LINEAR BEHAVIOUR OF ONE-SIDE COATED PAPER: ANISOTROPY

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The research work presents the study results of anisotropy of one-side coated papers for the purpose of offset printing. Through technological processes, e.g. paper production, finishing, coating, printing, paper becomes more homogeneous, which shows an equal transformation of mechanical tension forces. The stated is in good agreement with the measurements of paper anisotropy. The regularity is seen as the evenness of mechanical forces transmission through technological stages, e.g. calendering, coating, winding, printing etc. The processes of paper finishing do not influence paper anisotropy significantly; moreover, it remains preserved through the entire production and post-production, or it even slightly lowers after offset printing, which means that the findings presented in this study can help to better understand paper anisotropy before and after printing. Anisotropy and paper fibre connectivity in the paper core structure were studied and verified by several research methods, i.e. sonic velocity, SEM, MIT, tearing resistance etc, the results being in good relation with the theory of anisotropy in general.

Keywords: anisotropy, sonic velocity, mechanical-physical properties, coated paper

INTRODUCTION

Paper substrates are preferred due to high strength, flexibility, low cost and recyclability, especially in graphic arts, printing, archiving, writing, magazines, books etc. However, they have a complex structure with cellulosic units arranged on multiple levels, including molecules, fibrils, fibres and fibre networks – the two or three-dimensional structures developed from nanometres to several centimetres. The hierarchical ordering forms during the production in a pulp and paper mill, where specific interactions within a paper network can be tuned by modifying pulp composition, by paper machine operations. Individual fibres and network properties determine the final paper performance, they may often be flocculated and/or anisotropically distributed, which is reflected in the mechanical properties of the paper. The anisotropy of deterministic features can be assessed by modern means.[1] In the world of material science and engineering, many phenomena are highly dependent upon direction, i.e. orientation. Systems that are directionally dependent are called anisotropic. In paper technology, fibre orientation is a key factor, and it may be MD − machine direction, or CD − cross direction. The intrinsic inhomogeneity of the media is originally induced by the anisotropy of the system.[2] Studying the mechanical behaviour of anisotropic materials under static and dynamic loads is important when considering engineering practice. However, in the early 20[th]century, anisotropy was predominantly studied by the scientific world, rather than used in engineering design.[3]

One of the imperfections of paper processing is the heterogeneity of paper properties, which is a great concern when manufacturing wide forming board; nevertheless, it occurs more or less in the production of any type of paper. This is explained firstly, by the difference in the pulp flow through the pipes and on the paper machine, e.g. stock inlet, and secondly, by the irregularity in thickness, grammage, moisture content, fibre orientation etc, as a result, differences in the stiffness values occur.[4] Paper with its macro- (e.g. fibres) and nano-composites (e.g. fillers and agents) exhibits time-dependent mechanical properties, which can affect extremely the functionality and durability. The degree of change in anisotropy and mechanical properties depends on many factors, e.g. temperature, pressure and stress conditions, to which the paper is subjected during the process of manufacturing and usage.

Unsuitable processing conditions may cause paper to curl, wrap, wrinkle or even tear, even before any external force is applied.[5]

RESEARCH METHODS

The study of anisotropy of one-side coated paper samples was performed on the basis of five research methods, e.g. sonic velocity, breaking force and elongation, scanning electron microscopy (SEM), and folding endurance and tearing resistance. The presented methods were chosen as the most appropriate methods to describe the anisotropy of one-side coated paper samples, which were produced at B&B Vevče paper mill.

Sonic velocity

Sonic velocity is one of the methods to determine polymer anisotropy. The molecular orientation is characteristic of oriented polymers, e.g. cellulose fibres.[6] Anisotropy in paper structure is a consequence of different energy values between atoms and molecules. A strong covalent bond along a macromolecule and a weak van der Waals intermolecular effect result in anisotropy. Without the anisotropy of energy effects, the orientation comprehension would be insignificant and there would be no anisotropy of physical nature. A paper strip sample (10 mm wide) is set between two piezoelectric crystals (Rochell salt and bimorph KNa tartar). An impulse generator sends a perpendicular signal to the transmitter. The receiver converts the sonic wave to an electric signal. The intensifier then strengthens the received electrical signal and transforms it into a perpendicular signal. The converted signal goes from the modulator to the oscillator. The impulse oscillator sends the impulse to the transmitter etc., with the frequency of 160 Hz.[7] The time required for a signal to travel from the transmitter to the receiver was measured sporadically, in 1 cm steps, between 15 and 2 cm. Sonic velocity is calculated based on the distance between the transmitter-receiver and the time needed for the impulse to travel from one to another (Eq. 1).

