

Oxygen Delignification and Bleaching of Industrial Hemp Pulps

Abstract

The oxygen delignification of unbleached kraft pulps produced from industrial hemp stalks and hemp 'wood' was studied, as well as the susceptibility of such pulps to bleaching. Hemp stalk and wood pulp showed comparable susceptibility to delignification with oxygen in alkaline media and good bleachability in the elemental chlorine free (ECF) and the total chlorine free (TCF) bleaching processes. Good bleachability was also shown by hemp bast fibre pulp. The final yield and intrinsic viscosity of bleached pulps produced from industrial hemp were also determined and compared with the properties of pulps produced from tree wood. It was found that the final yield of bleached hemp stalk pulp was higher than that of conventional bleached birch- and pine papermaking pulps. However, the retention of high intrinsic viscosity in hemp pulps can be achieved by varying the conditions of the oxygen delignification and bleaching processes.

Key words: hemp pulps, oxygen delignification, bleaching, final yield, intrinsic viscosity.

■ Introduction

An increase in paper production, as well as stricter environmental protection regulations and the decreasing area of forest per capita may make it difficult to obtain the traditional raw material (i.e. wood) used in papermaking in the future. As a consequence, research aiming to increase fibrous semi-manufactured product yields has focussed on improving the selectivity of wood delignification and stability of polysaccharides, which has led to the development of technology involving the use of polysulphides and anthraquinone, solutions which are said to facilitate more rational wood processing. However, the relatively low increase in pulp yield (2 - 4%) from wood obtained using these methods seems insufficient to overcome the potential shortage of wood raw material facing papermaking.

Therefore, the search for additional sources of fibres for use in papermaking is now concentrated on the development of plantations of rapidly growing trees, increasing the recycling of waste paper, and the wider use of non-wood plants. With respect to the latter, industrial hemp has potential [1], with annual fibre production per hectare ranging from 5 to 15 t [2, 3]. For the Polish climate, annual production of up to 10 t has been estimated [4].

Industrial hemp is an annual plant cultivated generally for use in the textile industry [5, 6]. Worldwide industrial hemp is defined as plants of the *Cannabis sativa* species with a < 0.2% content of tetrahydrocannabinols (psychoactive substance), which makes such plants unsuitable for narcotic purposes. In Poland there are three registered varieties

– *białobrzaska*, *beniko* and *silesia*, all of which are cultivated at the Institute of Natural Fibres in Poznan [7]. As shown in the literature, the use of industrial hemp in paper production has been previously considered [8], with studies also investigating the technological aspects of such a process. Much of the activity in this area has been undertaken by Canadian researchers [9 - 11], whose work largely concerns the evaluation of the chemical composition of industrial hemp, the anatomical structure and cell morphology of a Canadian variety of this plant, as well as the technological aspects of processing industrial hemp into unbleached papermaking pulps. Similar research on the application of industrial hemp for papermaking purposes has also been conducted in England, France, Germany [8], Holland [12] and Australia [13]. In Poland, investigation of the processing of industrial hemp into bleached papermaking pulps via a chemithermomechanical method has been carried out by workers of the Pulp and Paper Research Institute, with two patents granted for methods developed by these authors [14, 15].

Recently, research has also been undertaken at the Institute of Papermaking and Printing of the Technical University of Lodz with the aim of replacing a part of semi-manufactured products used in the production of graphic woodfree paper, i.e. bleached pulps derived from wood, with other semi-manufactured products such as bleached pulps derived from waste paper and annual plants.

This paper presents the results of research into the oxygen delignification and bleaching of industrial hemp kraft pulps. The results presented may have

significance for the creation of a theoretical basis for the process of the delignification and bleaching of industrial hemp kraft pulps and could also be useful when determining the conditions and parameters of these processes in the industry.

■ Experimental

Pulps

The following kraft pulps produced from industrial hemp (*Cannabis sativa*) were used:

- kappa number 24.2 pulp from hemp stalks cut into 3 - 6 mm segments (marked as Hs3-6),
- kappa number 25.9 pulp from wood of hemp stalks not subjected to the retting process (Hw-nr),
- kappa number 26.6 pulp from wood of hemp stalks subjected to the retting process (Hw-r),
- kappa number 25.3 pulp from birch wood (B),
- kappa number 32.3 pulp from pine wood (P).

