	0,729
Fibre width [µm]	20,8	19,8	19,5

Table 5. Dimensional characteristics of fibres refined at 49 °SR after recycling.

Relative distribution of fibres length and width were moved into lower values (fig. 24 and 25) due to the additional beating at 49 °SR.

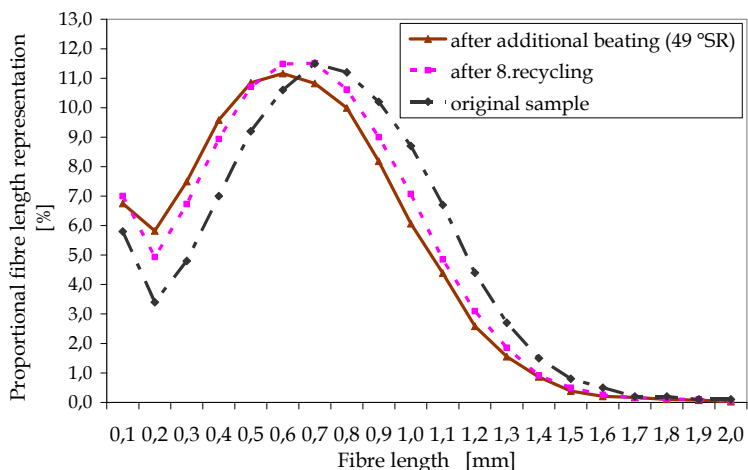


Fig. 24. Relative distribution of pulp fibres length (49 °SR, 120 °C).

Table 5 and figures 24 and 25 indicate that intensive additional beating at 49 °SR after 8-times recycling explicitly decrease the distribution of longer and wider fibres and increase the distribution of shorter and thinner fibres. Higher drying temperature (120 °C) causes that the fibres were more keratinized and fragile. Intensive additional beating at 49 °SR occurred not only to fibrillation, but also to shortening.

Although the values of pulp fibres dimensional characteristics were decreased, increased beating effect influenced positively pulp fibres mechanic properties. Increased fibres fibrillation induced the increase of inter-fibres bonding surface which caused the augmentation of breaking length and tearing index (see tab. 6).

Characteristics		Original sample	After 8 th recycling	After refining at 49 °SR
Breaking length	[km]	0,97	2,00	5,22
Tearing index	[mN.m ² .g ⁻¹]	1,60	4,51	6,77

Table 6. Mechanic characteristics of fibres refined at 49 °SR after recycling.

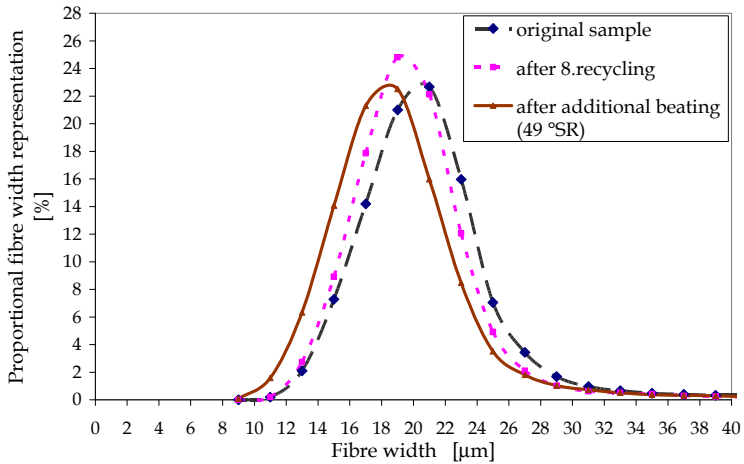


Fig. 25. Relative distribution of pulp fibres width (49 °SR, 120 °C).

Additional beating of 8-times recycled fibres at 49 °SR evoked that the average value of breaking length increased 2.6-times and tearing index 1.5-times.

Intensive additional beating influenced also porosity. Increased inter-fibres bonding decreased the area between fibres thereby the air permeability of sheet structure decreased. The porosity of experimental sheets prepared after beating at 49 °SR demonstrated significant decrease from 5 935 ml.min⁻¹ to 1 425 ml.min⁻¹ (fig. 26).

