Durability of Cellulose and Synthetic Papers Exposed to Various Methods of Accelerated Ageing

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Abstract: The paper presents a study of the stability of cellulose and synthetic papers exposed to various methods of accelerated ageing. Particular consideration was given to the optical and mechanical stability of six paper samples (one film synthetic paper, two fibre synthetic papers, one lignin-free paper of higher quality and two security cellulose papers), which have undergone changes during accelerated ageing. The papers were artificially aged using standard techniques of accelerated ageing, e.g. moist-heat (80 °C and 65% RH), dry-heat (105 °C) and treatment with a xenon arc lamp (35 °C CT, 50 °C BST, 35% RH). The ageing was performed for the periods of 1, 2, 3, 6 and 12 days. The changes in the optical (ISO brightness, Yellowness Index), surface (roughness, paper topography) and mechanical stability (zero-span tensile strength, elongation at break, folding endurance) of papers were measured during the periods of accelerated ageing. The results show that the differences between synthetic and cellulose papers exist. On average, the dry-heat ageing had the highest influence on ISO brightness and Yellowness Index on synthetic papers, while the treatment with a xenon lamp had the strongest influence on cellulose papers. A comparison of mechanical properties showed that synthetic papers are more durable than cellulose paper; they had higher zero-span tensile strength and folding endurance, and showed substantially better ageing resistance to dry-heat and moist-heat accelerated ageing than cellulose papers. It was also noticed that the surface roughness increased after all three accelerated ageing processes.

Keywords: synthetic paper; cellulose paper; accelerated ageing; optical properties; mechanical properties; paper topography

1 Introduction

As with all other organic materials, paper is subjected to a number of fundamental deterioration processes. Under normal conditions of storage, these processes are very slow; however, they eventually and inevitably still lead to the well-known ageing effects, e.g. yellowing and loss of strength [1]. Heat and moisture are two of the most important environmental influences on the stability of papers [2]. At artificial or accelerated ageing methods, a material is exposed in a climate-chamber to extreme conditions in the terms of temperature and humidity for a certain period of time, during which the changes in the material are measured. Artificial ageing tests are often used to determine the permanence of paper, i.e. its rate of degradation, as well as to predict the long-term effect of a conservation treatment [1]. Moreover, exposure to light can cause fading and can shorten the use-life of paper. The degree of fading varies with the type of illumination and is greater with higher intensity light [2]. During accelerated ageing, the measured variables can include exposure time, exposure to UV irradiation over specific wavelength range and exposure to moisture as a number of cycles or time [3].

J. Malešič et al. [4] studied the photo-induced degradation of cellulose. The research demonstrated that extensive oxidative degradation of cellulose, accompanied by the formation of hydroxyl radicals, occurs during the exposure to light with $\lambda > 340$ nm. The studies showed that the rate of degradation, carbonyl formation and brightness decrease may be reduced with the addition of magnesium carbonate. Dr. S. Kaufmann and A. Bossmann [5] studied the light resistance of synthetic fibres under extreme exposure conditions. M. S. Islam et al. [3] studied the influence of accelerated ageing on the physico-mechanical properties of alkali-treated industrial hemp fibre reinforced poly(lactic acid) (PLA) composites. After the accelerated ageing, tensile strength, flexural strength, Young's modulus, flexural modulus and fracture toughness were found to decrease, whereas impact strength increased for aligned untreated long hemp fibre/PLA (AUL) and aligned alkali treated long hemp fibre/PLA (ALL) composites. B. Havlíonova et al. [6] studied the mechanical properties of papers (one alkaline and three different acidic samples) exposed to various methods of accelerated ageing. The increased temperature and relative humidity caused a significant loss of folding endurance, especially for acidic papers. S. Soares et al. [7] studied the degradation of cellulose in the form of transformer insulating paper and Whatman filter paper in the air at the temperatures from 200 °C to 550 °C with and without the addition of 0.01 wt.% NaCl, $ZnCl_2$ and $CuCl_2$, using the solid-state NMR and FTIR spectroscopy. Major changes occurred at the temperatures higher than 250 °C, resulting in the loss of protons and the development of new saturated and unsaturated structures.

Our research study focused on the investigations of the stability of papers made from synthetic and/or cellulose fibres. The surface, optical and mechanical properties of three different synthetic papers and three different cellulose papers exposed to various methods of accelerated ageing were determined.

2 Experimental

2.1 Materials

In the present study, commercially available papers were used, three types of synthetic papers and three types of cellulose papers.

Paper 1: Yupo (manufacturer: Yupo Corporation, Japan) is a biaxially-oriented film synthetic paper. It consists of three extruded polypropylene (PP) layers with inorganic filler ($CaCO_3$) and does not contain wood pulp or other bio materials.

Paper 2: Pretex (manufacturer: Neenah-Lahnstein Company, Germany) is a double-side coated fibre synthetic paper made from a mixture of selected pulp and synthetic fibres (polyamide – PA and polyester – PES) in a combination with a special binder system.

Paper 3: Neobond (manufacturer: Neenah-Lahnstein Company, Germany) is a double-side coated fibre synthetic paper made from a mixture of selected pulp and synthetic fibres (polyamide – PA, polyester – PES and viscose – CV), reinforced with a special impregnation.