Kappa number 11 hemp bast fibre pulp (Hbf3) was also used in the bleaching experiments, obtained via the oxygen delignification of hemp bast fibres cut into segments of approximately 3 mm.

For comparison **Figures 1 - 5** also include results of the delignification and bleaching of birch- and pine kraft pulps. These data are derived from experiments carried out as part of another research project by the authors.

Pulping process

Pulping was carried out in a Hato laboratory digester in 2.5-L autoclaves. The active alkali charges for hemp stalks,

hemp wood (nr and r) and birch- and pine chips were 15, 18.5, 21, 18 and 22% for oven-dried raw material, respectively. For the kraft pulping experiments the sulphidity of the liquor was 25%, with a liquor-to-wood ratio of 5:1 for hemp raw materials and 4:1 for birch- and pine wood chips. In all the cooking experiments, the temperature was raised to 165 °C in the first 90 minutes and held there for a further 90 minutes. After cooking, the fibrous material was washed with deionised water, first on wire mesh and then by diffusion for 24 h, after which they were disintegrated.

Oxygen delignification (OD) of hemp stalks, hemp wood and birch- and pine pulps

A Jayme reactor was used for oxygen delignification. In all the experiments, the amount of pulp used was 40 g (oven-dry basis). Oxygen delignification experiments were carried out at a consistency of 8%, an oxygen pressure of 0.6 MPa and at a temperature of 100 °C. At the beginning of each experiment, a 0.1% charge (on oven-dry pulp) of MgSO₄ dissolved in 300 ml of water was mixed with the pulp, after which a NaOH charge (on oven-dry pulp) was added to the rest of the water. The pulp was then mixed with chemicals, placed in the reactor and oxygen pressure applied. After 60 minutes of delignification, the pressure was released, the reactor opened and the pulp discharged, filtered and washed with four aliquots of 1000 ml deionised water before being stored in a plastic bag for further treatment.

Oxygen delignification of hemp bast fibres

A sample of 100 g (oven-dried basis) of hemp bast fibres was placed in a polyethylene bag and then the following was added sequentially: 0.1% MgSO₄ (in the form of an aqueous solution), 1% sodium hydroxide solution and distilled water in an amount ensuring the 10% concentration of fibrous slurry desired. The contents of the bag were then mixed by squeezing and placed in the Jayme reactor. The autoclave was closed, filled with oxygen and heated to a maximum temperature of 100 °C for 30 minutes, at which temperature it remained for a further 60 minutes. After 60 minutes of delignification, the pressure was released, the reactor opened and the pulp discharged, filtered and washed with four aliquots of 1000 ml deionised water and

stored in a plastic bag for further treatment.

Chlorine dioxide bleaching (D₀E_pD₁)

A total of 20 g (dry content) of disintegrated pulp was placed in a double polyethylene bag together with deionised water. After kneading the pulp, chlorine dioxide was charged with three percent ClO₂, used for bleaching oven-dried pulp. Sixty-five percent of this was added at the D₀ stage and the rest at the D₁ stage at 8% consistency. No adjustment of the pH of the pulp suspension was made. After 1 minute of further kneading, the pulp was placed in a water bath with a constant temperature of 75 °C. The bag was kneaded again after a further 5 and 30 minutes. After 60 and 90 minutes of bleaching in the D₀ and D₁ stages respectively, the bag was opened. The pulp was then washed via the same method used in the oxygen delignification process and subsequently placed in a new plastic bag for further treatment.

After the D₀ stage, the pulp was treated by a hydrogen peroxide-reinforced alkali process (E_p stage). Deionised water, sodium hydroxide (1.5% on oven-dried pulp) and hydrogen peroxide (0.6% on oven-dried pulp) were added to the bag containing the pulp (10% pulp consistency). After kneading, the bag was placed in a water bath (75 °C) and kneaded again after 10 and 30 minutes. After a total of 90 minutes of treatment, the pulp was washed using the same method as described for the OD process.

Bleaching of pulps with hydrogen peroxide (P stage)

The peroxide bleaching stage was conducted using bleach liquor consisting of 3% H₂O₂, 2.5% NaOH, 0.2% MgSO₄ and 1% Na₂SiO₃ (all chemical charges are expressed as a percentage on pulp, on an oven-dry basis). Each pulp sample (20 g of oven-dried pulp) and the accompanying bleaching chemicals were mixed with deionised water in a polyethylene bag to obtain a final consistency of 10% before being immersed in a water bath of 80 °C, in which they were held for three hours and hand-mixed at 30 minute intervals. At the end of the treatment, the pulps were washed as described previously.

