Laboratory Refining of Bleached Softwood Kraft Pulp in Water and a Series of Alcohols of Different Molecular Weights and Polarities: Effects on Swelling and Fiber Length

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Typical bleached pinewood kraft pulp from a paper mill was immersed in either water or different alcohols, such as methanol, ethanol, n-propanol, and n-butanol, and then refined in a PFI mill. After refining, changes in the internal fibrillation of the fibres were evaluated by measurements of water retention values (WRV), while fibre shortening was determined by measurements of the average weighted fibre length. The objective of this study was to determine the influence of a liquid used for refining on the principal refining effects such as the internal fibrillation and fiber shortening. The highest increase in the internal fibrillation was observed for the pulp samples refined in water, which has the higher dipole moment than the alcohols. For these samples, WRV increased from 93% to 201%, while the average weighted fiber length was reduced by only 0.6 mm. When the pulp was beaten in n-butanol, which was the least polar liquid among the liquids investigated, liquid retention value increased by only 23.5%, while the average weighted fibre length was reduced by 1.37 mm. These results showed the importance of water in the beating of cellulose fibres and demonstrated that the outcomes of this process depended on the dipole moment of the fiber immersion liquid.

Keywords: Papermaking pulp; Beating; Refining; Water; Dipole moment; Internal fibrillation; Fiber shortening

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INTRODUCTION

Paper is a versatile material used in everyday life, industry, and the economy. Global production and consumption of paper products amounts to 400 Mt and is continually increasing (Macklin 2012; Fornalski 2014). Apart from the functionality and relatively low prices, paper products are produced from environmentally friendly materials, such as fibrous biomass, mainly wood, and wastes, such as recovered paper.

All technological operations of the paper manufacturing process take place in water systems. Currently, water consumption amounts to approximately 20 m^3 per ton of paper produced (Thompson *et al*. 2001; Gavrilescu *et al*. 2008). Taking into account its availability and relatively low price, water is used as a cheap medium for transportation (suspension pumping), cooling, sealing, and washing. Relatively less attention is paid to the role of water as a compound in unit operations of the paper manufacturing process (Hubbe and Heitmann 2007). Therefore, in this study, the impact of water and selected alcohols on the outcomes of the papermaking pulp beating process were compared.

The Nature and Significance of Papermaking Pulp Beating

The mechanical treatment of pulp in water, or "beating", is a basic process in paper manufacturing. This process has been conducted since paper was invented, *i.e.*, the 2nd century A.D. Although pulp beating conditions have been modified many times, the mechanism of this process has not changed. Paper made from unbeaten fibres has a bulky structure due to the low apparent density, and very low strength properties, such as breaking force, burst, and tear resistance, *etc.* Paper of sufficient quality can only be produced from beaten cellulosic pulp, as this process strengthens the interactions that develop between cellulose fibres as the paper is dried (Mohlin 1975; Lumiainen 2000; Laine *et al*. 2005).

Along with the beating conditions, the raw materials used for paper manufacturing have also changed over time, with cotton, flax, and hemp fibres being substituted by wood fibres (Biermann 1996; Perez and Fauchon 2003). Moreover, the equipment used for this process has changed dramatically; the obsolete beating devices have been replaced by modern conical and disc refiners, in which pulp slurries, containing 4 to 6% dry weight, are pressed into suitably shaped gaps between the rotor and stator (Bajpai 2011; Andersson *et al.* 2012). The drawback of these devices is the low energy efficiency, which may be as low as 0.1% (Batchelor *et al*. 1997; Batchelor 2001; Scheihing 2005; Ek *et al*. 2009). The energy input into this process is very high and usually amounts to 100 to 500 kWh/t, which accounts for up to 40% of the total electric energy consumed by a paper mill (Cannell 1999; Illikainen *et al*. 2007). The results of measurements of the energy used for refining, which were collected over several decades, provide evidence that it was not remarkably reduced when the traditional technology was replaced or supplemented by treatments with ultrasound, enzymes, pulp freezing, steam explosion, pressure pulsation, cavitation, *etc.* (Szwarcsztajn and Przybysz 1970; Focher *et al*.1988; Kokta and Ahmed 1998; Mohlin and Pettersson 2002; Martin-Sampedro *et al*. 2011; Gandini and Pasquini 2012; Joutsimo and Asikainen 2013).