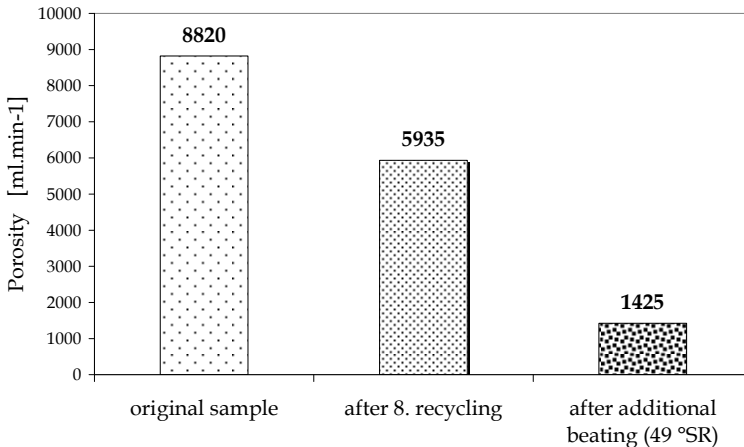


Fig. 26. Sheets porosity.

Negative effect of intensive additional beating at 49 °SR displayed on sheets brightness too (see fig. 27).

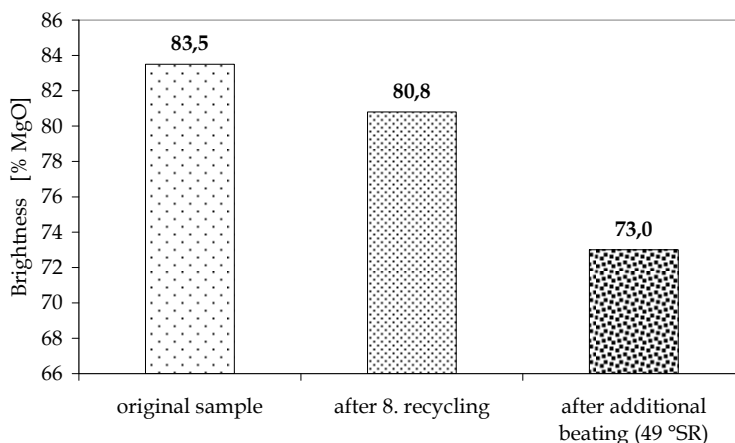


Fig. 27. Sheets brightness.

Beating at 29 °SR and drying temperature 120 °C induced the brightness decrease of kraft hardwood pulp about 2,7 % MgO. Additional beating at 49 °SR and following drying decreased the brightness value about 7,8 % MgO. This effect could be explained by enlargement of fibres surface due to the beating which influenced diffusion reflection of fallen luminous flow.

4. Conclusion

Achieved results of kraft hardwood pulp recycling demonstrate that all monitored characteristics deteriorate with increasing recycling level.

Although the pulp fibres were refined only at 29 °SR during 8-times recycling, it was observed the decrease of average fibre length and the increase of relative distribution of shorter and thinner fibres.

Negative influence of recycling combined with increased drying temperature manifested on mechanic characteristics. Increased fibre fragility due to the hornification caused the decrease of breaking length and tearing index during recycling.

Repeated drying during recycling increased the pulp sheets porosity due to the fibre hornification and shrinkage. Decreased swelling ability was caused by cell wall pores closing and their limited re-opening ability in water contact.

Repeated refining and drying influenced negatively average polymerization degree of cellulose. This fact displayed by the decrease of relative longer fibres distribution.

The negative effect of recycling on optical characteristics of bleached pulp (brightness, colourity) was amplified by increased drying temperature. Pulp colour moved into yellow shape during recycling.

Additional beating at 49 °SR of 8-times recycled pulp fibres showed that these fibres retained sufficient potential of strength properties with parallel decrease of porosity and brightness.

In practice the paper contains beside of pulp fibres, also many auxiliary paper agents that are combined with other factors (way of treatment, warehousing) and could negatively influenced some recycled fibres properties.

The growth of paper production in the future will not be possible without utilization of recycled kraft pulp fibres. The majority of them are originated from hardwood. The treatment of these recycled fibres should take into account the dominant influence of beating (additional beating). Achieving of optimal beating degree 28 – 29 °SR assures the extension of fibres life cycle (increase of recycling levels).

Drying temperature is other important recycling factor and is closely linked on the changes of fibres swelling ability and paper porosity. This effect influences significantly technological parameters of paper production and should be take into account during the designing of paper machines using recycled fibres.