Peracetic acid treatment (Pa stage)

Peracetic acid (purchased from Fluka Chemica) treatment was conducted in polyethylene bags containing 0.3% dis-

tilled peracetic acid on pulp (as active oxygen) and the quantity of water required to achieve a pulp consistency of 10%. No adjustment of the pH of the pulp suspension was made after the addition of peracetic acid. After kneading, the pulp was placed in a water bath with a constant temperature of 75 °C. After 90 minutes of treatment, the pulps were washed in the same manner outlined for the OD process. The concentration of active oxygen in the peracetic acid was determined using the method described by Amini and Webster [16].

Removal of metal ions (chelation stages)

Chelation stages (Q) were performed at pulp consistencies of 10% for one hour at 75 °C. At the beginning of the treatment, a 0.5% charge of EDTA was applied to the pulp, and the pH was adjusted to 5 using H₂SO₄. After 60 minutes of treatment, the pulp was washed as described previously.

Analyses

Standard methods were used to measure both the kappa number of the pulps PN-85/P50095 (Equiv. ISO 302-1981) and the intrinsic viscosity PN-92/P-50101/01 (Equiv. ISO 5351/1:1981). The pulp brightness (R457 nm) was determined according to the ISO 2470 standard using Spectrocolor apparatus.

Results and discussion

Bleached kraft pulps obtained from wood are mainly used in the production of white paper, such as xerographic paper. In order to determine if, or to what extent, these pulps can be replaced by alternative ones, the authors studied the process of production and properties of bleached pulps obtained from hemp stalks, hemp wood and hemp bast fibres.

In the first part of the work we found that in the case of hemp stalks and hemp wood, it was necessary to process these kinds of raw materials using the same methods applied to wood, i.e. with the kraft pulping process as the first stage of delignification. However, obtaining easily bleachable pulps without need for the pulping process appears to be possible in the case of hemp bast fibres [17].

In this study, the aim was to study the oxygen delignification and bleaching processes of hemp pulps obtained via kraft pulping. Hemp stalks and wood

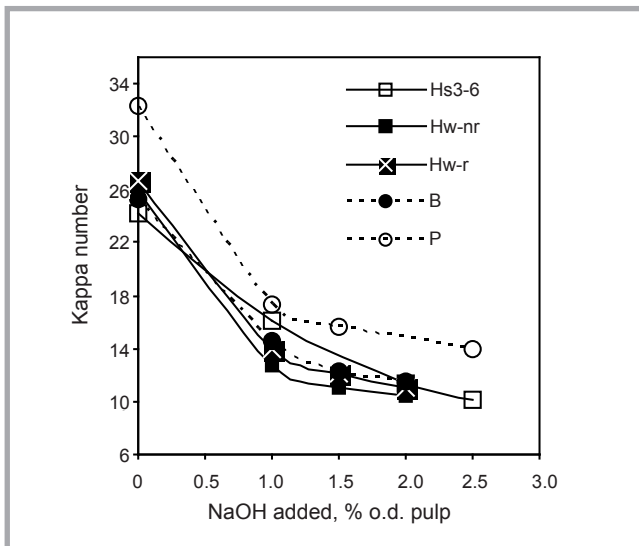


Figure 1. Changes in the kappa number of kraft pulps obtained from whole hemp stalks (Hs3-6) and hemp wood (Hw) in oxygen delignification process compared with results of the oxygen delignification of birch- and pine pulp (B, P)

