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EFFECT OF THE THERMAL AGEING ON SELECTED CHARACTERISTICS OF RECYCLED OFFICE PAPER

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ABSTRACT

The work was focused on monitoring of changes of selected characteristics of recycled office paper occurring during the modelled thermal ageing.

The effect of modelled thermal ageing was manifested mainly by the change of optical characteristics when brightness of recycled paper surface decreased by 40%. The coordinate values L*, a* and b* of the color space moved into the black, red and yellow region of the spectrum in achieving of total color differences E* 14.0 during modelled ageing.

Thermal ageing due to hornification and shrinkage of fibers significantly affected the value of air permeability (increasing by 31.5%), the value of swelling of paper (decreasing by 37%), the value of tear index (decreasing by 26%), the value of total crystallinity index (decreasing by 26%) and the value of oxidation index (increasing by 24%).

Modelled thermal ageing slightly reduce the pH values of the surface of the paper (by 5.2%), the values of breaking length (by 5.3%) and the values of intensity of the hydrogen bonds (by 2.6%).

The biggest changes of monitored characteristics were observed after the first 6-hour interval of modelled thermal ageing.

Key words: recycled office paper, modelled thermal ageing, brightness, colour, breaking length, tear index, air permeability, swelling, crystallinity.

INTRODUCTION

Nowadays, the increased use of recycled paper is the global trend in production and use of paper. It is modern, interesting and also educational. People are becoming more aware of the idea of the environmental protection, which is closely linked to the collection and re-use of old paper which would otherwise become waste. Great attention is paid to re-use of the fibres of paper, i.e. paper recycling, because it leads to saving of the raw material and to the reduction of water and energy consumption per unit production of paper. Waste paper is becoming an interesting article not only for the country with plenty of forests, but especially for countries with shortages of wood raw material.

In the year 2014 212,000 tons of waste paper, which represented up to 1.8 times of its domestic consumption, were exported from Slovakia. Although the collection of paper in Slovakia is at a very good level, waste paper is only processed for hygiene and packaging papers due to build technologies.

In the technologically advanced European countries waste paper is a valuable fibre raw material that is used not only for the production of hygienic paper and packaging, but also for the production of graphic papers. In the framework of CEPI (Confederation of European Paper Industries), there has recently been consumed more waste paper than primary cellulose fibres for paper production. In 2014 the declared utilization rate of waste paper was of 52.2% and the recycling rate up to 71.7% (CEPI Key Statistics 2014).

The recycled paper may contain the papermaking raw material recycled more than once in different representation which is not constant (MILICHOVSKÝ 1994). It can also contain a number of non-cellulosic impurities. These may be the remains of dyes, toners, coatings, fillers, sizing agents, which were not sufficiently removed by deinking or were on purpose introduced into the paper making stock for improving of paper quality and they also affect the properties of the paper during the ageing.

The paper is subject to ageing by time and repeated recycling, which is considered as the undesirable phenomenon in relation to its widespread use. The results of the work of many authors (BLECHSCHMIDT 1979, NORDMAN 1976, LAIVNS 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, GEFFERTOVÁ and GEFFERT 2012, 2016) show that the properties of the secondary fibres of waste paper differ from the characteristics of the primary cellulose fibres. This must be taken into account in their reprocessing for paper.

The change in optical characteristics, manifested by its yellowing, is the most visible demonstration of ageing in all kinds of paper (TESAŘÍK 2012). VIZÁROVÁ *et al*. (2003) also report the changes of colourity as the biggest changes of the various parameters during the ageing of paper.

Some authors (e.g. KRKOŠKA 1998, OLMSTEAD and GRAY 1997) deal with the causes of paper discolouration in their works, attributing the colouring to multiple chromophores arising from chemical reactions of lignin, cellulose and hemicelluloses, initiated by heat, light, radiation and pH. GEFFERTOVÁ, GEFFERT (2015, 2016) also point to significant optical changes of bleached pulps and white office paper during recycling in the modelled accelerated ageing. Many authors see the connection between paper yellowing as a result of oxidation of the cellulose and the subsequent increase of carbonyl and carboxyl groups (MORAVOVÁ *et al*. 1990, MARGUTTI *et al*. 2001, BUKOVANSKÝ 2000, VÝBOHOVÁ and GEFFERTOVÁ 2015). They point to the increased acidity of the surface of the paper, which results from the degradation of macromolecules of cellulose, hemicelluloses and lignin. ZERVOS (2010), SHAHANI *et al*. (1995), HROBOŇOVÁ *et al*. (2009) report the formation of the large amounts of degradation products depending on the nature of the sample and the ageing conditions. REHÁKOVÁ *et al*. (2003) point to the biggest changes in the optical characteristics of the samples of groundwood papers, while VIZÁROVÁ *et al*. (2005) state that pure cellulose and white paper have the higher stability and resistance to the combined action of heat and light in comparison with groundwood papers. SOLÁR (2004), MARGUTTI *et al*. (2001) also point out the negative effect of the oxidation products of cellulose and hemicelluloses, decrease in brightness and yellowing of the paper as a result of the formation of chromophores with the increased capability to absorb visible radiation.