Paper 4: G-print (manufacturer: Stora Enso, Finland) is a coated lignin-free paper made from 100% virgin cellulose fibres.

Paper 5: Catanelle (manufacturer: Fabriano, Italy) is an uncoated security paper made from 100% E.C.F. chemical bleached pulp. The paper has multitonal watermark and contains fluorescent security fibres.

Paper 6: Small Money (manufacturer: Gmund, Germany) is a lignin-free security paper made from a mixture of old german marks, waste paper and cellulose fibres.

2.2 Methods

The experiments, which were focused on the surface, optical and mechanical paper properties, were performed in compliance with ISO standards. The paper samples were aged using standard techniques for accelerated ageing: moist-heat based on the standard SIST ISO 5630-3 (80 °C and 65% relative humidity), dry-heat based on the standard SIST ISO 5630-1 (105 °C) and ageing with a xenon lamp in a Xenotest® Alpha apparatus based on the standard ISO 12040 (35 °C Chamber Temperature, 50 °C Black Standard Temperature, 35% relative humidity). For all three types of accelerated ageing, the exposure time was 1, 2, 3, 6 and 12 days [8-10].

The optical properties of papers were evaluated based on ISO Brightness and Yellowness Index YI E313 [13-14]. The measurements were performed in accordance with the standard ISO 2470 (ISO Brightness, R_{457}) with an X-Rite spectrophotometer at D65/10° and in accordance with the ASTM Method 313 (YI E313) with a spectrophotometer Spectroflash 600 – Datacolor International at D65/10°.

The influence of dry-heat and moist-heat ageing on the mechanical properties was determined using an Instron 5567 tensile testing machine. A paper strip with 15 mm in width was clamped with the span length as close to zero as possible. The zero-span tensile strength was determined according to ISO 15361. The tensile properties were measured in the machine (MD) and cross directions (CD) of papers. The folding resistance was measured on the MIT folding endurance tester in the machine and cross direction of papers (load: 2 kg, except for the aged Paper 6 in MD: 0.5 kg).

The chemical composition of paper surface before and after 12 days of accelerated ageing was determined with the ATR-FTIR technique on a FTIR spectrometer PerkinElmer SpectrumGX. The standard FTIR spectrometer settings were as follows: range 4000-500 cm^{-1}, 64 scans, resolution 4.00 cm^{-1}.

The unaged and aged papers were imaged using a Scanning Electron Microscope JOEL, JSM 6060LV at 100× magnification and 10 kV voltage. The captured JPEG images were re-saved into 8 bit images and analysed using ImageJ software (Mean Grey Values, Standard Deviation and Median Value). The topography of samples was evaluated at the area of 1120 × 750 pixels with Surface Plot diagrams. The average surface roughness (R_a) of unaged and aged papers was measured with a Surface Roughness Tester TR200.

3 Results

3.1 Influence of Accelerated Ageing on Optical Properties of Papers

The deterioration of paper upon ageing is initiated with an irreversible change of their mechanical, chemical and optical properties [11]. In the first part of the investigation, the influences of various accelerated ageing techniques on the optical properties (ISO Brightness, Yellowness Index) of papers were investigated. Figures 1-3 summarise the influence of three accelerated ageing techniques (dry-heat treatment, moist-heat treatment and treatment with a xenon lamp) on the ISO Brightness of the papers.