Water Contribution to Fibrous Pulp Beating Mechanism

The increase in the papermaking potential of the beaten fibrous pulp is caused by the growth of total free energy from bonds connecting cellulose fibers. The total energy depends on the specific energy of these bonds, the bonded area between the fibers in paper, and its structure, as calculated from Eq. 1 (Emerton 1957),

$$E_t = f(E_{sp}, A_{sp}) \quad (1)$$

where E_t is the total bond energy between the fibers in paper (J/g), E_{sp} is the specific bond energy between the fibers in paper (J/m^2), and A_{sp} is the bonded area between the fibers in paper (m^2/g).

The development of an appropriate bonded area (A) requires the proper flexibility of fibers, and to some extent, it depends on the fines content, which increases after refining. Properly flexible and plasticized fibres, which are created during the forming and pressing processes, enable formation of the paper web with a uniform structure, in which fibres adhere to each other on a large area (Seth 2006; Schmied *et al*. 2013). The bonds, which determine the high strength of the finished product, are fixed in the contact points between fibres during the drying process.

The ability of solid bodies to deform depends on, among other factors, the ease of reciprocal dislocation of their structural elements. The relatively high stiffness of unbeaten cellulose fibres results from durable bonding of their basic elements, which includes fibrils,

macrofibrils, lamellas, cell membranes, *etc*. Therefore, the breaking of bonds between the structural and morphological elements of the cellulose fibres is the essence and purpose of refining. This phenomenon is called internal fibrillation of fibres (Szwarcsztajn and Przybysz 1970; Wang 2006; Rusu *et al*. 2011).

Hydrogen bonds in plant fibres mainly form between hydroxyl groups of adjacent polysaccharide chains (Przybysz 2012). The formation of hydrogen bonds takes place in water environments during plant growth, when fibre cell membranes are formed. Hydrogen bonds form when these membranes consolidate and their water content decreases. This phenomenon reaches its apogee after the drying of plant material. It also occurs in papermaking pulps, which contain mainly cellulose and hemicelluloses.

The opposite phenomenon takes place when the water content increases in the fibre cell membrane during pulp soaking and refining. Polar water molecules penetrating the cellulose fibre structure cause the cleavage of hydrogen bonds between the fibrous structural elements. As a result, these hydrogen bonds, which are available to water, gradually transform into water bridges with reduced energy. In papermaking, this phenomenon is called internal fibrillation and gives rise to fibre swelling.

In industrial practice, swelling begins just after immersion in water (Kang and Paulapuro 2006; Ek *et al*. 2009; Yang 2014). Water fills the capillary system of fibres and swells the cellulose and hemicelluloses in water and low-ordered areas. The swelling of hydrophilic fibre components creates high stresses in the internal structure, which in turn causes the limited growth of transverse fibre dimensions. The loosening of the structure of fibres only under the influence of water is, in general, insufficient to produce sufficiently strong paper from these fibres (Batchelor *et al*. 1997).

Along with swelling in water, mechanical treatment is also necessary to intensify the internal fibrillation process. The results of mechanical treatment, which takes place during beating and consists of fibre compression, friction, bending, *etc.*, are similar to the outcomes of fibre grinding. Both mechanical treatment and grinding of cellulose pulp in a ball mill without water results in major fibre shortening and, at the end, the pulverization of fibres (Rusu *et al.* 2011).

Simultaneous internal fibrillation, which is influenced by water and fibre shortening caused by mechanical action, takes place during pulp refining. Considering the quality of paper, this process should bring about intensified internal fibrillation and very limited fibre fragmentation.

The amount of internal fibrillation is measured by changes in water retention values (WRV) during cellulose pulp refining (Stone *et al*. 1968; Przybysz 2012). This parameter defines the amount of water absorbed by cellulose fibres in relation to their dry weight. Fibre shortening is measured by the decrease in the mean fibre length.