The changes in the mechanical and physico-chemical characteristics also occur in the ageing of pulp and various kinds of paper, whether caused by the influence of light (MALEŠIČ *et al*. 2005, HUNT 1979, GEFFERTOVÁ and GEFFERT 2016) or by heat (GEFFERTOVÁ and GEFFERT 2013, 2015). This relates to the so-called hornification, in which there is the compaction of the cell wall and increase of the rigidity of the fibres. At the same time the fibres shrink and the porosity of the paper increases (GEFFERTOVÁ and GEFFERT 2012, ALINCO 2002). Hornification of the fibres affects the relationship with water and reduces their ability to swell (OKOYAMA 2002). Many scientists (STONE and SCALLAN 1968, DE RUVO and HTUN 1983, Geffert *et al*. 2013) attribute the loss of the ability of the pulp fibres to re-swell to the closure of the pores in the cell walls and the inability of many pores to open again when re-wetted.

The changes in the optical, mechanical and physico-chemical properties of paper during the ageing are influenced not only by the actual fibre compound but also by instability and decomposition of present paper adjuvants.

Due to the long-time process of the natural ageing of paper that runs tens to hundreds of years (MATTON *et al*. 1991) the accelerated ageing is modelled under external influences such as heat, humidity and radiation.

The aim of this paper is to point out the changes in the selected characteristics of recycled office paper, which occur during the modelled thermal ageing.

EXPERIMENTAL

Recycled office paper "Image recycled" (100% recycling) containing various amounts of different fibers types used several times, was used to monitor the modelled thermal paper ageing. It is uncoated paper with basis weight 80 $g \cdot m^{-2}$, not containing brighteners and suitable for everyday printing (laser, inkjet), for high capacity and two-sided printing and copying.

The modelled thermal ageing was based on the STN ISO 5630-4, procedure B, under which dried paper samples were exposed to 150°C for 24 hours. The prescribed treatment time (24 hours) was divided into 6-hour time intervals, after which the paper samples were subjected to the determination of the selected characteristics, in order to determine the rate of changes of the observed characteristics.

After the modelled thermal ageing the series of test paper sheets were conditioned for 24 hours in the standard atmosphere for testing pulp, paper and paperboard (STN ISO 187: 1990, EN 20187) at (23±1)°C and humidity (50±2)% .

Selected characteristics were determined at each series of test paper sheets of the 6-hour modelled thermal ageing:

basis weight	STN EN 536 (50 0310)
pH of the paper surface	STN 50 0374
brightness	STN ISO 3688 (50 0240)
colouring	Color Reader CR–10
breaking length	STN EN ISO 1924-2 (50 0340)
tear index	STN ISO 1974 (50 0348)
air permeability	STN ISO 5636-1 (50 0322)
swelling	a method according to Solár *et al*. 2006

FTIR spectra of the paper samples were obtained by the ATR-FTIR technique on a Nicolet iS 10 (Thermo Fisher Scientific) spectrometer equipped with a Smart iTR sampling accessory (Thermo Fisher Scientific) with diamond crystal. The spectra were measured and recorded at a resolution of 4 cm^{-1} at wavenumbers range 4000–650 cm^{-1} and evaluated by spectroscopic software OMNIC 8. The obtained data from the IR spectra were used for the calculation of total crystallinity index (TCI - ratio of the absorbances at 1372 cm^{-1} and at 2900 cm^{-1}), hydrogen bond intensity (HBI - proportion of the absorbance of FTIR bands at a wave number 3337 cm^{-1} and at a wave number 1335 cm^{-1}) and oxidation index (OI - ratio of the intensity of absorption bands at 1730 cm^{-1} and at 1620 cm^{-1}). The measurements were performed on eight replicates per each sample.

RESULTS AND DISCUSSION

There was a change in the basis weight of recycled office paper during the modelled thermal ageing by treatment at 150°C in the monitored time interval (Fig. 1). Average change of the basis weight at the monitored time had linear course. The basis weight was reduced by 0.66 $g \cdot m^{-2}$ during the 24-hour thermal exposure. GEFFERTOVÁ and GEFFERT (2015) report the average change up to 1.6 $g \cdot m^{-2}$ in the basis weight of the white office paper at the thermal modelling of ageing during the 24 hours. This difference is related to the quality of the fibres in the paper, to the content of the paper-making auxiliary agents (inorganic, organic) and also to blocking of the free -OH groups due to hornification. For example, the ash (inorganic portion) of white plain paper was 11.2%, whereas of the recycled office paper 16.2%.