5. Acknowledgment

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6. References

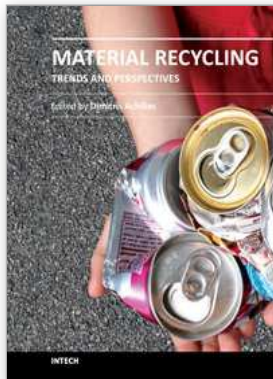
- Ackermann, Ch., Gottshing, L., Pakarinen, H. (2000). Papermaking potential of recycled fiber. In *Recycled fiber and deinking*, Papermaking Sci. Technol.Ser., Fapet Oy, Helsinki, Ch. 10, 2000. ISBN 952-5216-07-1, p. 358-438
- Albersheim (1965). In Kačík, F., Kačíková, D. (2007). Charakteristika a analýza celulózy a jej derivátov. Monografia.1. vyd. Zvolen: TU vo Zvolene, 2007. 94 s. ISBN 978-80-228-1819-3
- Alinec, B. (2002). Porosity of swollen pulp fibers revisited. In *Nordic Pulp and Paper*. ISSN 0283 2631, 2002, vol. 17, (1) p. 71-73
- Alinec, B., van de Ven, T.G.M. (1997). Porosity of swollen pulp fibers evaluated by polymer adsorption. In *The Fundamentals of Papermaking Materials*, Trans. 11th Fundamental Research symp., Cambridge, 1997, baker, C.F.(ed.) Pira International, Leatherhead, Surrey, UK
- Attwood, D. (1983). Fiber recycling. In *Recycling in the production of pulp and paper*. Eucepa symposium, Praha 1983, p.91
- Blažej, A. et al. (1975). *Chémia dreva*, 1.vyd. Bratislava:Alfa, 1975. 221 s
- Blažej, A., Krkoška, P. (1989). *Technológia výroby papiera*. 1.vyd. Bratislava : Alfa, 1989. 584 s. ISBN 80-05-00119-3
- Blažej, A., Šutý, Š. (1973). *Rastlinné fenolové zlúčeniny*. 1.vyd. Bratislava: Alfa, 1973. 236 s
- Blechsmidt, O. (1979). *Altpapier-Faserstoff für die Papiererzeugung*. VEB Fachbuchverlag, Leipzig 1979

- Bos, A. (1972). Reflectance spectra of cellulose. *Appl. polym. Sci.* 16, 2567-2576. In *Wood Chemistry, Ultrastructure, Reactions*, Gruyter. Berlin, New York, 613 p. ISBN 0-89925-593-0
- Čabalová, I., Geffert, A. (2009). Zmeny priemerného polymerizačného stupňa listnáčových a ihličnáčových buničín v procese recyklácie. In *ACTA FACULTATIS XYLOLOGIAE*, ISSN 1336-3824, 2009, 51 (2): 79-85
- Čabalová, I., Kačík, F., Sivák, J. (2009). Zmeny distribúcie mólových hmotností celulózy pri recyklácii buničínových vlákien. In *ACTA FACULTATIS XYLOLOGIAE*, ISSN 1336-3824, 2009, 51 (1): 11-17
- Daňhelka, J., Kössler, I., Boháčková, V. (1976). Determination of molecular weight distribution of cellulose by conversion into tricarbonyl and fractionation. In *Journal of polymer Science: Polymer Chemistry Edition*, 14, s. 287-298
- De Ruvo, A., Htun, M. (1983). Fundamental and practical aspects of paper-making with recycled fibers. In: *The Role of Fundamental Research in Paper Making*, Brander(ed.), Mechanical Engineering Pub., Ltd., London, Vol.1, s. 195-225
- Dupont, A. L. (1996). Degradation of Cellulose at the Wet/Dry Interface. In *Restaurator. International Journal for the Preservation of Library and Archival Material*. ISSN 0034-5806, 1996, 17, s. 145-164
- Dupont, A. L., Mortha, G. (2004). Comparative evaluation of size-exclusion chromatography and viscometry for the characterisation of cellulose. In *Journal Chromatogr. A.*, ISSN 0021-9673, 2004, 1026 (1-2), p. 129-141
- Falkehag, S.I., Marton, J. (1961). Lignin structure and reactions. *Advances in Chemistry series*, R.F. Gould (Ed.), American Chem. Soc. Publications, Washington, p.75
- Götttsching, L. (1976). Einfluss des Altpapier-Recycling auf Suspensions und Papiereigenschaften. In *Sekundärne vlákna a ich využitie v papírenskom priemysle*. Eucepa symposium, Bratislava 1976
- Götttsching, L., Stürmer, L. (1975). *Wochnbl. Für Papierfabrik* 103, 1975, č. 23/24, s. 909
- Hnětkovský, V. (1983a). Speciální otázky zpracování sběrového papíru. PPC, Praha 1983
- Hnětkovský, V. (1982). Zúžitkování sběrového papíru jako základní vlákniny v papírenském průmyslu. PPC, Praha 1982
- Hnětkovský, V. et al. (1983b). *Papírenská příručka*. 1. vyd. Praha : SNTL, 1983. 864 s
- Hon (1994). In *Kačík, F., Kačíková, D. (2007). Charakteristika a analýza celulózy a jej derivátov*. Monografia. 1. vyd. Zvolen: TU vo Zvolene, 2007. 94 s. ISBN 978-80-228-1819-3
- Howard, R.C. (1990). The effects of recycling on paper quality. In *J. Pulp paper Sci.* 16(5), p 143-149
- Howard, R.C. (1994). Fundamental problem in recycling. In *Prog. Paper Recycling* 3 (3), p. 66-70
- Howard, R.C. (1995). The effects of recycling on paper quality. In *Technology of paper recycling*. R.W.J. Mc Kinney (ed.), blackie Academic, London, Ch. 6, p. 180-203
- <http://swivel.com/charts/2381-Paper-Consumption-per-capita-by-Country>
- <http://www.cepi.org/content/default.asp> - Key Statistics 2009. European Pulp and Paper Industry