The objective of this work was to demonstrate the impact of water on pulp refining outcomes. Therefore, the pulp was refined in either water or certain alcohols such as methanol, ethanol, n-propanol, and n-butanol. This made it possible to find the interplay between the characteristics of a liquid used for refining and the internal fibrillation (disruption of hydrogen bonds inside the fibers and swelling) and disintegration of fibers (their shortening). The dipole moment of water is higher than the dipole moments of the alcohols, and therefore water was expected to promote fiber swelling, while the highest elasticity of fibers in water environment was presumed to counteract their shortening. It was also expected that pulp refining in n-butanol might lead to the weakest fiber swelling and the most advanced shortening.

EXPERIMENTAL

Cellulosic Pulp

A typical air-dried bleached pine kraft pulp was used in the study. The following parameters were measured for the unbeaten pulp:

- Dryness – 96.0% according to ISO 638:2008; the standard deviation of results of four measurements was 0.1%.
- Lignin content – Kappa number of 0 according to ISO 302:2004; the measurements were conducted in triplicate, and the standard deviation was 0.1.
- Swelling in water (WRV – Water Retention Value) – 93% according to ISO 23714:2014; the standard deviation of results of four measurements was 0.6%.
- Average fiber length – 2.30 mm, measured according to ISO 16065-2:2014 standard, using a Morfi Compact Black Edition device; the measurements were performed in triplicate and the standard deviation was 0.01 mm.
- Degree of polymerization – 1250, measured according to ISO 5351:2010; the standard deviation of results of four measurements was 30.

Alcohols

To determine the role of water in papermaking pulp beating, water was replaced with a series of alcohols with increasing molecular weight and decreasing molecule polarity (Table 1). All the used alcohols were pure for analysis and produced by Avantor Performance Materials Poland.

Table 1. Selected Properties of the Used Liquids (McMurry 2012)

Liquid	Chemical Formula	Molecular Mass (μ)	Electric Permittivity (F/m)	Dipole Moment (D)	Dielectric constant (K)
Water	H-OH	18	80	1.85	78.4
Methanol	CH3-OH	32	33	1.7	32.6
Ethanol	CH3-CH2-OH	46	24	1.69	24.6
n-Propanol	CH3-CH2-CH2-OH	60	20	1.68	21.0
n-Butanol	CH3-CH2-CH2-CH2-OH	74	18	1.66	17.5

Refining in Water

Reference samples were soaked in water for 24 h before refining. After the incubation, the samples were disintegrated in a laboratory fiberizer R1 (Labormeks, Poland), at 23,000 revolutions according to ISO 5263-1:2004. The concentration of the disintegrated samples was adjusted to 10% dry weight before refining in a PFI mill under standard conditions, according to ISO 5264-2:2011.

The results of preliminary refining tests showed that the standard Schopper-Riegler number of 30°SR was reached in 3 min (4320 revolutions). Paper of basis weight equal to 75 g/m^2, which was produced from this pulp using a Rapid-Kothen apparatus, according to ISO 5269–2:2004 standard, was characterized by the highest static strength properties. Its breaking length was 8100 m, tear resistance was 580 mN and burst was 480 kPa.

The measurements of water retention value were carried out before and after refining according to ISO 23714:2014 using a MPW 350 centrifuge (MPW, Poland). Four

measurements were performed for each sample and average values and standard deviation of results were calculated.

The fiber length was measured according to ISO 16065-2:2014 standard, using a Morfi Compact Black Edition device (Techpap, France). The measurements were carried out in triplicate and mean values and standard deviation were calculated.

Refining in Alcohols

To remove the residues of water and promote soaking in alcohols, the pulp samples were kept before refining for 24 h in a desiccator containing silica gel. Such treatment of pulp does not cause any additional hornification of fibers or any changes leading to a decrease in papermaking potential of pulp in comparison to air-dry pulp (Kucner *et al.* 2014). Aliquots (400 mL) of methanol, water-free ethanol, n-propanol, or n-butanol were mixed with 22.5 g of dry pulp, and the samples were incubated for 24 h. During this time, the liquids penetrated the structure of the fibers and caused swelling. After the incubation, the samples were disintegrated and refined for 3 min (4320 revolutions) analogically as the samples treated in water.

The liquid retention (swelling) and fiber length of these samples were determined using the same methods as for the samples refined in water. The liquid retention in pulp was determined according to the same standard (ISO 23714:2014) as in case of WRV assays, however in this case the amount of retained alcohols was determined.