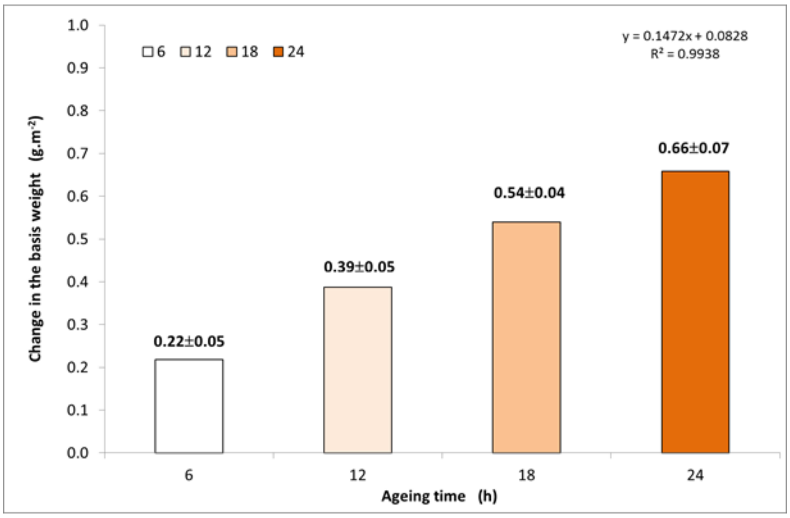

Fig. 1 Changes of basic weight of the recycled office paper by ageing.

The pH of the paper sheet surface was another monitored parameter. Due to thermal exposure there is a radical depolymerization of polysaccharides which is associated with dehydration and hydrolysis of hemicelluloses and amorphous content of cellulose. As reported by many authors (FENGEL and WEGENER 1984, MORAVOVÁ 1990, JABLONSKÝ *et al*. 2008) there is created a number of acid components, such as 2-furaldehyde, 5-hydroxymethyl-2-furaldehyde, levulinic acid and lactic acid. As a result of their formation there is a drop in the pH of the paper surface during the thermal and light modelling of ageing of pulp fibres and paper (GEFFERTOVÁ and GEFFERT 2013, 2015, 2016). If the pH of the paper surface is acidic, MCCOMB and WILLIAMS (1981) point to the possibility of acid hydrolysis of pulp fibres during storage and use too.

Fig. 2 shows the average values of the pH after the individual time intervals of the modelled thermal ageing.

The original sample of recycled paper had an average pH value of 7.35. The impact of the modelled ageing by heat was demonstrated by a decline in the pH of the paper surface in the whole monitoring range. The most significant change of the pH was recorded after the first time interval (2.4%). The average pH value of the paper surface after 24-hour ageing was 6.97 and overall reduction of the pH amounted 5.2%.

The most visible change in paper ageing was the change in brightness (Fig. 3).

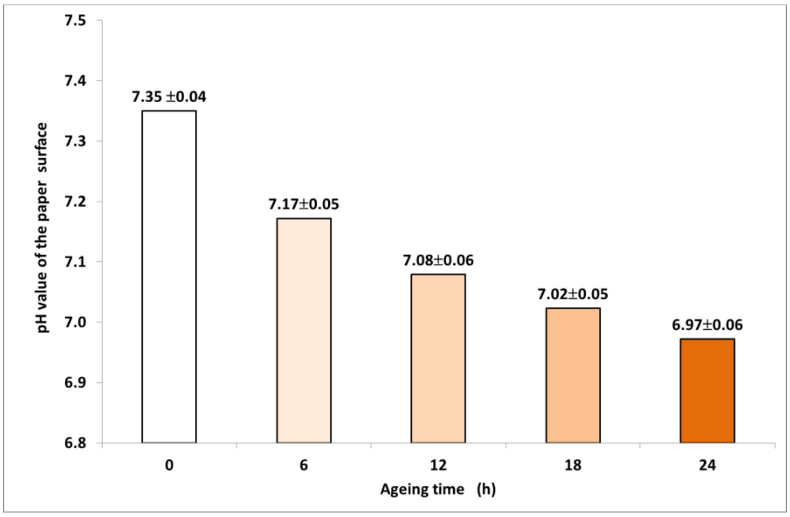

Fig. 2 pH changes of surface of the recycled office paper by ageing.

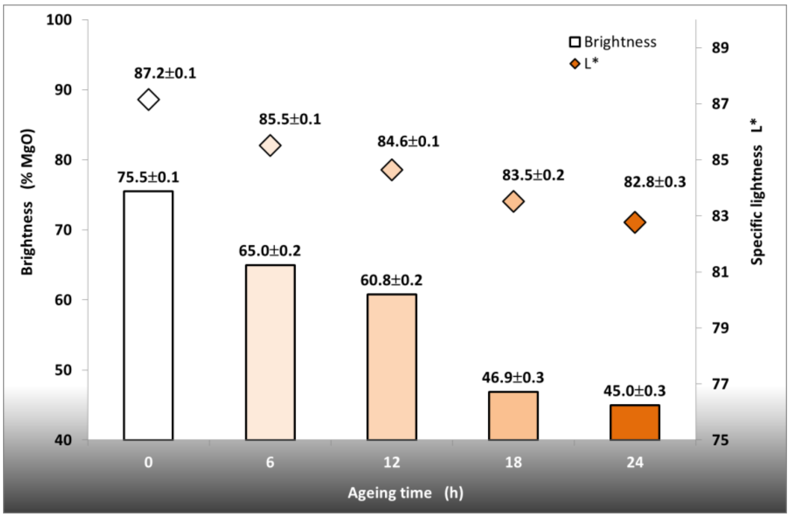

Fig. 3 Changes of brightness and L* of the recycled office paper by ageing.