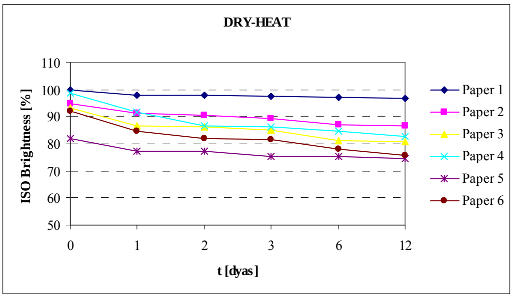


Figure 1

Influence of dry-heat accelerated ageing on ISO Brightness of papers

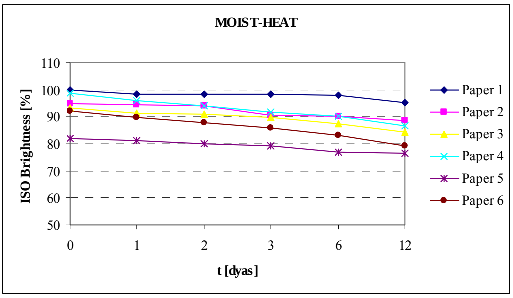


Figure 2

Influence of moist-heat accelerated ageing on ISO Brightness of papers

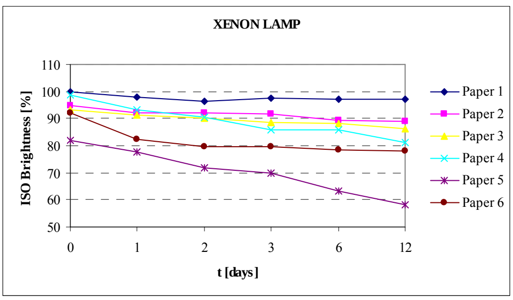


Figure 3

Influence of accelerated ageing with xenon lamp on ISO Brightness of papers

An important feature of cellulose fibres in the paper is their degradation due to ageing [8]. One of the major sources of decay of materials made from natural fibrous materials is the effect of light [4]. Paper made from cellulose fibres has the tendency to undergo yellowing (brightness reversion) upon exposure to the sunlight. There is a general agreement that the coloration occurs due to the remaining lignin constituents in the pulp, although neither the precise nature of the chromophores responsible for this nor the exact mechanism for their formation has been conclusively established [12]. The ISO brightness values for papers before the ageing were as follows: Paper 1 = 99.9%, Paper 2 = 94.9%, Paper 3 = 93.1%, Paper 4 = 98.6%, Paper 5 =82.0% and Paper 6 = 92.2%. Paper with the highest ISO brightness, i.e. the film synthetic paper (Paper 1), retained the highest brightness at all three accelerated aging techniques after each day of aging. For most papers, the dry-heat treatment (cf. Figure 1) caused a higher loss in ISO brightness than the moist-heat treatment (cf. Figure 2) and the treatment with a xenon lamp (cf. Figure 3). With the dry-heat treatment (105 °C) and at the moist-heat treatment (80 °C, 65% RH), the most obvious decrease in ISO brightness was established for the cellulose paper containing old value paper and waste paper (Paper 6). Within 12 days, brightness dropped by 16.3 units for the dry-heat treatment and by 13.1 units for the moist-heat treatment, which corresponds to a perceptible change. The treatment with a xenon lamp (35 °C CT, 50 °C BST, 35% RH) influenced most substantially the ISO brightness of both cellulose papers (Paper 4, Paper 5). The highest loss in ISO brightness was obtained for the security paper (Paper 5), where the value dropped by 23.9 units. It was established that all three synthetic papers are more durable than the cellulose papers of higher quality. According to the producer, both fibre synthetic papers contain pigment colors, no optical brighteners and still have good light fastness after many years. Normally, temperatures up to 100 °C do not influence the paper properties, and a short-term increase to 200°C only leads to paper surface discoloration [13]. The papers produced from cellulosic fibres with various additives are determined by the extent of oxidative and hydrolytic reactions taking place upon ageing [6]. Two general mechanisms are involved in the degradation of cellulosic materials by light in the visible and ultraviolet ranges. In the short-wave UV region, the breakdown is believed to occur due to the photolysis of cellulosic chains, leading to the cleavage of carbon-to-carbon or carbon-to-oxygen linkages, without any particular evidence that the reaction with oxygen is vital to the process. The other type of reaction is thought to involve the presence of a substance which can act as a photosensitiser and which, in the presence of oxygen and moisture, leads to the production of hydrogen peroxide, which in turn degrades the cellulose by oxidation [14].

In terms of visual appearance, absorption in the blue part of the light spectrum causes yellowness. Visually, yellowness is associated with scorching, soiling and general product degradation by light, chemical exposure and processing [15]. The Yellowness Index is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white toward yellow. This test is most commonly used to evaluate the color changes in a material caused by a real or simulated outdoor exposure. Lightfastness normally decreases with increasing atmospheric humidity, the extent of the effect depending on the dye-substrate system, which is very pronounced for cellulosic fibres [16].

The Yellowness Index according to the ASTM Method E313 is calculated as follows:

$$YIE313 = \frac{100(C_X X - C_Z Z)}{Y} \tag{1}$$

where X, Y, Z are the CIE tristimulus values, C_X and C_Z are coefficients (D65/10°: $C_x = 1.3013$, $C_Z = 1.1498$) [17].

Figures 4-6 summarise the influence of three accelerated ageing techniques (dry-heat treatment, moist-heat treatment and treatment with a xenon lamp) on the Yellowness Index of the papers.

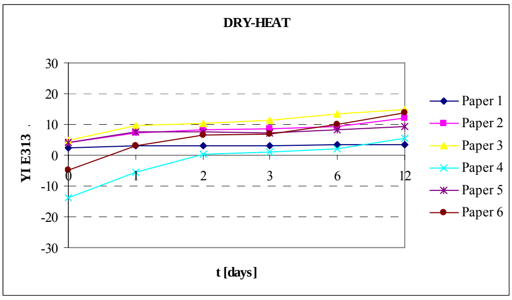


Figure 4

Influence of dry-heat accelerated ageing on Yellowness Index of papers

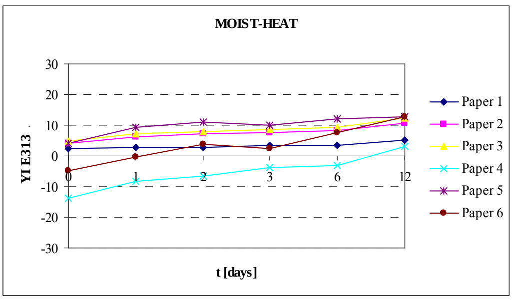


Figure 5

Influence of moist-heat accelerated ageing on Yellowness Index of papers

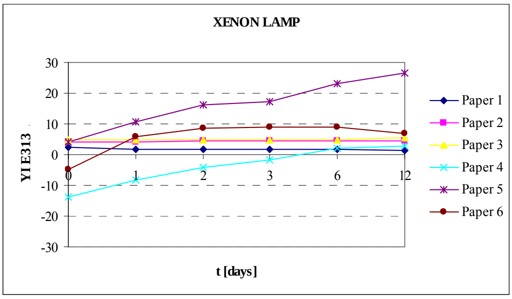


Figure 6
Influence of accelerated ageing with xenon lamp on Yellowness Index of papers