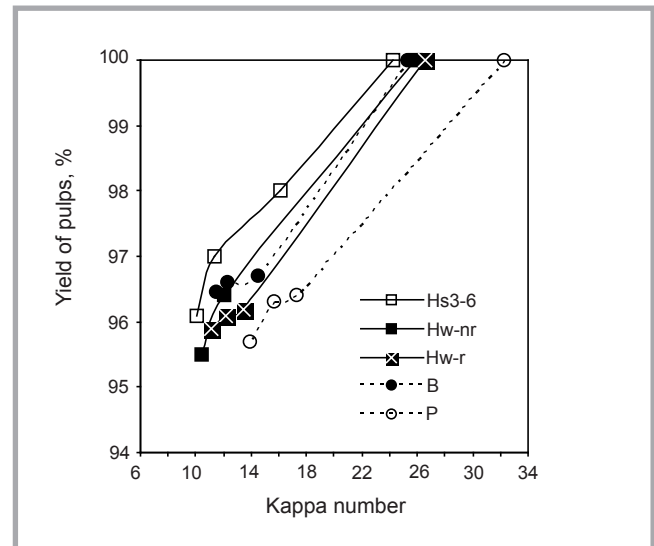


Figure 2. Changes in kraft pulp yield in the oxygen delignification of hemp stalks (Hs3-6) and hemp wood (Hw) pulps, compared with corresponding changes in the yield of birch- and pine pulps (B, P).

were delignified by the pulping process to a kappa number of approximately 25, i.e. the same as birch pulp. The pulps obtained were subsequently subjected to oxygen delignification in conditions differing only in terms of the amount of NaOH added. The results of these experiments are presented in **Figure 1**, which also shows results of the oxygen delignification of birch- and pine pulps for comparison.

The data presented in **Figure 1** show that all hemp pulps (Hs3-6, Hw-r, Hw-nr) are delignified with oxygen in a manner characteristic of this process, i.e. with a relatively large amount of lignin removed from the pulp in the initial stage and significantly lower amounts removed in the second. The pattern of the delignification

of pulps obtained from hemp stalks (Hs3-6) and wood (Hw) is similar to that of the delignification of birch pulp (B).

Figure 2 shows comparative yields of oxygen-delignified pulps obtained from hemp and tree wood pulps.

Analysis of **Figure 2** reveals that pulps derived from hemp wood (Hw-nr, Hw-r) have a yield comparable to that of birch pulp, i.e. approximately 96%, when delignified to a kappa number of 10 - 12. A slightly higher yield (approx. 1%) was obtained from hemp stalks (Hs3-6) of similar kappa numbers.

An important suitability parameter of pulps produced from industrial hemp is their bleachability. The research outlined

here enables a comparison to be made of the bleachability of pulps produced from semi-manufactured hemp products and that of birch- and pine kraft pulp. In this study, oxygen-delignified hemp- and birch pulps of kappa number 10 - 12 and pine pulp of kappa number 13 were used. Pulp samples were bleached with chlorine dioxide (the elemental chlorine free (ECF) bleaching) and hydrogen peroxide (the total chlorine free (TCF) bleaching) as the main bleaching agents. In the ECF bleaching (D stages), a ratio of 3% ClO₂ to oven-dried pulp was used.

The results of pulp bleaching, i.e. their R457 brightness levels, are presented in **Figure 3** compared with their initial (unbleached) brightness values.

As can be seen in **Figure 3**, the initial brightness of each pulp differed significantly. Immediately noticeable is the especially low brightness of pulps obtained from hemp stalks subjected to the retting process, i.e. hemp wood (Hw-r) and hemp bast fibres (Hbf3), of around 29%. The initial ISO brightness of the remaining pulps ranged from circa 38 to 50%, being the highest in the case of birch pulp. The pulp samples were initially subjected to bleaching with chlorine dioxide (sequence D₀EpD₁).

Figure 3 shows that after bleaching with a ratio of 3% chlorine dioxide to oven-dried pulp, pulps Hs3-6, Hw-r and Hbf3 had brightness levels 2.4 - 4.7% lower than that of birch pulp. Despite these re-