The average brightness of the original recycled office paper was 75.5% MgO and during the modelled thermal ageing decreased to 45.0% MgO, which represented up to 40.4% decrease in the original brightness of recycled office paper. The smallest reduction in the brightness of the paper surface was determined in the last time interval and represented only 4% change.

Reduction in the brightness alternatively the colour change of the surface paper can be characterized more objectively by the coordinates of the CIELAB colour space. Values of specific lightness L* represent the black and white coordinate. Fig. 3 shows the change in L* of the surface of recycled copy paper due to the thermal ageing.

The average value of specific lightness of the original sample of recycled copy paper was 87.2 and during the 24-hour ageing it decreased to 82.8, which represented 5% change in this characteristic. The largest reduction in L* was observed after the first 6-hour interval of ageing and from the overall change in lightness it amounted 38.6%.

Darkening of the paper surface by the influence of the modelled thermal ageing and the acquisition of yellowish orange shades of the different intensity is associated with a shift of coordinates L*, a* and b* in the colour space, wherein the specific lightness L* is black and white coordinate, a* is the red and green coordinate and b* is blue and yellow coordinate of the colour space.

Fig. 4 shows the course of the coordinates a* and b* of the colour space after the individual time intervals of ageing.

Based on the course it can be concluded that coordinate a* under the impact of ageing in the whole the monitored range shifted to the red region of the colour space. This shift represents a 2-fold increase of its original value (from -0.6 to 0.6).

The blue and yellow coordinate moved to the yellow of the colour space during ageing. It moved from the original average of 3.4 to 16.7 after a 24-hour thermal ageing, which is almost four times the original value of this coordinate. The biggest change in b* coordinate was recorded after the first time interval and considering the whole shift it represented almost 50%.

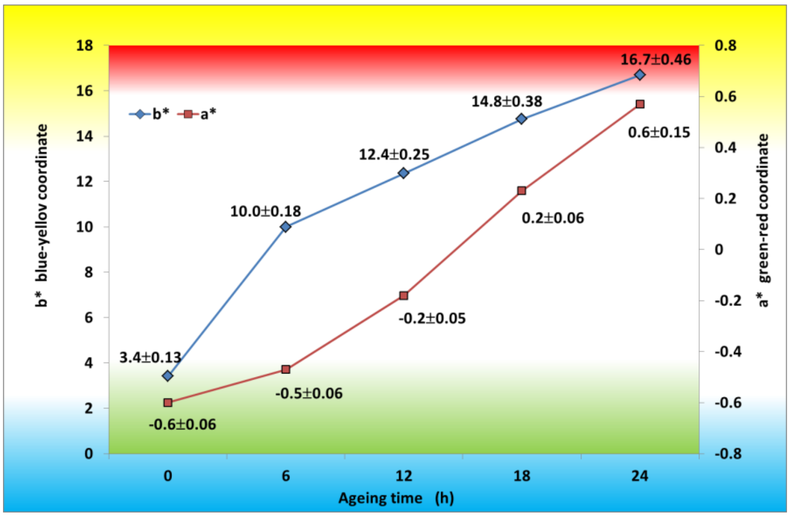

Fig. 4 Changes of coordinates a*, b* of the colour space by ageing.

When comparing the colours KUBOVSKÝ and URGELA (2004) considered the colour difference to be a parameter of the fundamental importance. The total colour difference ΔE, reflecting the changes in all three coordinates of the colour space due to the colour of the original sample, is expressed as follows.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + \left(b_2^* - b_1^*\right)^2}$$

Fig. 5 shows the overall colour differences after individual time intervals of ageing.

A colour difference reached the value of about 14.0 after ageing for 24 hours, while the values of the colour difference above the value of 12 can be described as different colours (ALLEGRETT *et al*. 2009). The changes of ΔE ranged from 2.5 to 2.1 between individual time intervals and they fit into the range 2< ΔE >3, which is defined as "colour difference visible with high quality screen."

The modelled thermal ageing of recycled office paper is also reflected in its mechanical characteristics such as breaking length and tear index.

Fig. 6 shows the average values of breaking length and tear index of recycled copy paper in monitored time intervals of the modelled thermal ageing.

The breaking length value of the original paper was 5.7 km and after 6 hours of the thermal ageing it increased to 6.0 km. The increase can be justified by hornification and shrinking of fibres due to heat, which resulted in the increased ability of paper to withstand the higher tension load. Other thermal action had a negative effect on the fibre strength and on breaking length values which fell only to 5.4 km after 24 hours.