The tested papers slightly differ in yellowness; Paper 1: YI E313 = 2.4, Paper 2: YI E313 = 4.3, Paper 3: YI E313 = 4.9, Paper 4: YI E313 = –13.8, Paper 5: YI E313 = 4.1 and Paper 6: YI E313 = –4.7, the values leading to the conclusion that Papers 1-3 and 5 are more yellowish, while Papers 4 and 6 are more bluish. Paper yellowing is a natural process of paper ageing, which is caused by the sunlight, moisture and air. On average, the best stability among synthetic papers was obtained by the film synthetic paper (Paper 1) made from PP fibres, while among the cellulosic papers, by Paper 5. The results obtained for Paper 5 showed that Paper 5 yellowed more slowly under the dry-heat treatment and the most under treatment with the xenon lamp. After 12 days of treatment with the xenon lamp, the value for Paper 5 was YI E 313 = 26.51. The reason is in the paper structure; Paper 5 is not coated, which influenced the results. The Yellowness Index for Paper 6 for all three ageing methods increased polynomially. Among all the tested papers, only Paper 6 contained recycled fibres. Papers 2 and 3 contained polyamide (PA) and polyester (PES) fibres apart from cellulosic fibres. Polyester (PES) fibres have greater light resistance than polyamide (PA) and cellulosic fibres, and photooxidation takes place at higher temperatures. It was noticed that the yellowing during the dry-heat and moist-heat treatment was the most progressive for Paper 4 and Paper 6, and the treatment with the xenon lamp for Paper 4 and Paper 5. Under all treatments, Paper 4 and Paper 6 turned from bluish to yellowish after accelerated ageing. The loss of brightness and paper yellowing during the ageing procedures is attributed to the presence of chromophores formed by the degradation of paper components (cellulose, hemicellulose, lignin) [11]. The degradation starts under the presence of light or no light and in the presence of increased temperature and humidity [18]. Pure cellulose absorbs visible light only to a small extent, while the absorption in the near UV spectral region is more pronounced. The absorption in the blue spectra causes the yellowing [4]. Lightfastness normally decreases with increasing atmospheric humidity, the extent of the effect depending on the dye-substrate system, which is very pronounced with cellulosic fibres [16]. Photodegradation is influenced by the surface-area-to-volume ratio to such a great extent, since the mechanism of degradation is largely photo-oxidative, and the surface area of the fibre in contact with air would hence be a very important factor in the chemical reactivity and its inherent kinetics. The greater the surface area facing a light source, the greater the actinic energy absorbed and the more vigorous the photodegradation reaction [14].

3.2 Influence of Accelerated Ageing on Mechanical Properties of Papers

The mechanical properties of paper can vary significantly by selecting different types of fibres and fibre preparation. Tensile strength is indicative of fibre strength, fibre bonding and fibre length. Fibre length and coarseness also influence the tensile strength of paper [11]. The tensile strength of paper is the maximum force per unit width that a paper strip can resist before breaking when applying the load in the direction parallel to the length of a strip. A special case of tensile strength is the zero-span tensile strength, which is a good indicator of the average strength of individual fibres. Table 1 shows the influence of dry-heat accelerated ageing, while Table 2 shows the influence of moist-heat accelerated ageing on the zero-span tensile strength, elongation at break and stress at break of papers.

Table 1
Influence of dry-heat ageing on zero-span tensile strength, elongation at break and stress at break of papers

Samples	**Fibre orientation**	**Days of ageing**	**Zero-span tensile strength [N]**	**Elongation at break [mm]**	**Stress at break [N/mm^2]**
Paper 1	*MC*	0	250.3	6.7	131.4
	CD		87.4	15.8	45.9
	MC	*6*	297.7	8.1	156.8
	CD		102.9	20.9	54.2
	MC	*12*	294.6	8.0	155.1
	CD		104.2	19.6	54.9
Paper 2	*MC*	*0*	116.3	1.0	91.2
	CD		78.8	2.0	61.8
	MC	*6*	196.0	1.3	100.5
	CD		140.6	1.7	72.1
	MC	*12*	186.7	1.2	95.8
	CD		126.1	1.5	64.6
Paper 3	*MC*	*0*	65.1	1.7	40.4
	CD		45.3	2.0	28.1
	MC	*6*	79.4	1.6	59.2
	CD		50.3	1.8	31.2
	MC	*12*	79.5	1.6	49.4
	CD		51.2	2.0	31.8