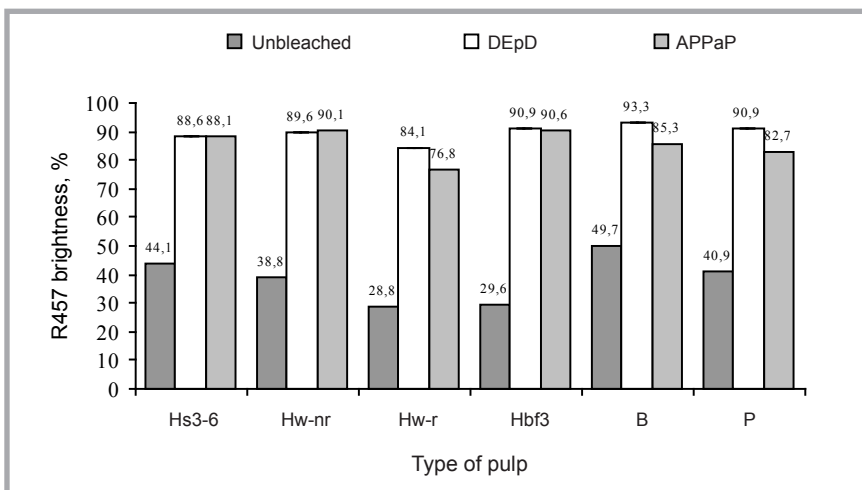


Figure 3. Results of the ECF and TCF bleaching of pulps obtained from whole hemp stalks (Hs3-6), hemp wood (Hw), hemp bast fibres (Hbf3) and birch- and pine wood.

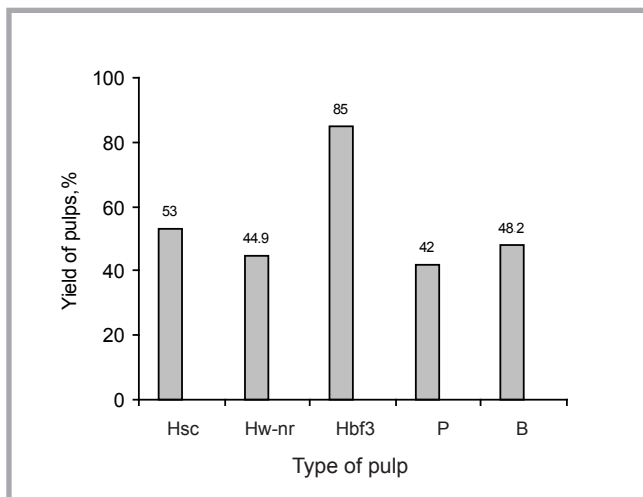


Figure 4. Comparison of the final yield of bleached pulps produced from hemp raw materials and the yield of bleached pulps produced from birch- and pine wood.

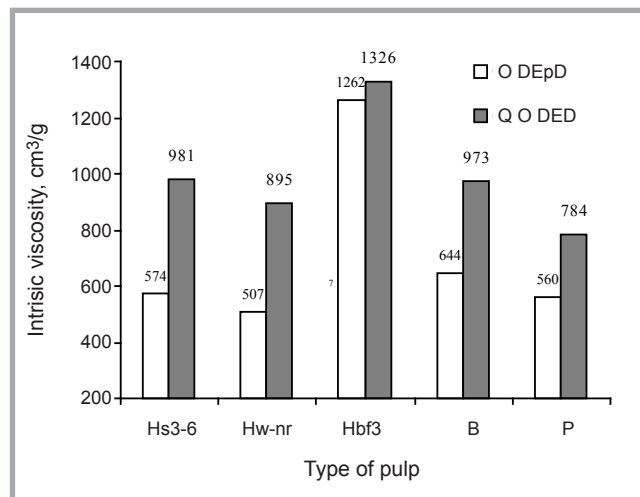


Figure 5. Comparison of the intrinsic viscosities of bleached hemp pulps and those of bleached birch- and pine pulps.

sults, it should be stated that the bleachability of these hemp pulps is very good. The higher brightness of birch pulp could be partly attributed to its comparatively greater initial brightness.

Pulp produced from hemp wood obtained from hemp stalks subjected to the retting process (Hw-r pulp) showed significantly worse susceptibility to bleaching with ClO_2 , because bleaching with 3% ClO_2 resulted in a pulp brightness of approximately 84% ISO.

As already mentioned, the susceptibility of pulps to TCF bleaching was also studied. Due to the fact that the complete bleaching of pulps solely with hydrogen peroxide is difficult to achieve; an additional peracetic acid treatment stage (Pa stage) was introduced into the bleaching sequence after the first peroxide stage. The former appeared to be a good lignin activator in our previous work [18 - 20]. Therefore the bleaching scheme was as follows: AP_1PaP_2 .