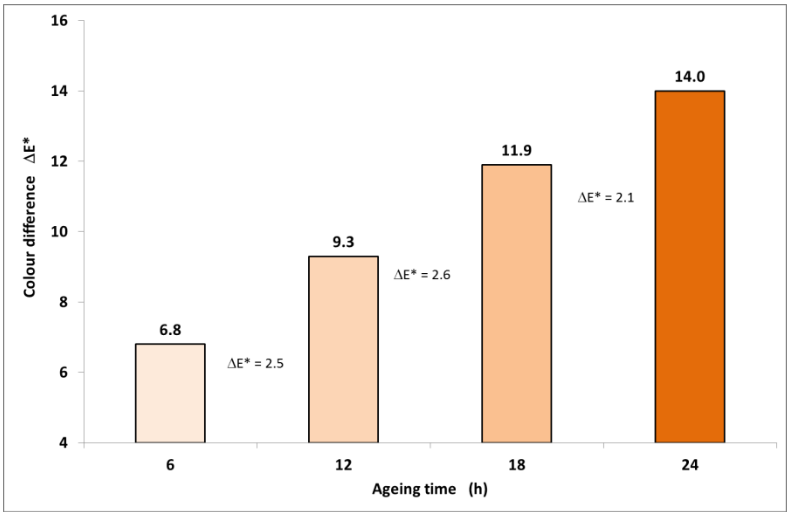

Fig. 5 Changes of colour difference ΔE* of the recycled office paper by ageing.

PYCRAFT and HOWARTH (1980) also found out that the elevated temperature of drying results in the reduction in the strength of primary and recycled paper too.

Ageing was demonstrated by more intense drop of tear index than breaking length in whole monitored range. Its average value dropped from 5.8 to 4.3 $mN \cdot m^2 \cdot g^{-1}$ after 24-hour thermal loading which compared to the value of the original sample represented the reduction of 26%. The smallest changes were recorded in the last monitored intervals.

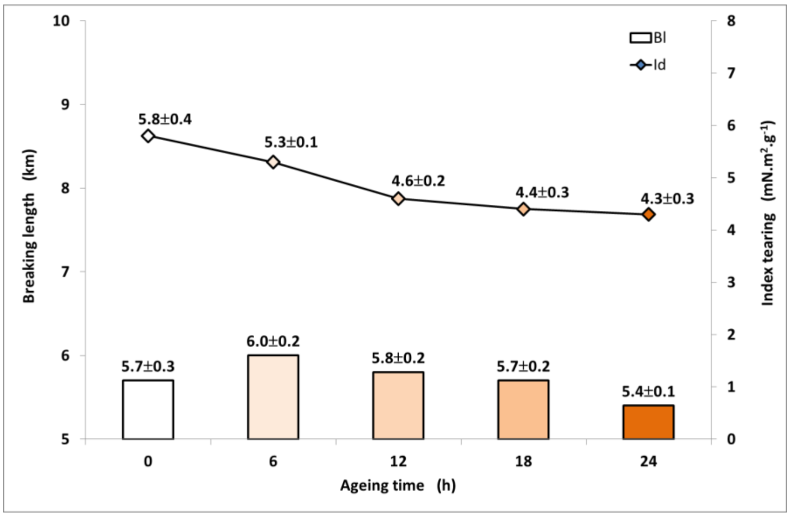

Fig. 6 Changes of breaking length and tear index of the recycled office paper by ageing.

According to SOUCEK (1977) the tear strength depends on the type of the treatment of the fibres, while the significant drop occurs by bleaching, sizing and intensive drying.

The production of recycled office paper uses various fibres with different treatment and with different technology of bleaching, sizing and filling (Fig. 7). The actual modelled ageing by heat increased their brittleness, which in turn led to decrease in the mechanical properties.

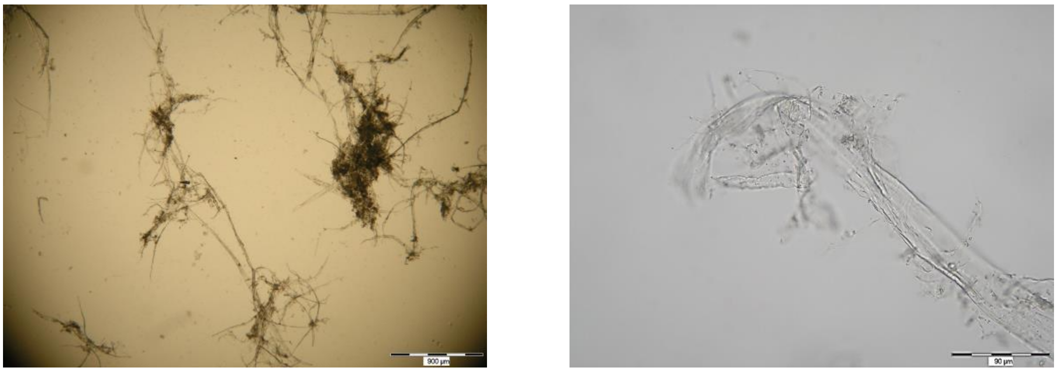

Fig. 7 Character of fibres in recycled office paper.