- Hubbe, M. A. (2006). Bonding between Cellulosic Fibers in the Absence and Presence of Dry-Strenght Agents-A review, In *BioResources*. ISSN 1930-2126, 2006, 1 (2), s. 281-318
- Hubbe, M. A. et al. (2003). Changes to unbleached kraft fibers due to drying and recycling. In *Prog. Paper Recycling*. 2003, vol 12 (3) s. 11-20
- Hubbe, M. A. et al. (2007). What happens to cellulosic fibers during papermaking and recycling? A Review. In *BioResources*. ISSN 1930-2126, 2 (4), p.739-788
- Hubbe, M. A., Zhang, M. (2005). Recovered kraft fibers and wet-and dry-strenght polymers. In *TAPPI 2005 Practical Papermarkes Conf.*, TAPPI Press, Atlanta
- Hubbe, M.A., Heitmann, J.A. (2007). Rewiew of factors affecting the release of water from cellulosic fibers during paper manufacture, In *BioResources*. ISSN 1930-2126, 2 (3), s. 500 -533
- Chen, Y., Wang, Y., Wan, J., Ma Y. (2009). Crystale and pore structure of wheat straw cellulose fiber during recycling. In *Cellulose*. Vol.17 (2) s.329-338
www.SpringerLink.com
- Chovanec, D. (1975). Výskum rozdielov v morfológii vlákien listnatých drevín. In IV celulózo-papierenské dni. Vranov 1975, s. 113
- ISO 5351/2-1981 (E) (1981): Cellulose in dilute solutions - Determination of limiting viscosity number. Part 2: Method in iron (III) sodium tartrate complex (EWNN_{mod NaCl}) solution
- Jayme, G., Büttel, H. (1968). The determination and the meaning of water retention value (WRV) of various bleached and unbleached cellulosic pulps, *Wochenbl. Papierfabr.* 96 (6) s. 180-187
- Kačík, F., Geffertová, J., Kačíková, D. (2009). Charakterizácia celulózy a buničín metódou gélovej permeačnej chromatografie a viskozimetrie. In *Acta Facultatis Xylogologiae*. ISSN 1336-3824, 2009, 51 (2) s. 93-103
- Kačík, F., Kačíková, D. (2007). Charakteristika a analýza celulózy a jej derivátov. Monografia.1. vyd. Zvolen: TU vo Zvolene, 2007. 94 s. ISBN 978-80-228-1819-3
- Karlsson, H. *Fibre Guide*. (2006). Fibre analysis and process applications in the pulp and paper industry. AB Lorentzen & Wetre, Box 4, SE-164 93, KISTA, Sweden, p.120, ISBN 91-631-7899-0
- Kato, K.L., Cameron, R.E. (1999). A review of the relationship between thermally-accelerated ageing of paper and hornification. In *Cellulose*, ISSN 0969-0239, 6 (1), p. 23-40
- Khantayanuwong, S. (2002). Effects of Beating and Recycling on Strength of Pulp Fibers and Paper, *Kasetsart J. (Nat. Sci.)* 36, s. 193-199
- Khantayanuwong, S. (2003). Determination of the Effect of Recycling Treatment on Pulp Fiber Properties by Principal Component Analysis. In *Kasetsart Journal*. Bangkok (Nat. Sci.) 37, 2003, s. 219-223
- Khantayanuwong, S. et al. (2002). Changes in Crystallinity and Re-swelling Capability of Pulp Fibers by Recycling Treatment. In *JapanTappi Journal* 56 (6), s. 103-106
- Klofta, J.L., Miller, M. L. (1993). Effects of deinking on the recycle potential of papermarking fibers. In *Res. Forum Recycling*, DAPPI, 1993, s. 207-220