$$C = \frac{\Delta l}{\Delta t}$$

(1)

where:
C − sonic velocity,
l − distance between piezoelectric crystals,
t − time needed for signal to travel from transmitter to receiver.

Sonic velocity depends on the ability of paper to store the kinetic energy, as well as on that of material elasticity to store the potential energy. From classic mechanics, we can deduce the relation between the module and sonic velocity in solid state, as written in Eq. 2.

$$E = C^2 \times \rho$$

(2)

where:
E − module,
C − sonic velocity,
ρ − specimen density.

Breaking force and elongation

Paper behaves as an anisotropic material due to the presence of hemicelluloses, lignin and non-crystalline, e.g. amorphous, regions. The factors affecting paper strength are the degree of refining, formation on the paper machine, web shrinkage in the drying section and paper humidity.[8] Excessive beating of cellulose fibres causes reduction in the breaking force and elongation and is proportional with the fibre length or with a square root of average fibre length.[9,10] The mechanical response of a paper strip to external tension is described by breaking force and elongation (often called stress-strain curve). The breaking force-elongation curve characterizes the mechanical properties, describing the general strength of paper. It is the maximum force per unit width that a paper strip (15 mm wide) can resist before breaking, when applying load in the direction parallel to the strip length. The measurement is based on applying a constant rate of loading or a constant rate of elongation.[11,12]

Scanning electron microscopy

Paper has a complex hierarchical structure and the finishing layer controls the end use functionalities, e.g. hydrophobicity. Better understanding of the multi-scale surface anisotropy patterns is obtained by monitoring the topography with a non-contact method, e.g. scanning electron microscopy (SEM). The complexity is characteristic not only of the paper bulk, but also of the surface, where it determines end use properties, such as visual appearance (e.g. gloss, colour and flatness), printability (e.g. capillary action, ink drying and absorption), processability (e.g. friction) and barrier resistance (e.g. water absorption, gas penetration and grease).[1] It is important to monitor paper surface to control the quality at the production site and provide insight into ways to improve the surface

properties. The paper qualities and interfacial properties depend on the surface topography, which has a multiscale structure that can be altered by coating or calendering.[1,13] The large surface features or waviness result from long-range fibre alignments during the paper machine operations and originates in the base sheet. The fine length-scale phenomena of small and high frequency surface irregularities or roughness are characteristic of coating pigments and pigment packing. The multilevel anisotropy of latex coatings with calcium carbonate pigments was evaluated with SEM. The one-side coated papers present a linear or bilinear function, depending on the rod- or blade-coating process.[13]

Folding endurance – MIT method

A finished product exhibits objectionable flaking, cracking or splitting along the spine of the fold. The problem may be the surface stress primarily affecting the ink and overcoat, or it may be the result of fibre stress and rupture, causing the uplifting of paper fibre and coating. The three primary paper characteristics contributing to foldability are inherent fibre strength, the fibre ability to effectively delaminate at the score and sheet pliability. Fibre strength is influenced by the species selection, and enhanced by the moderate levels of refining and wet pressing to obtain fibre fibrillation and bonding. Paper pliability can be accomplished by increasing paper moisture, since water has the effect of elasticizing the fibres. Paper coatings are typically rich in pigments, such as calcium carbonate, which are bound to the paper surface with latex and/or natural starch. Except for latex, these materials tend to be brittle and therefore challenged to absorb the forces created during the folding process. Therefore, it follows that a higher coat weight sheet tends to be more prone to cracking issues as compared to lower coat weight sheet. In general, the folding endurance of lightweight papers, i.e. 70 g/m^2 and lower, is stronger and more resistant when paper is folded in CD, whereas the folding endurance of heavyweight papers, i.e. 100 g/m^2 and higher, resists better when paper is folded in MD.[14] The MIT method, which was used in our research, is based on the oscillating folding head, which repeatedly folds a paper sample back and forth with the folding angle of 135° until it breaks. In comparison with the Schopper method, the MIT method allows a greater variability in paper samples, and the tension can be adjusted to the