Before evaluation of fiber length, the alcohols were removed from pulp samples through washing with water. Two liters of deionized water were used to wash 0.4 g of pulp. The samples of pulp refined in n-butanol were successively washed with n-propanol (500 cm^3), methanol (500 cm^3) and at the end with deionized water (2 dm^3).

RESULTS AND DISCUSSION

The results presented in Fig. 1 demonstrate that the swelling of cellulose fibres was more advanced in water than in the tested alcohols. The strongly polar, small water molecules broke hydrogen bonds between the structural elements of cellulose fibres, which in turn increased their swelling degree. The water retention value reached 93%. This meant that 1 g dry weight of these fibres could absorb approximately 0.93 cm^3 of water. The liquid retention value of the pulps soaked in methanol or n-butanol achieved only 30% and 21.5%, respectively. Thus, the pulp swelling ability of the alcohols decreased with increased molecular weight and decreased dipole moment.

The decrease in the pulp swelling ability and the decrease in the dipole moment of alcohols correlated with the reduced pulp swelling (fibrillation) in the refining process (Fig. 1) because the ultimate LRV (liquid retention value) for the pulps beaten in water, methanol, and n-butanol were 201.5%, 102.5%, and 45%, respectively. Thus, the LRV of the beaten pulps decreased with the increase in the molecular weight and decrease in the dipole moment of the alcohol.

The effect of the dipole moment of the solvent on changes in liquid swelling (ΔLRV) caused by pulp beating is presented in Fig. 2. The values of ΔLRV for water, ethanol, and n-butanol were 108%, 55%, and 25%, respectively. The increase in the swelling degree of the pulp was lower when the dipole moment of the solvent was lower, and the cellulose fibres are not expected to swell in the alcohols with dipole moments below 1.5 to 1.6 D.

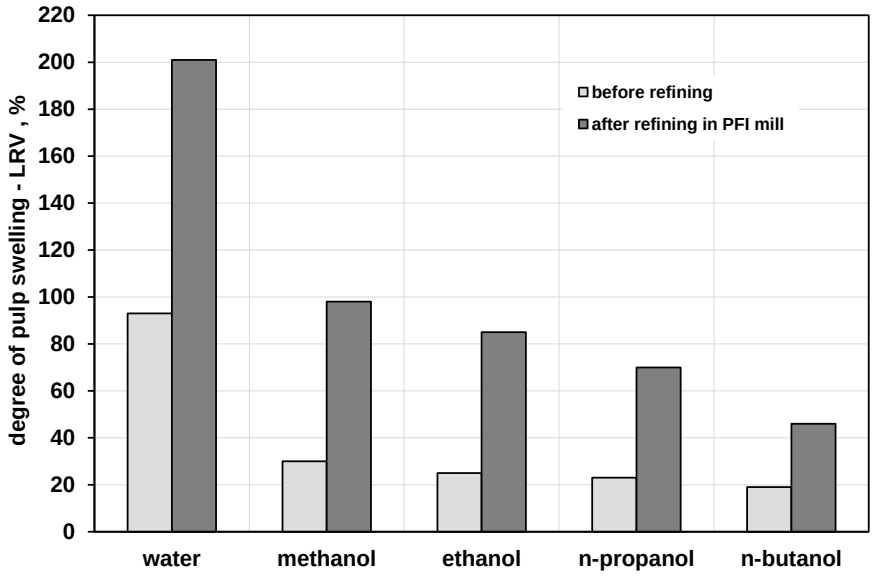

Fig. 1. Liquid retention value (LRV) of the bleached kraft pulp in the selected liquids before beating and after beating in a PFI mill for 3 min