Paper 4	*MC*	*0*	95.7	0.7	70.9
	CD		59.1	1.0	43.7
	MC	*6*	120.1	0.7	89.4
	CD		73.4	0.9	54.7
	MC	*12*	113.8	0.7	84.8
	CD		69.1	0.8	51.5
Paper 5	*MC*	*0*	118.0	0.8	73.5
	CD		88.3	1.6	55.0
	MC	*6*	157.0	0.9	98.5
	CD		109.7	1.2	68.8
	MC	*12*	148.6	0.9	93.2
	CD		102.9	1.1	64.6
Paper 6	*MC*	*0*	101.0	0.7	52.6
	CD		71.3	1.1	37.2
	MC	*6*	118.6	0.7	61.5
	CD		87.4	0.9	45.3
	MC	*12*	118.8	0.7	58.0
	CD		79.2	0.8	41.1

Table 2

Influence of moist-heat ageing on zero-span tensile strength, elongation at break and stress at break of papers

Samples	**Fibre orientation**	**Days of ageing**	**Zero-span tensile strength [N]**	**Elongation at break [mm]**	**Stress at break [N/mm^2]**
Paper 1	*MC*	0	250.3	6.7	131.4
	CD		87.4	15.8	45.9
	MC	*6*	296.5	8.0	156.1
	CD		101.2	19.4	53.3
	MC	*12*	292.2	7.7	153.9
	CD		104.1	20.7	54.8
Paper 2	*MC*	*0*	116.3	1.0	91.2
	CD		78.8	2.0	61.8
	MC	*6*	203.9	1.3	104.6
	CD		142.5	1.7	73.1
	MC	*12*	186.2	1.3	95.5
	CD		133.7	1.7	68.6
Paper 3	*MC*	*0*	65.1	1.7	40.4
	CD		45.3	2.0	28.1
	MC	*6*	79.8	1.6	49.6
	CD		50.5	1.9	31.4
	MC	*12*	80.4	1,6	49.9
	CD		50.4	1.9	31.3

Paper 4	*MC*	*0*	95.7	0.7	70.9
	CD		59.1	1.0	43.7
	MC	*6*	118.9	0.7	88.6
	CD		72.5	1.0	54.0
	MC	*12*	117.5	0.7	87.5
	CD		69.3	0.8	50.1
Paper 5	*MC*	*0*	118.0	0.8	73.5
	CD		88.3	1.6	55.0
	MC	*6*	159.9	0.9	100.3
	CD		114.0	1.1	71.5
	MC	*12*	153.6	0.8	96.3
	CD		109.5	1.1	68.7
Paper 6	*MC*	*0*	101.0	0.7	52.6
	CD		71.3	1.1	37.2
	MC	*6*	123.2	0.7	63.8
	CD		86.8	0.9	45.0
	MC	*12*	118.9	0.7	61.6
	CD		82.3	0.9	42.7

The mechanical properties of investigated papers are substantially influenced by individual characteristics of cellulose and synthetic fibres, concentration and chemical properties of fillers and additives, as well as by the paper network structure. The differences in tensile properties between the papers are high, especially in the machine direction (MD) of papers. The paper properties, such as tensile strength, vary significantly between the machine and cross directions of papers. This is attributed to fibre orientation; however, the fact that in the machine direction paper is dried under much higher resistance than in cross direction is often of even greater importance [19]. The highest zero-span tensile strength and stress at break belonged to the film synthetic paper made from the PP fibres in the form of extruded layers. The film synthetic paper was also much more extensible than other investigated papers. The lowest zero-span tensile strength and stress at break belonged to the film synthetic paper (Paper 3), whereas all other papers had similar tensile strength. The differences in elongation at break are a consequence of paper composition; Paper 2 and Paper 3 contained cellulose and synthetic fibres, whereas Papers 4-6 contained only cellulose fibres, which are less flexible and less extensible. Polyester, polyamide and polypropylene fibres have high strength and excellent strength retention properties, and are mostly used as non-absorbable suture [20]. It is well known that the effect of exposure to moisture and heat or a combination of these parameters may damage paper stiffness and strength [3]. During ageing, the loss of paper strength is a consequence of the degradation processes of its main structural component, the fibre [21]. From Tables 1 and 2, it is evident that the dry-heat and moist-heat ageing influenced the tensile strength and extension of papers. Synthetic papers are more thermally stable and more durable to light and moisture, and they have in normal use higher dimensional stability than cellulose papers. They also have superior resistance against tear and damage [22]. Moisture generally reduces the tensile strength of the hydrophilic fibre. The exception is the most natural cellulose fibre, where in the wet the tensile strength increases due to the layer structure of the secondary cell wall. Humidity does not affect the tensile strength of hydrophobic fibres (polyester), since in the wet the tensile strength does not change [14]. The values of the zero-span tensile strength reflect the detailed structure of a paper and mainly the properties of its individual fibres, i.e. dimension and strength of fibres, their arrangements and interfibre bonding. The effects of accelerated ageing processes on paper are interpreted in terms of bond scission between fibres, chain scission producing weaker fibres and degradation of smaller molecules. At first, only the degradation in amorphous regions takes place, leaving more ordered structure, resulting in crosslinking by additional bonds leading to increased strength and brittleness.

Table 3 shows the loss in the folding endurance of papers after 6 and 12 days of accelerated ageing.