thickness of the sample. The folding endurance is enhanced with increased paper fibre refining, as a function of interlacing of the bonds between paper fibres. The non-fibrous additives, such as fillers, sizing and coatings to the papermaking furnish or finished paper surface, reduce folding endurance. Moisture loss also considerably decreases the folding endurance. The degree of desired folding endurance depends on the paper end use requirements.[15]

Tearing resistance – Elmendorf method

The Elmendorf method is used to determine the paper tearing resistance. The tearing resistance is the mean force required to tear a specimen consisting in a stack of four papers with an initial cut. The tearing force is generated by the release of the quadrant pendulum to which one half of the paper sample is clamped, the other half being attached to the stationary clamp. The Elmendorf tear test exerts a shearing force perpendicular to the paper surface, simulating an actual tearing action. An initial cut in the MD is the MD tear test and vice versa.[9,10]

EXPERIMENTAL
Materials

To study the paper viscoelastic properties, three different wood-free paper samples were taken from the production line. Paper composed of sulphate cellulose pulp of conifer (spruce) and deciduous tree (eucalyptus), and of production rejects (mixture of spur and eucalyptus) were analysed. The paper samples were internally sized with synthetic size, based on alkyketendimer (AKD) in neutral pH media, with the surface starched on a Billblade machine. A one-side coating (a mixture of natural calcium carbonate, synthetic latex, water and auxiliary materials) was applied off-line and then glazed on a supercalender. The measurements were performed on uncoated (UN), off-line one-side coated (CO) and on coated side printed (PR) paper samples. A five-colour offset printing machine Heidelberg SpeedMaster CD 102-5+LX, with an excluded varnishing part, was used for the printing purposes.

Methods

Several studies have been performed to evaluate paper anisotropy, as some authors tried to evaluate and describe paper anisotropic behaviour with different measuring methods, e.g. pulsed holographic interferometry,[16] paper multi-axial yield surface measurement,[17] wavelet analysis,[13,18] strain orthotropic elasto-plastic model,[19] ellipsoidal anisotropy,[20,21] AFM, polarized light microscopy, wavelength and angle dependent optical reflectometry,[21] tensile testing of

cellulose films[22] and laser ultrasonic method.[23] Nevertheless, none of these studies explains paper anisotropy as the research presented in this paper. Sonic velocity was measured with an impulse detector Morgan Dynamic Modulus Tester, Pulps Propagation Meter PPM-5R (H. Morgan Comp. USA). The measurements were performed on the surface of paper samples, with the frequency of 10 kHz, every 20º between 0º and 180º.

Tensile strength, expressed as breaking force, was measured on an Instron apparatus. The samples were stretched to the rupture point, where the breaking force and corresponding elongation were measured and recorded with a dynamometer Instron 6022. The dynamometer reads data continuously from the beginning (l = 180 mm) to the end of the test, i.e. break.

The SEM microscopy analysis was performed on a JEOL JSM 6060 LV under various magnifications (i.e. between 100 and 3000×) at 10 kV. The specimens were coated with a 13.5 μm thick layer of gold under argon atmosphere.

The MIT-folding endurance was measured according to the ISO 5626 standard. The specimens were tested before (UN, i.e. uncoated) and after the coating (CO, i.e. coated). The measurements were conducted on an ETS Interlaken Technologies MIT machine. Folding endurance indicates paper durability and a decline in paper folding endurance displays in paper deterioration and a decrease in mechanical-physical properties.

Tearing resistance was done according to the ISO 1974 standard and the samples were analysed on a Henry Baer & Co. Ltd apparatus, and similarly to the MIT-folding endurance, just for UN and CO paper and in two fibre directions, i.e. MD and CD. Tearing resistance measures the energy to propagate an existing crack through the paper and the path it takes is often variable, especially in CD, while in MD, the tearing is more in a straight line.