- Kučerová, V., Halajová, L. (2009). Sledovanie zmien recyklovaných buničín metódou gélovej permeačnej chromatografie. In *Acta Fakultatis Xylogologiae*, ISSN 1336-3824, 2009, 51, (2), 87-92
- Laivins, G. V., Scallan, A. M. (1993). The mechanism of hornification of wood pulps. In *Products of Papermaking*, Oxford, 1993, C.F.Baker (ed.) Pira International, Leatherhead, Surrey, UK, Vol. 2 p. 1235-1259
- Lešíkár, M. (2006). Perspektívy balení potravín do obalů z papírů a lepenek. In *Papír a celulóza*. ISSN 0031-1421, 2006, 61, (2), s. 59
- Margutti, S., Conio, G., Calvini, P., Pedemonte, E. (2001). Hydrolytic and oxidative degradation of paper. In *Restaurator*. ISSN 0034-5806, 2001, (22) 2, s. 67-131
- Marx et al. (1966). *Naturwissenschaften* 53, 1966, s. 466. In *Blažej et al. Chémia dreva*. 1.vyd. Bratislava:Alfa, 1975. 221 s
- Matsuda et al. (1994). Effects of Thermal and Hydrothermal Treatments on the Reswelling Capabilities of pulps and Papersheets. In *Journal of Pulp and Paper Science*, ISSN 0826-6220, 1994, 20 (11), p. J323-J327
- MD (2010). Stav a vyhlídka průmyslu papíru a celulózy v některých vybraných zemích světa. In *Papír a celulóza*. ISSN 0031-1421, 2010, 65 (12), s. 352-354
- Milichovský, M. (1994). Recirkulace a recyklace - výzva současnosti. In: *Papír a celulóza*. ISSN 0031-1421,1994, 49 (2), s. 29-34
- Nazhad, M. M. (2005). Recycled fiber quality-A review, In *J. Ind. Eng. Chem.* 11 (3), s. 314-329
- Nazhad, M. M., Paszner L. (1994). Fundamentals of strength loss in recycled paper. In *Tappi Journal*, ISSN 0039-8241, 1994, 77 (9), p. 171-179
- Nordman, L. (1976). The applicability of recycling fiber to different papwe qualities. In *Sekundárne vlákna a ich využitie v papierenskom priemysle*. Eucepa symposium, Bratislava 1976
- Okayama, T. (2001). Characteristicsof pulp fiber with high recycling performance. *Journal Shigen Junkan* s. 39-40
- Okayama, T. (2002). The Effects of Recycling on Pulp and Paper Properties. *Japan TAPPI Journal*. ISSN 0022-815X, 2002, 56 (7), p. 986-992
- Paavilainen, L. (1993). Conformability-flexibility-of sulfate pulp fibers. In *Paperi Puu*.ISSN 0031-1057, 1993, 75 (9-10), p. 896-702
- Pauler, N. (2002). Paper optics. AB Lorentzen&Wetretre, Elanders Tofters, Östervála, Sweden 2002, p. 93, ISBN 91-971765-6-7
- Peng,Y.X., Valade, J.L.,Law, K.N. (1994). Effekcts of recycling and blending of virgin fibers on paper properties, In *China Pulp and Paper* 13 (2), p. 3-9
- Phipps, J. (1994). Effects of recycling on the strength properties of paper. In *Paper Technol.* 35 (6), p. 34-40
- Požgaj, A. et al. (1997). Štruktúra a vlastnosti dreva. 2. vyd. Bratislava : Svornosť, 1997. 485s. ISBN 80-07-00960-4
- Putz H.-J. (2000). Recovered paper grades, quality control, and recyclability. In: Götsching, L & Pakarinen, H (eds.) *Papermaking Science and Technology*, Book 7, Recycled Fiber and Deinking. ISBN 952-5216-07-1, 2000, p. 61-87
- Rowell, R.M., (2005). *Handbook of wood chemistry and wood composites*. 2005, Taylor & Francis Group. ISBN 0-8493-1588-3