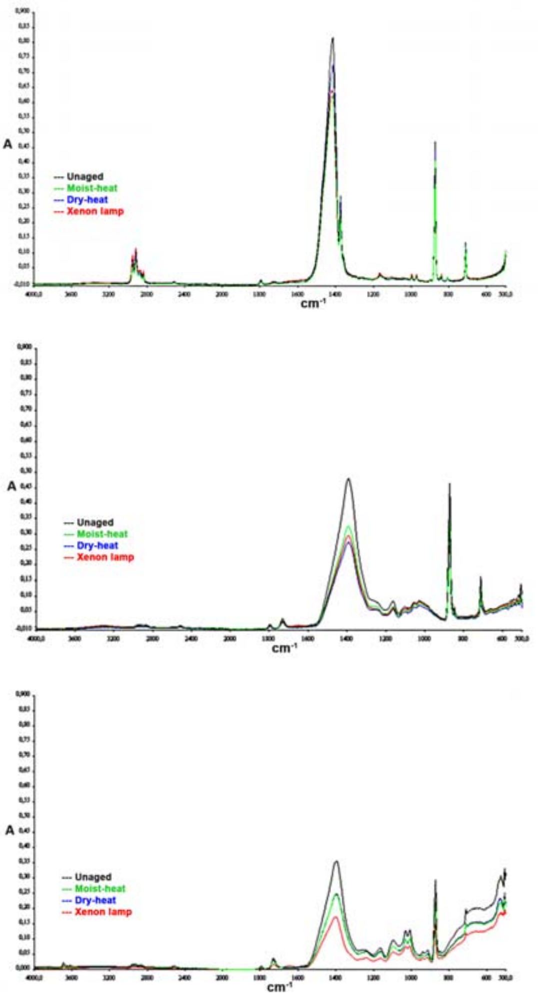
Table 3
Number of double folds of papers after moist-heat and dry-heat ageing

Numbers of double folds after breaking (load: 2 kg)						
Samples	**Fibre orientation**	**Unaged papers**	**Moist-heat ageing**		**Dry-heat ageing**	
			6 days	**12 days**	**6 days**	**12 days**
Paper 1	MC CD	Did not break	Did not break	Did not break	Did not break	Did not break
Paper 2	MC CD	3543 743	3479 196	3139 166	2335 119	1807 99
Paper 3	MC CD	Did not break	Did not break	Did not break	Did not break	Did not break
Paper 4	MD CD	641 280	643 218	550 188	295 193	246 135
Paper 5	MD CD	2140 625	939 75	755 52	701 53	614 22
Paper 6	MD CD	781 114	354 69	217 60	120 36	33 14

Folding endurance represents the most sensitive indicator of paper breakage upon ageing. The effects of accelerated ageing processes on paper are interpreted in terms of fibre chain scission producing weaker fibres and covalent crosslinking by additional bonds leading to increased brittlenes [6]. The results presented in Table 3 show the highest folding resistance to ageing for film synthetic paper (Paper 1) and fibre synthetic paper (Paper 3). Neither paper broke under the load of 2 kg at 5,000 double bonds, meaning that these two papers had higher strength, were more flexible and more bonded. It was found that dry-heat ageing processes had a higher impact on the folding endurance of papers than moist-heat ageing. The most obvious decrease in the number of double folds was obtained for security cellulose papers (Paper 6), as it contained recycled fibres. For all papers, the load was 2 kg, except for Paper 6; it was in MD direction 0.5 kg.

3.3 FTIR Spectroscopy

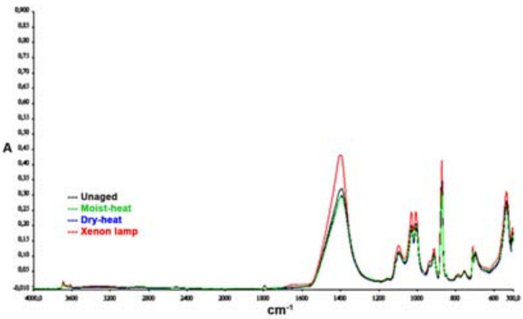
Infrared (IR) spectroscopy is useful in the elucidation and identification of the molecular structure and in the applications of quantitative analyses. The FTIR spectra of unaged papers, as well as papers after 12 days of various accelerated ageing, procedures are illustrated in Figure 7.



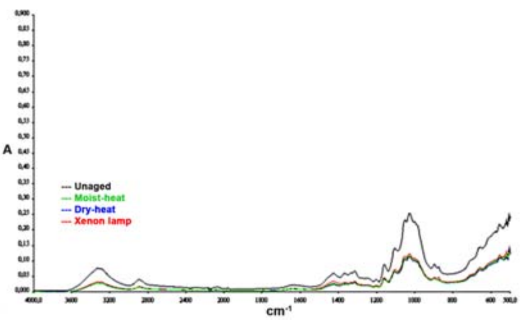
a)

b)

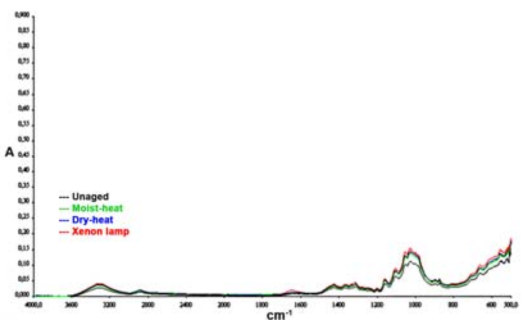
c)



d)



e)



f)