RESULTS AND DISCUSSION
Sonic velocity

For the quantitative determination of anisotropy characteristics of paper, the sonic velocity method was used. The measured differences are the result of a crack coincidence arrangement on paper surface, thickness, bulk of fibres or fillers and mainly an increase in the particle number (fillers, pigments). The more perforated (free space between fibres, air bubbles in filler) and cracked (coating and/or printing layer) the paper surface is, the longer the time required for a sonic wave to get from the transmitter to the receiver. The measurements of sonic velocity (Table 1 and Fig. 1) provide an insight into the influence of an individual process

stage, e.g. paper production, coating, calendering and printing, on paper anisotropy properties. The highest measured speed (i.e. 3.76 km/s) was on uncoated paper in MD as a result of the phase transformation at high pressures. Therefore, the uniformity of paper changes after offset printing is the consequence of the pressure forces in the coating and printing nip, which tend to range between 2 and 4 MPa. When comparing the sonic velocity of all three types of studied paper samples, the difference at 0° and 180° is of 0.05 km/s for the uncoated, 0.03 km/s for the coated, and 0.17 km/s for the printed samples. Printing ink influences the sonic velocity results, decreasing sonic speed, as coated particles have fewer covalent bonds, and with the addition of ink, the thickness of paper samples increases, causing the results presented.

Breaking force and elongation

From the diagram presented in Fig. 2, it can be concluded that, of the three tested specimens, uncoated paper has the lowest values of breaking force (in MD = 66.75 N and in CD = 32.26 N), as well as elongation at break (in MD = 1.72% and in CD = 7.97%). On the other hand, the coated paper sample has a breaking force by 9.00 N in MD lower than that of printed paper. However, in CD, the coated paper has a breaking force by 3.68 N higher than that of printed paper. A higher breaking force in MD is the result of alluvium of the printing ink (composition of flax oil, pigment, binding agent, diversified waxes and the addition of different substances to attain optimal rheological characteristics and gloss). The cause for that should be sought in ink, which is dried with oxide, after the printing. The result is an increasingly fortified paper structure, since ink also links paper structure and makes it more even. However, in the printing direction, i.e. in CD, the reduction of breaking force (3.68 N) and elongation (0.12%) of the printed paper in comparison with the coated one is mainly caused by one of ink components. Flax oil has in this case the function of a lubricant. The number of junction points in the net of cellulose fibres decreases after printing and consequently, paper becomes less resistant to external mechanical deformation enabling fibres to slide by each other. In the literature, the breaking force and elongation data can be found only in two directions (MD (0°) and CD (90°)). In the research of the anisotropy of a breaking force (Fig. 3) and elongation at

break (Fig. 4), we also performed measurements of angle distribution between 0° and 180°. The results indicate that the values at 30° do not match the values at 150°. The differences, which are the result of paper inhomogeneity and structure changes between angles (30° and 150°), are noted for breaking force: 4.65 N (UN), 5.62 N (CO), 0.76 N (PR) and for elongation: 0.11% (UN), 0.24% (CO), 0.29% (PR).

Even though the mechanical properties of the studied paper should weaken with each additional technological process of the production and finishing, the results of our investigation show the opposite. The diagrams of angle distribution of breaking force (Fig. 3) and elongation (Fig. 4) permit the following conclusions: 1) uncoated paper has the lowest values of breaking force and elongation (lower unity and homogeneity); 2) coated paper has the highest values of breaking force (coating makes paper more linked); and 3) between 30° and 90°, printed paper has the highest values of elongation at break, but at higher angles (over 90°), uncoated and printed paper levels with the coated one. The cause for such behaviour lies in the coating layer and its influence on the paper mechanical properties. The thickness of ink on a paper surface is between 0.7 and 1.3 µm (offset printing), while the medium depth of roughness of a coating layer is of approximately 1 µm.[24] Printing ink evens out the remaining irregularity of the surface, making the paper more homogeneous.