Another monitored parameter was air permeability, which depends on the number and size of the through pores in the structure of paper. The inter-fibre spaces in the paper are filled with quite a number of auxiliary paper making materials (fillers, sizing agents etc.) which by its amount and nature influence the air permeability in the paper.

Fig. 8 shows the values of air permeability through the recycled office paper at individual time intervals of ageing.

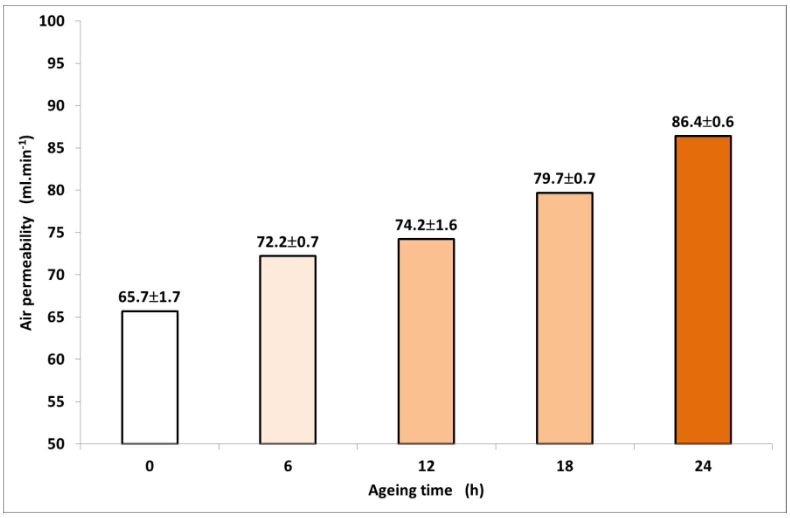

Fig. 8 Changes of air permeability of the recycled office paper by ageing.

From the data in Fig. 8 it can be stated that the modelled thermal ageing resulted in the increase in the value of air permeability. The original sample of recycled paper had air permeability of 65.7 ml·min^{-1} and during 24 hours of ageing the value of the air permeability increased by 20.7 ml·min^{-1}, representing the increase up to 31.5%. The largest increase in the air permeability was determined after the first time interval (9.9%) and amounted up to 31.4% of the total change in the air permeability per 24 hours.

The increase of air permeability of recycled paper due to the thermal exposure as of other monitored parameters is related to hornification and shrinkage of the fibres resulting in the increased porosity. ELLIS and SEDLACEK (1993) reported that repeated drying reduces the circuit of the fibres of about 7%.

Recycled office paper contains besides a very heterogeneous mixture of fibers also a number of other ingredients that improve its quality but reduced air permeability. It was also confirmed by the value of the air permeability (692 ml·min^{-1}) of white office paper made from the primary pulp fibres (GEFFERTOVÁ and GEFFERT 2015) and in pulp sheets prepared from unbeaten pulp which had an average value of permeability up to 8433 ml·min^{-1} (GEFFERTOVÁ and GEFFERT 2012).

The modelled thermal ageing also affected the relationship of the recycled fibres to water, which was reflected by the change in the swell ability of monitored paper. Swelling is the percentage change of the paper dimensions in water between the present and the initial dimensions of paper samples.

Fig. 9 shows the time progression of swelling of recycled office paper from individual intervals of ageing. Original sample paper had the highest swell ability, which after 200 second contact with water reached 38.6%. Depending on the time of ageing, the ability of paper to swell decreased and for the sample with 24-hour ageing extra term it had the value of 24.3% only. This reduction represented the decrease of up to 37% compared with the original sample. The most significant reduction of swelling was determined after the first interval of ageing (6 h) and accounted up to 46% of the total change of swelling ability. The smallest thermal effect on the swelling was in the last interval of ageing.

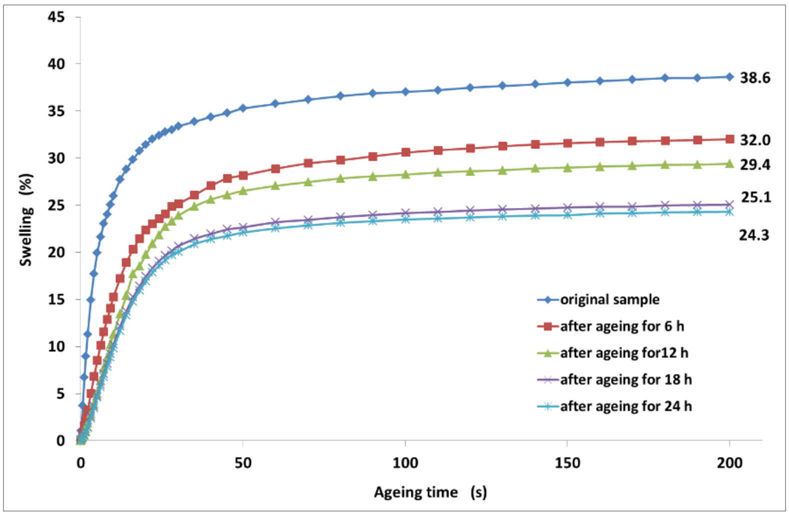

Fig. 9 Changes of swelling of the recycled office paper by ageing.