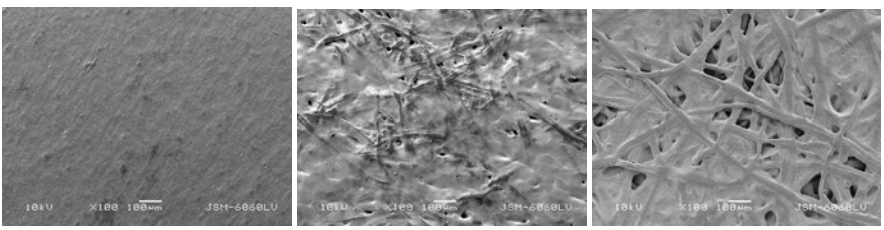
Figure 7

FTIR spectra of unaged and for 12 days acceleratedly aged papers: *a)* Paper 1, *b)* Paper 2, *c)* Paper 3, *d)* Paper 4, *e)* Paper 5 and *f)* Paper 6

The applications of all accelerated ageing procedures led to the most obvious decrease in absorption for Paper 1 (cf. Figure 7/a) in the regions 1500-1400 cm^{-1}, especially under the treatment with the xenon lamp. The band at the 1400 cm^{-1} for unaged Paper 1 obtained 0.500 of absorption, while for the treatment with the xenon lamp obtained 0.385 of absorption. Only for Paper 1, the absorption peak was noticed at 2922 cm^{-1}, which represents the CH_2-gruoup vibration in the main PP polymer chain [23]. In comparison with all other papers, Paper 1 obtained the highest intensity of absorption. For Paper 2 (cf. Figure 7/b), the most obvious decrease in absorption after accelerated ageing procedures was observed in the region 1550-1000 cm^{-1}. For example, at the band at 1400 cm^{-1}, the following values were obtained: A = 0.472 (unaged), A = 0.320 (moist-heat), A = 0.269 (dry-heat) and A = 0.290 (xenon lamp). For Paper 3 (cf. Figure 7/c), a decrease in the absorption in the region 1500-500 cm^{-1} was observed. The curves for moist-heat and dry-heat treated papers behaved similarly, while the curve for the xenon lamp treated papers decreased the most. From Figure 7/d, it can be seen that for Paper 4, the absorption under treatment with the xenon lamp increased in the region 1600-500 cm^{-1}, while the curves for the moist-heat and dry-heat treated papers decreased. The intensity of bonds in the cellulose finger print is in the region 1500-800 cm^{-1}.While the hydrolytic degradation results in the breaking of (1→4) β-glycosidic bonds and the occurrence of the formation of aldehyde groups, the oxidative degradation of cellulose results in the opening of the β-D-glucopyranose ring, causing the formation of carboxylic and aldehyde groups. These bands are located in the region 1750-1617 cm^{-1} [24]. For Paper 5 (cf. Figure 7/e), all three types of accelerated ageing behaved similarly. In all regions, the absorption was lower than for unaged paper. In contrast to Paper 5, the unaged Paper 6 obtained lower absorption than the aged samples. From all FTIR spectra, it can be seen that for Papers 1-3 and 5, the absorption of aged samples decreased compared to the unaged sample. The treatment with the xenon lamp reflected the growing absorption for Paper 4 and all three ageing procedures for Paper 6.

3.3 Paper Surface Topography

The mechanical properties of different paper samples are substantially influenced by the characteristics of individual fibres, nature, concentration and chemical properties of fillers and additives, and by the paper network structure [6]. Figures 8 and 9 present the SEM images of the unaged papers and their surface plot diagrams. Surface plot displays a three-dimensional graph of intensities of pixels in a greyscale or pseudo color image.



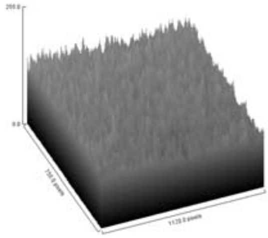
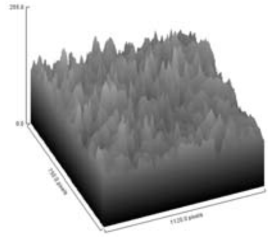
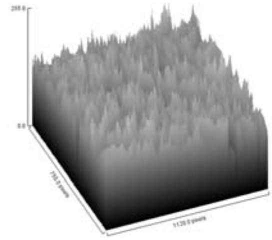
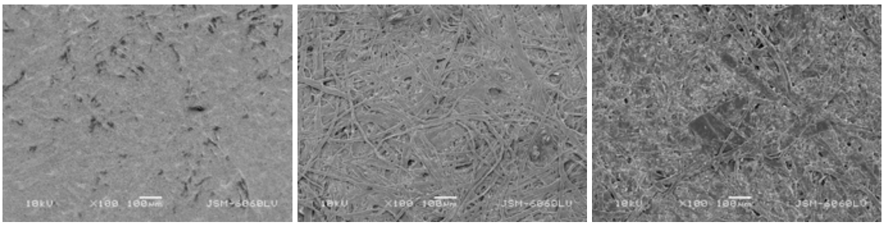
a)  *b)*  *c)* 