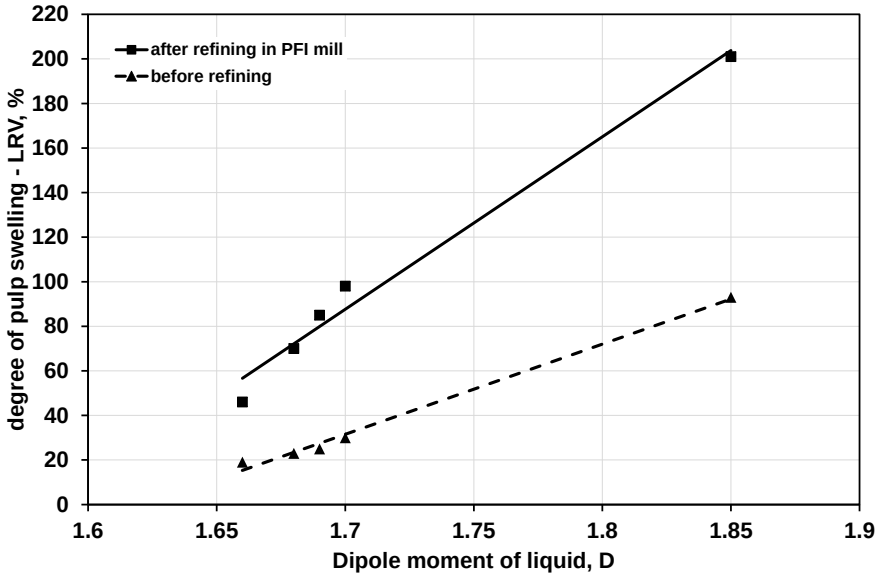

Fig. 2. The degree of swelling (LRV) of the tested pulp before and after beating as a function of the dipole moment of the investigated liquids

The comparison of the values of average fibre length of pulp beaten in either water or alcohol (Fig. 3) demonstrated that water outperformed the latter. After beating in water, this parameter decreased from 2.3 mm to 1.66 mm, while in methanol and n-butanol, it decreased to 1.35 mm and 0.98 mm, respectively. Thus, the tendency of fibres to fragment (shorten) increased with the rise in molecular weight of the alcohol and the decrease in the dipole moment.

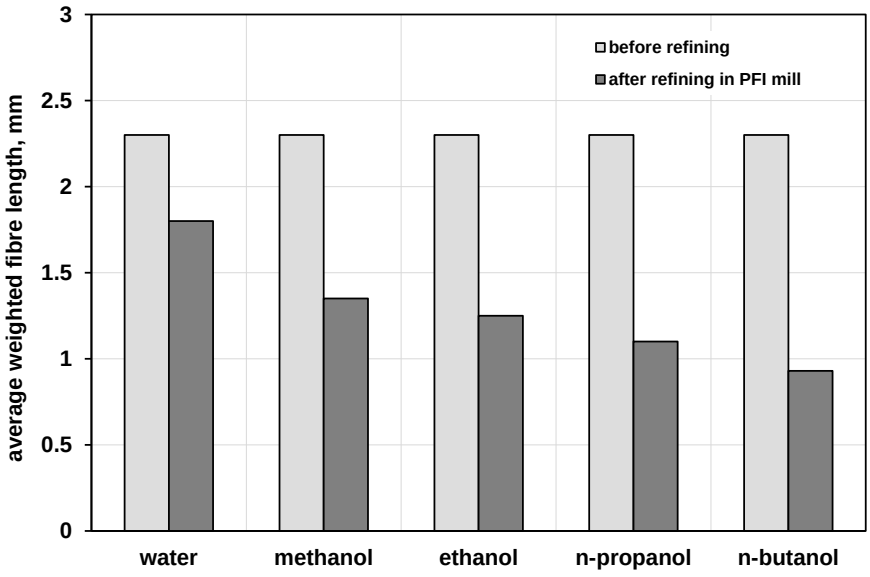

Fig. 3. The average length of fibres with fines contained in the bleached kraft pulp after refining in water and alcohols in a PFI mill for 3 min

Because the growing LRV reflected the increased degree of pulp fibrillation and the decreased fibre average length reflected the gradual fibre shortening, the relationship between these parameters described the nature of the beating process.

The interplay between the dipole moment of the liquid and shortening of the cellulose fibres, caused by the beating process, is presented in Fig. 4. A lower dipole moment resulted in a greater decrease in the average fibre length of the refined pulp. In the case of water, the decrease in the average fibre length was 0.5 mm, while for butanol, the decrease was more than 2-fold higher (1.3 mm).