The fibres subjected to the thermal ageing became a less hydrophilic. Hornification of the fibres was accompanied by pores closure in the cell walls and mutual blocking of free -OH groups. The ability of absorbing more water into the structure was reduced. According to OKOYAMA (2002) this inactivation of the fibre surface is related to the irreversible hornification that was proved by exceptional increase of contact angle with water. STONE and SCALLAN (1966, 1968) DE RUVO and HTUN (1983), GEFFERTOVÁ and GEFFERT (2012a) in their works came to the similar findings. The loss of the ability of pulp fibres to re-swell is caused by hornification and shrinkage of fibres, closure of pores in the cell walls and inability of many pores to be again opened in re-wetting, which is characteristic of the fibre ageing (JABLONSKÝ *et al*. 2014).

The study of structure of the cellulose macromolecule and identification of the functional groups can be carried out by FTIR spectroscopy (KAVKLER and DEMŠAR 2012, CIOLACU *et al*. 2011, KUČEROVÁ and VÝBOHOVÁ 2014). Proportion of the crystalline and amorphous regions in the cellulose macromolecule and its arrangement is expressed by intensities of the absorption bands at characteristic wavenumbers in FTIR spectrum (COLOM *et al*. 2003, OH *et al*. 2005). Total crystallinity index (TCI) is defined by the ratio of the absorbances at 1372 cm^{-1} (-CH deformation vibrations in crystalline cellulose) and at 2900 cm^{-1} (CH stretching vibrations) (NELSON and O'CONNOR 1964).

Fig. 10 shows the comparison of the ATR-FTIR spectra (1850–800 cm^{-1}) of the papers, which were treated at various duration. All absorption bands used for calculation of TCI, HBI and OI are marked.

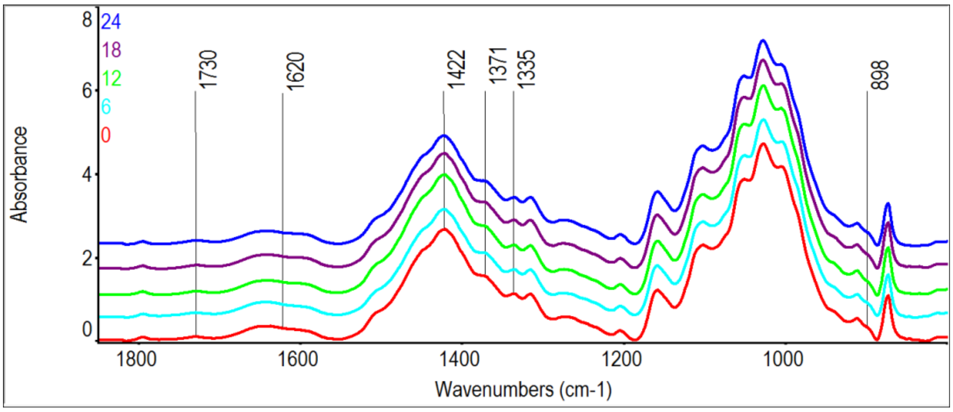

Fig. 10 ATR-FTIR spectra (1850–800 cm^{-1}) of the recycled office paper by ageing.

Fig. 11 shows the effect of modelled thermal ageing on total crystallinity index (TCI) and hydrogen bond intensity (HBI) in cellulose chains.

On the basis of results of the ATR-FTIR analysis, it can be concluded that the decrease of crystallinity was occured during thermal treatment. The decrease in TCI after 24-hour thermal treatment was 25.7% (from 1.110 to 0.825).

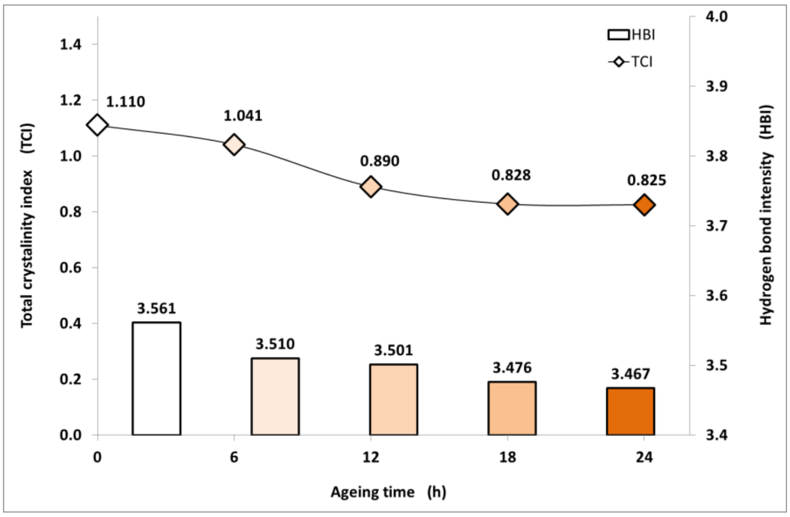

Fig. 11 Changes of TCI and HBI of the recycled office paper by ageing.