Table 1

Measurements of sonic velocity (C) on uncoated (UN), one-side coated (CO) and printed (PR)

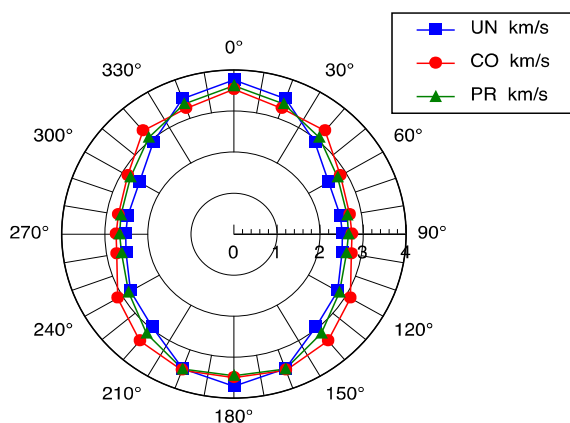| α [°]	C [km/s]		
	UN	CO	PR
0	**3.76**	3.53	3.62
20	3.51	3.26	3.38
40	2.92	3.42	3.08
60	2.54	2.85	2.78
80	2.51	2.73	2.67
90	2.52	2.74	2.66
100	2.55	2.77	2.65
120	2.78	3.12	2.83
140	2.96	3.40	3.16
160	3.49	3.53	3.50
180	3.71	3.50	3.45

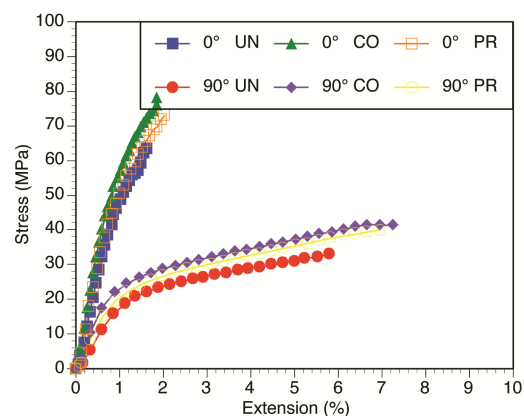Figure 1: Angle distribution of sonic velocity
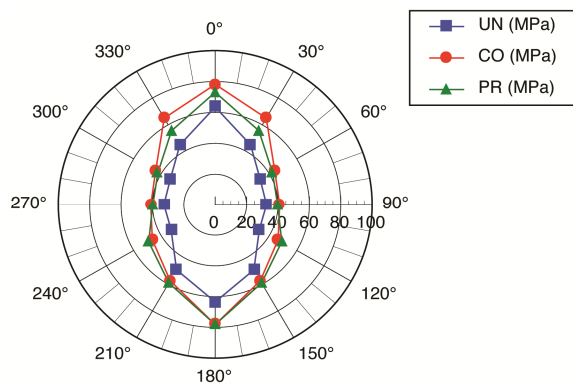

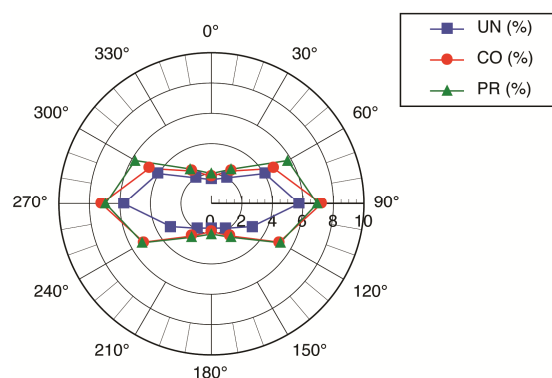Figure 2: Stress vs. extension

Figure 3: Angle distribution of stress at break

Figure 4: Angle distribution of extension at break

Table 2
Folding endurance of uncoated (UN) and one-side coated (CO) paper – MIT

	MD				CD				
	m [g]								
	0	800	1000	1250	1500	0	800	1000	1250	1500
UN									
$\overline{\mathrm{X}}$	**5675**	246	32	18	8	**2947**	145	29	10	7
S_x		27.578	4.464	4.740	2.173		28.267	2.489	3.556	1.889
CV		11.21	13.95	26.33	27.16		19.49	8.58	35.56	26.99
CO									
$\overline{\mathrm{X}}$	**2209**	128	28	13	7	**897**	68	25	11	6
S_x		69.323	10.429	3.617	2.819		30.045	10.221	3.026	2.573
CV		54.16	37.25	27.82	40.27		44.18	40.88	27.51	42.88