Figure 8
SEM images of unaged synthetic papers and their surface plot diagrams: a) Paper 1, b) Paper 2, c) Paper 3



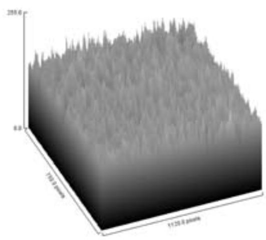
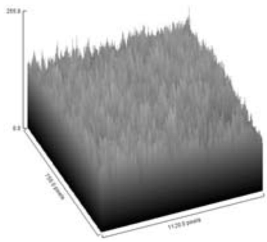
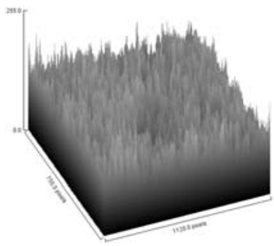
a)  *b)*  *c)* 

Figure 9
SEM images of unaged synthetic papers and their surface plot diagrams: a) Paper 4, b) Paper 5, c) Paper 6

Table 4
Results of analysed SEM images of papers and average surface roughness

Samples	**Ageing**	**Mean**	**StdDev**	**Median**	**Ra [µm]**
Paper 1	*Unaged*	118.42	22.95	117	0.44
	Moist-heat	129.29	17.60	128	0.75
	Dry-heat	111.17	22.90	109	0.70
	Xenon lamp	118.49	10.20	117	0.43
Paper 2	*Unaged*	143.13	37.20	142	1.84
	Moist-heat	167.11	31.20	171	1.93
	Dry-heat	140.47	40.50	143	1.81
	Xenon lamp	142.96	27.10	143	2.35

Paper 3	*Unaged*	136.52	35.84	137	4.77
	Moist-heat	150.61	32.50	149	5.64
	Dry-heat	133.27	44.60	133	6.05
	Xenon lamp	117.42	26.40	118	4.95
Paper 4	*Unaged*	140.80	35.55	140	0.85
	Moist-heat	123.62	9.80	125	1.17
	Dry-heat	130.22	35.70	128	0.91
	Xenon lamp	138.63	15.40	138	1.64
Paper 5	*Unaged*	130.43	42.67	129	2.94
	Moist-heat	105.70	30.30	101	2.75
	Dry-heat	109.08	29.40	106	2.90
	Xenon lamp	97.96	22.90	97	4.12
Paper 6	*Unaged*	115.64	46.40	108	3.07
	Moist-heat	147.30	37.60	141	3.14
	Dry-heat	131.12	42.90	124	2.97
	Xenon lamp	139.67	22.30	138	3.29

Legend:
Mean – Average grey value within selection. This is the sum of grey values of all pixels in the selection divided by the number of pixels.
StdDev – Standard deviation of grey values used to generate the mean grey value.
Median – Median value of pixels in the image or selection.
Ra – Average surface roughness.

In the scanning electron images of papers (cf. Figure 12), some differences can also be seen. Plot diagrams support the visual evaluation of roughness on the SEM images. 3D surface plot diagrams show the highest level of uniformity for Paper 1.

From Table 4, it is seen that all three synthetic papers (Papers 1-3) and one cellulose paper (Paper 6) obtained the highest mean grey values and also the median value under the moist-heat treatment. With ageing, the uniformity of surface topography improves, except for the dry-heat treated synthetic papers. For all papers, the highest uniformity was obtained after the treatment with the xenon lamp. It was noticed that the average surface roughness of synthetic and cellulose papers increased after all three accelerated ageing processes. All three cellulose papers (Papers 4-6) and one fibre synthetic paper (Paper 2) became rougher after the treatment with the xenon lamp, while the film synthetic paper (Paper 1) and fibre synthetic paper (Paper 3) under the dry-heat ageing. Accelerated ageing had the highest influence on the fibre synthetic paper (Paper 3), which had among all papers the highest roughness. The environmental action causes oxidation of the coating surface layers and in this way deteriorates the cohesion between the filler particles and polymer matrix, which results in increased roughness of the polymer coating surface [25].

Conclusions

In the present work, a comparison of the surface, optical and mechanical properties of synthetic and cellulose papers exposed to various accelerated ageing (dry-heat, moist-heat and xenon lamp) was studied. For most of the papers, the dry-heat treatment caused a higher loss in ISO brightness than the moist-heat treatment and the treatment with the xenon lamp. The yellowing of the paper and the brightness decrease upon ageing were more pronounced for cellulose papers than for synthetic papers. The film synthetic paper with the highest ISO brightness kept high brightness over 95% and showed no yellowing even after the ageing. The differences between papers were noted also for the mechanical properties of the papers. Ageing had little influence on the tensile strength and elongation at break; zero-span tensile strength increased, whereas a dramatic decrease in folding endurance was observed. Dry-heat ageing had a higher impact on the folding endurance of papers than moist-heat ageing. Synthetic papers had higher mechanical resistance to ageing than cellulose papers. It was also noticed that surface roughness increased after the ageing, especially at the synthetic paper with higher roughness.

The best durability in the dry-heat and moist-heat environment was obtained by the film synthetic paper. Both fibre synthetic papers also showed higher optical and mechanical resistance than cellulose papers.

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