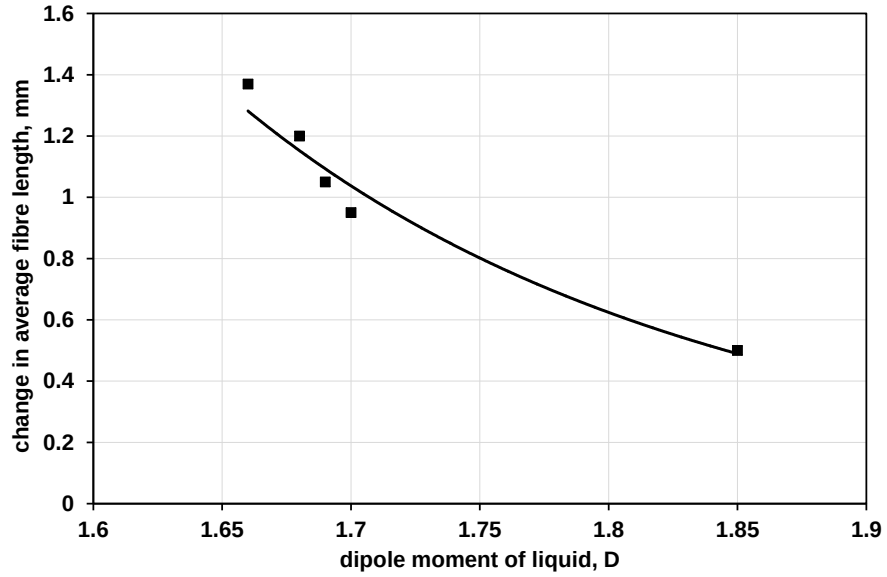

Fig. 4. The change in the average weighted fibre length of the pulp before and after beating as a function of the dipole moment of the liquid

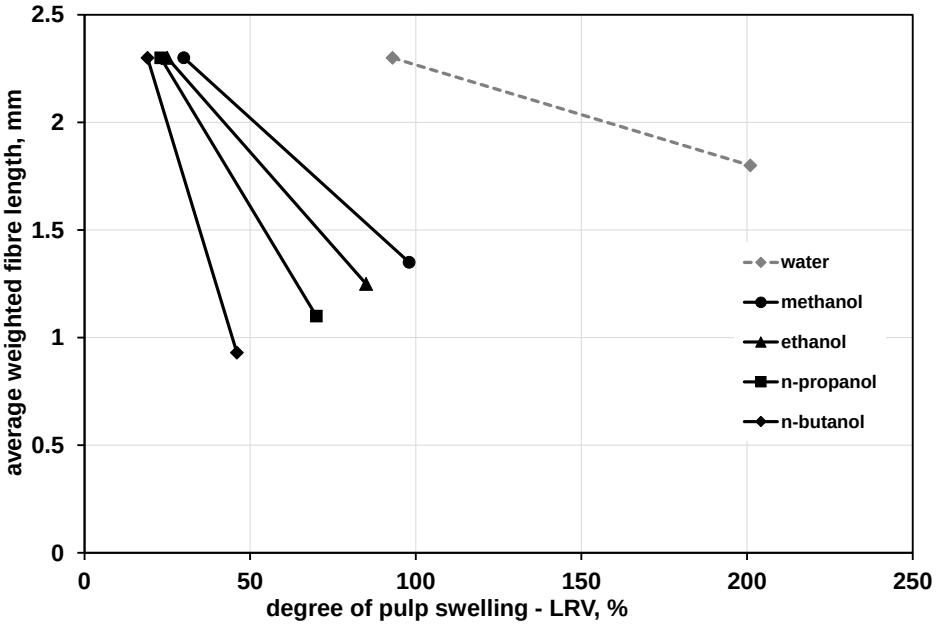

Fig. 5. The influence of water and selected alcohols on the relationship between the swelling degree (LRV) and the average fibre length of the beaten pulp

The relationship between liquid swelling and the average weighted fibre length of pulp beaten in water and the alcohols is presented in Fig. 5. This data showed that pulp refining should be conducted in water because, compared with the alcohols, the highest increase in liquid swelling (fibrillation) and the lowest decrease in the average weighted fibre length occurred in water.