Scanning electron microscopy

The morphology of uncoated, coated and printed papers is presented in Fig. 5. The fibres and fillers of uncoated papers are fully covered by the microdomain structure of the coating. Therefore, the creation of microdomains does not depend on eventual stresses between the fibrous substrate and the coating, but likely results from the agglomeration of nanoparticles during water evaporation. In fact, the basic mechanisms for the film formation of pigments in an aqueous dispersion contain three stages:

− evaporation of water, so that the dispersion becomes more concentrated and the particles become structurally ordered,
− deformation of the film on the substrate due to capillary forces, and
− interdiffusion of polymer molecules across the particle boundaries.

The non-continuous film changes the capillary surface forces and offers good printing properties, i.e. the microcracks may serve as drainage channels to evacuate ink solvents, while the ink pigments adhere well onto the microdomains.

Folding endurance − MIT method

Paper heterogeneity makes preparing two identical paper specimens impossible. Paper has a random distribution of paper components (i.e. fibres, paper fillers etc) in its spatial structure. The surface of the clamp is in the case of the MIT method of 2 mm^2, while, compared to it, the surface of the paper strip is in the range of "unlimited" dimensions. The probability of finding two equal regions in paper, e.g. with the same number of fibres, filler concentration and pigments, is exceedingly low. Therefore, the result is a high variance of average value, which is in our study the highest on the one-side coated paper, i.e. 69.323 (Table 2). As seen from the results presented in Table 2, uncoated paper attains the highest values of folding endurance, i.e. 5675 in MD and 2947 in CD, which is in good agreement with the theory, according to which uncoated papers present better mechanical properties in relation to coated. The reason lies in the measuring scale, which in folding endurance testing is on the same line with cellulose fibres, meaning that when measuring the uncoated paper,

the key element in resisting to folding endurance consists in fibres and their flexibility. Nevertheless, a thin film of the coating layer weakens the paper mechanical resistance and

increases paper stiffness. The result can be observed as cracking of the paper surface, which has a negative effect on the printing quality, i.e. wicking and bleeding.
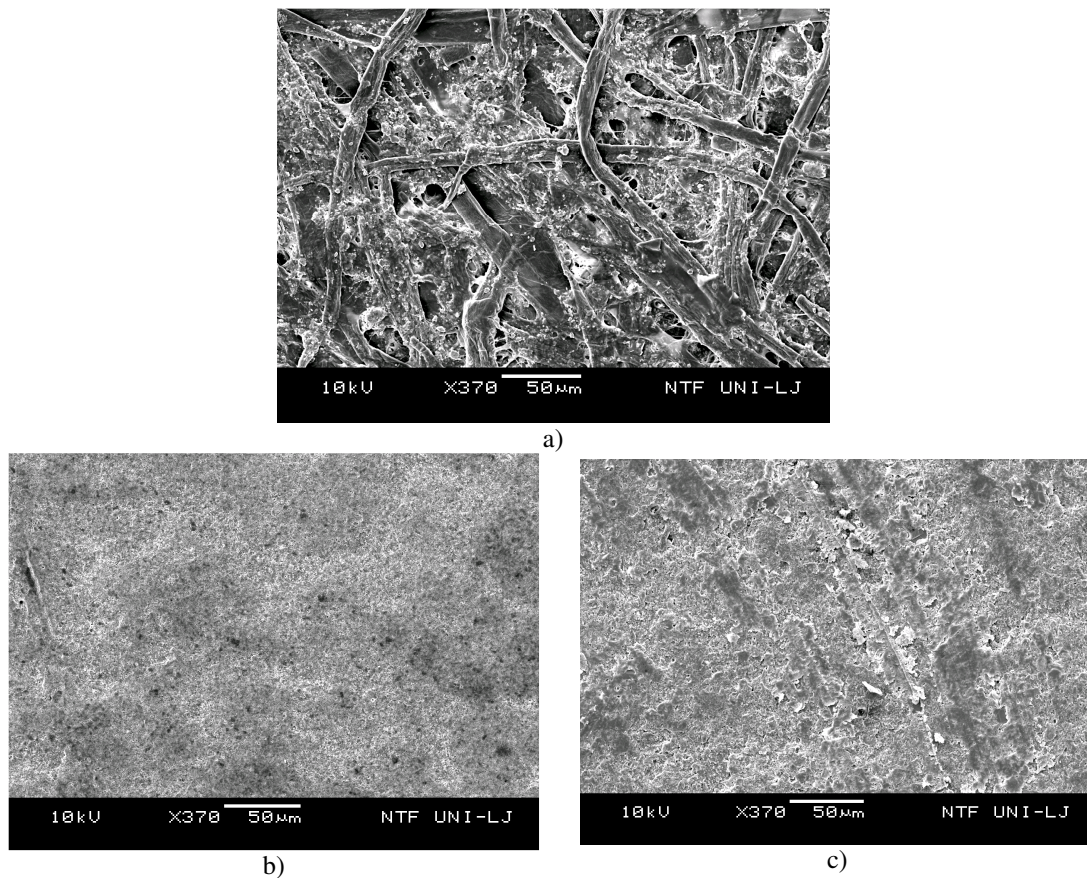