As shown in **Figure 3**, the susceptibilities of pulps produced from hemp (Hs3-6, Hw-nr, Hbf3) to TCF bleaching were surprisingly higher than that of birch pulp, with a brightness of the hemp pulps after bleaching of 88-91%, compared with only approximately 85 and 82% for birch- and pine pulps, respectively. As observed after chlorine dioxide bleaching, the Hw-r pulp had a demonstrably lower susceptibility to bleaching again.

In a separate experiment, the final yield of the bleached hemp pulps was determined and compared with the yield of

pulps produced from birch- and pine wood. Data are presented in **Figure 4**.

As shown in **Figure 4**, industrial hemp stalks potentially produces a bleached pulp yield approximately 5% higher than that derived from birch wood, and 11% higher than that from pine wood. Less favourable was the yield of pulp produced from the inner part of this plant, i.e. hemp wood, with yields around 3% lower than that of birch pulp. The highest bleached pulp yield derived from hemp raw materials was produced from hemp bast fibres (Hbf3). As shown in **Figure 4**, by subjecting these fibres to the processes of oxygen delignification and ECF bleaching, it is possible to obtain bleached pulp yields of approximately 85%, i.e. 43% and 37% greater than those of bleached pine- and birch pulp, respectively.

Finally, the intrinsic viscosities of hemp pulps were determined and compared with those of bleached pulps produced from birch- and pine wood, which were also bleached according to the method described in the experimental methods section. The results are presented in **Figure 5**.

As shown in **Figure 5**, the intrinsic viscosity of pulps derived from hemp stalks (Hs3-6) and hemp wood (Hw-nr) bleached according the method described in the methods section (OD_0EpD_1 sequence) was relatively low (500 - 600 cm^3/g) and comparable to that of birch- and pine pulps. The low viscosity of these pulps after bleaching is generally thought to be due to the presence of metal ions, such as iron, manganese and cop-

per in the unbleached pulps. These ions, especially in bleaching processes which involve H_2O_2 (e.g. oxygen delignification, alkaline extraction reinforced with H_2O_2), generate hydroxyl radicals ($\text{OH}\cdot$) which strongly depolymerise the cellulose.

In order to retain high viscosity levels of hemp pulp, the conditions of the oxygen delignification and bleaching processes of these pulps were modified. This modification consisted in the introduction of a Q stage before the oxygen delignification of the pulps, increasing the amount of MgSO_4 (an inhibitor of cellulose depolymerisation) added at the O_2 stage to 0.5% on oven-dried pulp and the removal of hydrogen peroxide at the Ep stage.

Figure 5 shows that the viscosity of Hs3-6 and Hw pulps after the introduction of such changes was greatly improved, with levels of 890 - 980 cm^3/g observed.

As can be seen from the data presented in **Figure 5**, these changes also affected the viscosity of bleached pulp made from hemp bast fibres (Hbf); although the increase was smaller than that observed in the other pulps. This suggests that the metal ion content of hemp bast fibres is lower than that of hemp stalks and hemp wood.

Conclusions

1. The oxygen delignification of pulps produced from the kraft pulping of hemp stalks and hemp wood proceeds in a way typical of this process, i.e. with a high amount of lignin removed

- in the first stage of the process and a considerably lower amount removed in the second stage.
- The yield of pulp produced from the oxygen delignification of cut hemp stalks is comparable to that of pulp produced from wood.
 - Oxygen delignified pulps produced from hemp show a similar susceptibility to ECF bleaching to those produced from birch- and pine wood, but a better susceptibility to TCF bleaching. Pulp produced from hemp wood obtained from hemp stalks subjected to the retting process is characterised by the worst levels of bleachability of all pulps produced from hemp raw materials.
 - Amongst hemp raw materials, the highest final yield of bleached pulp was obtained from bast fibres (85%) and stalks (53%), with the lowest yield obtained from hemp wood (approx. 45%). The yield of bleached pulp from hemp stalks is higher than that of bleached pine and birch pulps, by 11 and 5%, respectively.
 - The viscosity of bleached hemp pulps can be kept at a high level (890-980 cm³/g) when metal ions are removed before oxygen delignification, with 0.5% of MgSO₄ added in the OD process and H₂O₂ removed at the E_p stage.



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University of Bielsko-Biała
Faculty of Textile Engineering
and Environmental Protection

ul. Willowa 2, 43-309 Bielsko-Biała
tel. +48 33 8279 114, fax. +48 33 8279 100
E-mail: itimp@ath.bielsko.pl