The interplay between the fibrillation and fibre shortening can be described by the following equation,

$$L = LRV_p - a \cdot LRV \quad (2)$$

where L is the average weighted fibre length (mm), LRV_p is the initial pulp swelling degree (%), a is the factor describing the nature of beating process (ΔL/ΔLRV, mm/10%·LRV), and LRV is the pulp swelling degree (%). The coefficient a in Eq. 2 corresponds to the ratio of ΔLRV and changes in the average fibre length, and thus it described the nature of the pulp beating process (Fig. 6).

The data presented in Fig. 6 demonstrated that the nature of the changes in the structure of pulp, which took place during refining, was strongly influenced by the liquid used in this process. In water, the value of liquid swelling (fibrillation) increased by around 10%, while the average weighted fibre length decreased by only 0.05 mm. For comparison, in n-butanol the latter parameter decreased by 0.58 mm, around 11 times more. Thus, the ability to cause fibre swelling (fibrillation) decreased and the ability to cause fibre shortening increased in conjunction with the increase in the molecular weight of alcohol and the decrease in its dipole moment.

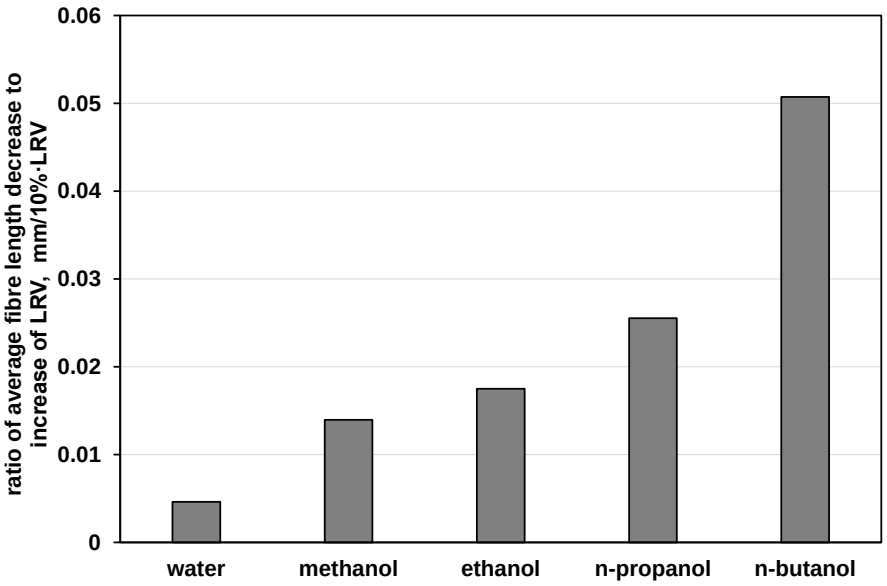

Fig. 6. The influence of water and tested alcohols on the relationship between the decrease in the average fibre length (ΔL) and the increase in swelling degree (ΔLRV) of the beaten pulp (coefficient a).

CONCLUSIONS

1. The highest liquid swelling of the unbeaten bleached softwood kraft pulp was obtained in water (93%). Liquid swelling decreased along with the increase in the alcohol molecular weight, and was only 21.5% in n-butanol.
2. The increase in liquid swelling caused by pulp beating was a measure of fibre fibrillation progress. Also, the change in liquid retention value (ΔLRV) was the highest after beating in water and decreased with increasing molecular weight of alcohol. After pulp beating in water, swelling (in this case WRV) increased by 108% (to 201%), while in butanol, liquid swelling increased by only 23.5% (to 45%).
3. The decrease in the average weighted fibre length caused by refining was a measure of pulp fragmentation. This parameter was the lowest for pulp beaten in water and increased with increased molecular weight of alcohol. The initial average fibre length was 2.3 mm and, after beating in water, it was reduced by 0.5 mm. Refining in butanol resulted in a decrease of this factor by around 1.4 mm.
4. The replacement of water with alcohols had a strong impact on the properties of the beaten pulp, which depended on the molecular weight and dipole moment of alcohol.
5. Water was found to be a very important factor that influenced the pulp beating process through synergistic action with mechanical treatment because of its unique structure and high polarity of molecules.

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