a)

b)

c)

Figure 5: Scanning electron microscopy of a) uncoated base paper, b) one-side coated and c) printed on coated side (magnification 370×)
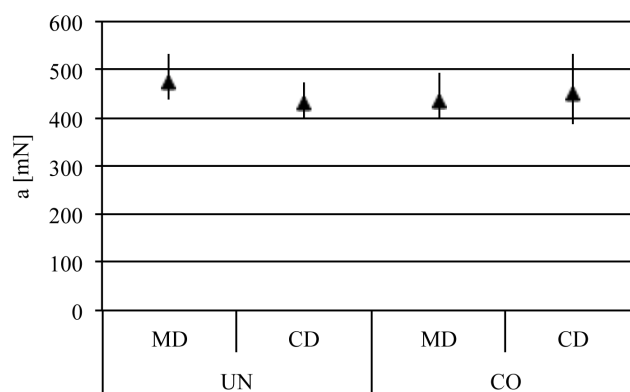

Figure 6: Tearing resistance (a)− Elmendorf

Tearing resistance – Elmendorf method

Tearing resistance was measured according to the ISO 1974 standard and the results confirmed the anisotropy of paper before and after one-side coating. The instrument measures the energy used

by the pendulum in tearing the test specimen and, as presented in Fig. 6, pulling the fibre out of the tearing line requires more energy, i.e. work, than breaking the fibre. The tearing resistance is for the uncoated paper in MD the highest, i.e. 476

mN, and the lowest for the uncoated in CD (i.e. 432 mN), while for the one-side coated paper, the coating layer offers uniformity to paper surface and is in accordance with the measured values, e.g. 436 mN in MD and 450 mN in CD. The tearing resistance method measures paper anisotropy on the basis of fibre distribution. The coating hardens paper flexibility and, as mentioned, paper stiffness. Since the tearing resistance is an indicator of runnability, i.e. web breaking, and gives an insight into fibre entanglement, we can see from the measurements that, with the addition of a coating layer, paper does not mechanically weaken, as it might be expected.

CONCLUSION

In the presented investigation, paper structure was studied before and after offset printing with variation in anisotropy. With each additional technological process of finishing (coating and printing), the mechanical properties of paper do not change considerably in MD. Similar behaviour is noticed in CD. These conclusions can be drawn from the angle distribution of breaking force (Fig. 3) and from the angle distribution of elongation at break (Fig. 4), where all the curves are nearly overlapping. The reasons for the existence of anisotropy of mechanical properties are numerous. When measuring and evaluating paper anisotropy with the presented research methods, it can be noted that the anisotropic behaviour of paper changes with each technological process, i.e. coating, calendering and printing, whereas in the end, the variation is not significant. This information is of great importance for the paper producer, as well as for the end user, i.e. printing houses. The results and research methodology are an example of practical usage of methods to determine and analyse paper anisotropy for the quality assessment of the papermaking process and technology.

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