VÝBOHOVÁ and GEFFERTOVÁ (2015) report the higher total crystallinity index (3.03) of white office paper which is made from the primary cellulose fibers. The authors report the relative increase of TCI during ageing of white office paper. This trend is not found in the case of recycled office paper, which is associated with impaired quality of recycled fibers that were probably exposured to multiple technological processing (beating, drying, defibering).

According to SOLÁR (2004), FENGEL and WEGENER (1984) the thermal degradation of cellulose occurs in the result of thermooxidation, dehydration and depolymerization reactions. Long-term exposure can lead to the extinction of crystalline regions and the gradual decomposition of the cellulose.

Another evaluation parameter, which reflects the intensity of the hydrogen bonds among cellulosic fibres is HBI. HBI is given by the proportion of the absorbance of FTIR bands at a wave number 3337 cm^{-1} (-OH stretching vibrations and hydrogen bonds) and at a wave number 1335 cm^{-1} (deformation planar vibration of -OH groups of amorphous cellulose).

The highest value of HBI was in the original sample of the recycled office paper. Subsequently the HBI values decreased slightly in the entire time interval of ageing and they amounted to 2.6% reduction after 24 hours of thermal exposure comparing to baseline levels (Fig. 11).

Decline in the HBI values is related to hornification of the fibres and partial closure of their structure.

Fig. 12 shows the oxidation index values (OI) for individual time intervals of modelled thermal ageing.

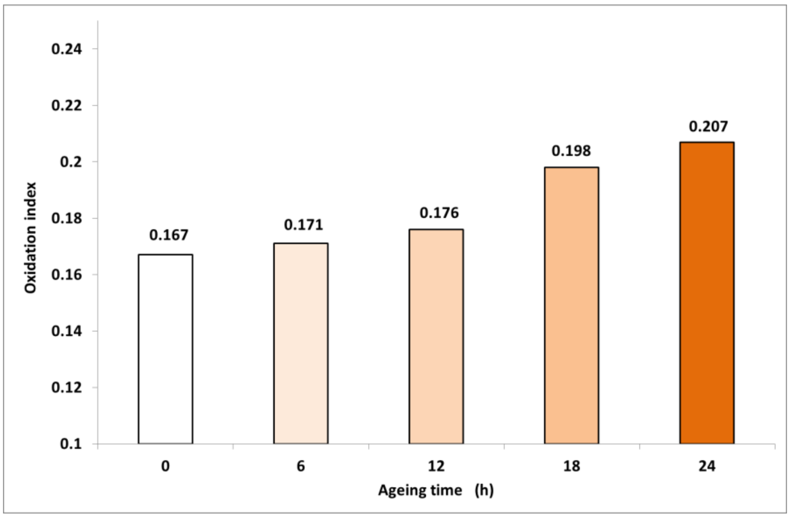

Fig. 12 Changes of oxidation index (OI) of the recycled office paper by ageing.

ŁOJEWSKA *et al*. (2005) defined the oxidation index (OI) as the ratio of the intensity of absorption bands at 1730 cm^{-1} and at 1620 cm^{-1}. The absorption band at a wavenumber 1730 cm^{-1} is assigned to C=O stretching vibrations of carboxyl and aldehyde groups and the band at a wavenumber 1620 cm^{-1} is assigned to C=O vibrations of carbonyl groups (HON *et al*. 2000, CALVINI and GORASSINI 2002). The increase of oxidation index was observed during modeled ageing of recycled office paper. The increasing OI by 24 % was determined after 24 hours of thermal exposure.

The increase of OI values is associated with a slight increase of band intensity at 1730 cm^{-1} and simultaneous decrease of band intensity at 1620 cm^{-1} that represents the increase of carboxyl and aldehyde group content comparing to the carbonyl groups. Decrease of band intensity at 1620 cm^{-1} may be affected also by the loss of bound water during paper ageing (CALVIN, GORASSINI 2002).

CONCLUSION

Based on the obtained results it can be concluded that there has been worsening of observed characteristics of recycled office paper during modelled thermal ageing:

- basis weight paper decreased
- acidity of the paper surface - the pH reduction increased
- brightness of the paper decreased
- colour of the paper changed - the shift to red, yellow and gray area of the colour space
- mechanical characteristics - breaking length and tear index decreased
- air permeability of the paper increased
- ability to swell decreased
- crystallinity of cellulose - TCI index decreased
- intensity of hydrogen bonds – HBI decreased
- number of carbonyl and aldehyde groups - OI increased.

The monitored characteristics of recycled office paper are worse comparing to characteristics of white office paper.

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