- Shao, S.Y., Hu, K.T. (2002). Hornification of recycled fiber, In *China Pulp Paper* (2), p. 57-60
- Solár, R. (2001). *Chémia dreva*. 1. vyd. Zvolen : TU vo Zvolene, 2001. 101 s. ISBN 80-228-1007-X
- Solár, R., Mamoň, M., Kurjatko, S., Lang, R., Vacek, V. (2006). A simple method for determination of kinetics of radial, tangential and surface swelling of wood. In *Dřeva industrija*. ISSN 0012-6772, 2006, 57 (2), p. 75-82
- Solár, R. et al. (2009). Alkaline and alkaline/oxidation pretreatments of spruce wood. Part 1: Chemical alterations of wood and its digestibility under conditions of kraft cook. In *WOOD RESEARCH*. ISSN 1336-4561, 2009, Vol. 54, (4) 2009. p. 142
- Souček, M. (1977). *Zkoušení papíru*. 1. vyd. Praha:SNL, 1977. 339 s
- Souček, M. (2009). Grafické papíry na bázi recyklovaných vláken, In *Papír a celulóza*. ISSN 0031-1421, 2009, 64 (6), s.164-165
- Stone, J. E., Scallan, A. M. (1966). Influence of drying on the pore structures of the cell wall. In: *Consolidation of the Paper Web*, Trans. Symp. Cambridge, Sept. 1965, f.Bolam (ed.), Tech. Sec. British Paper and Board Makers' Assoc. Inc. London, Vol. 1, s. 145-174
- Stone, J. E., Scallan, A. M. (1968). A structural model for the cell wall of water-swollen wood pulp fibers based on their accessibility to macromolecules. In *Cellulosa Chem. Technol.* ISSN 0576-9787, 1968, 2 (3), 343-358
- Stürmer, L., Göttching, L. (1979). Physical properties of secondaryfiber pulps under the influence of their previous history. Part 3: Influence of the paper manufacturing process, In *Wochenbl. Papierfabrik*. 107 (3), p. 69-76
- ŠK (2010). Rast cien buničiny o 40 % a zberového papiera o 80 % tlačia na ceny výrobcov papiera na Slovensku. In *Papír a celulóza*. ISSN 0031-1421, 2010, 65 (6), s. 162
- Takayuki O. (2002). The Effects of Recycling on Pulp and Paper Properties. In *Japan TAPPI Journal*, ISSN 0022-815X, 2002, vol. 56 (7), p. 986-992
- Woodward, T., W. (1996). Recycled fiber types, processing history affect pulp behavior during papermarking. www.paperrecovery.eu, 2007
- Zugenmaier, P. (2008). *Crystalline Cellulose and Derivatives: Characterization and Structures*. Springer Series. In *Wood Science*, Springer-Verlag Berlin Heidelberg 2008, 286 s. ISBN 978-3-540-73933-3. <http://www.springer.com/978-3-54-73933-3>



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The presently common practice of wastes' land-filling is undesirable due to legislation pressures, rising costs and the poor biodegradability of commonly used materials. Therefore, recycling seems to be the best solution. The purpose of this book is to present the state-of-the-art for the recycling methods of several materials, as well as to propose potential uses of the recycled products. It targets professionals, recycling companies, researchers, academics and graduate students in the fields of waste management and polymer recycling in addition to chemical engineering, mechanical engineering, chemistry and physics. This book comprises 16 chapters covering areas such as, polymer recycling using chemical, thermo-chemical (pyrolysis) or mechanical methods, recycling of waste tires, pharmaceutical packaging and hardwood kraft pulp and potential uses of recycled wastes.

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