INTERACTIONS BETWEEN OFFSET PAPERS AND LIQUIDS

Juraj Gigac, Monika Stankovská, Miroslava Kasajová
Pulp and Paper Research Institute
Bratislava, Slovak Republic

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ABSTRACT

Spontaneous transport of water and solution of isopropyl alcohol in water during interaction with uncoated and coated surfaces of offset papers was observed. Paper surface was characterized with regard to porosity, topology of pores and paper printability. Measurement of penetration dynamics of the both Newtonian liquids by monitoring of transmitted ultrasound of 2 MHz frequency allowed to specify USI70 and t95 parameters which correlate with surface roughness and printability of paper. The results of the ultrasound method are highly correlated (r = 0.890-0.956) with PPS printing roughness measured by the flow-through method, with Optical variability of surface roughness and with print density D of surface printed by the Prüfbau Print Tester.

KEYWORDS: Capillaries, light, liquids, paper, print quality, roughness, surface energy, ultrasound, wetting.

INTRODUCTION

Porosity and topology of pores, chemistry of surface together with surface tension and viscosity of liquids are playing an important role in paper saturation. Capillary penetration is a phenomenon occurring in paper production processes e. g. in coating, in treatment of paper in a size press, in printing and writing on paper, in gluing of fluting with liner in corrugated board production but also in using sanitary papers.

Liquids can penetrate paper by action of pressure forces or internal forces such as capillary forces sucking liquids into paper. If the contact angle between liquid and solid surface is below 90° spontaneous saturation by sucking liquid into paper occurs. According the Washburn–Lucas–Rideal law penetration depth into capillary at spontaneous saturation with inert liquid depends on square root of penetration time and on absorption coefficient of the porous body (Daub et al. 1986, Alava and Niskanen 2006). The absorption coefficient is a function of pores diameter, surface tension and viscosity of the liquid and of contact angle between the liquid and porous wall.
Mechanisms of liquids intake besides filling cavities of paper surface includes vapor diffusion into fibers through pores, diffusion of molecules of liquids on fibrous surfaces and diffusion of vapor into fibers through pores, so called fiber sorption (Daub et al. 1986). In case of sorption into pores thickness of paper remains unchanged. Oil sorption on fibers is not possible as wall pores are too small for oils. Water and water solutions can be uptaken by paper by pores and by fiber sorption. Water in dense and sized papers is sorpted first on fibers and afterwards in pores. In case of voluminous, the sequence in unsized papers is reversed. In interaction of hydrophilic cellulose fibers and binders in coating with water and water solutions occurs swelling and changes in dimension of pores. Assumption, that the contact angle is constant is not valid in the case of sized papers. Differences of surface in chemical and morphological condition are causing hysteresis of contact angle values. As a result of roughness and porosity variability as well as of changes of hydrophilic and hydrophobic areas in paper the value of the static contact angle is between the receding contact angle (when air displaces liquid) and the advancing contact angle when air is displaced by liquid (Radvan and Skold 1966).

The wetting front in paper was observed with optical coherence tomography (Fabritius and Myllyla 2006). Two optical methods, based on a steak-camera and optical coherence tomography for measuring sorption into paper were used (Fabritius 2007) where the last mentioned were proved as very promising for investigation of dynamical paper-liquid interactions which are spatially and temporally dependent processes.

Ultrasound methods for characterization of paper wetting have been reported long ago. Measurement of 7 kHz in-plane acoustic wave propagation showed high correlation with wetting rate constant according by Klemm test (Chatterjee 1971). Pan et al. studied liquid penetration with through transmitted 2 MHz ultrasound (Pan et al. 1985), further developed their device and made parallel measurements with ultrasonic and Bristow wheel methods (Pan et al. 1988). Commercial product based on their first existing device, where horizontal paper sample is soaked vertically in a liquid vessel. The ultrasound has advantage over other non-contact methods because it can examine mechanical changes where other methods were unable to do so. We introduced a “vertical” setup of device having the capability to measure with center frequencies of 0.5-14 MHz (Stor-Pellinen et al. 2000). The device with high power ultrasound field on liquid penetration could be used to measure swelling induced test sheet thickness increase. The ultrasound pulse scatters and diffracts when reflecting from a rough surface and energy loss by scattering and diffraction can be observed as a reduction in the reflected pulse amplitude. The impact of surface roughness on amplitude of an acoustic wave reflected at normal incidence is described in the literature by the following equation (Blessing et al. 1993):

\[
A = A_0 e^{-2k^2R_q^2(t)}
\]

where: \(A_0\) is the amplitude of the incident wave, \(k\) the wave number and \(R_q(t)\) the time-dependent surface roughness.

The aim of this work was to study penetration of water and water solution of isopropyl alcohol at contact with paper surface without external pressure and to determine surface roughness of coated and uncoated offset papers by the ultrasound technique as well as to compare results of the ultrasound method with Parker Print Surf (PPS) printing roughness, with optical surface roughness measured by the photoclinometric method and with print density of an area printed by the Prüfbau Print Tester.
MATERIAL AND METHODS

Coated and uncoated paper samples for sheet offset printing were kindly gifted by following paper producers: Mondi SCP, M-real Biberist, Hallein and Stockstadt, Arctic Paper Kostrzyn. Surface free energy of coated papers was 34.4-39.1 mJ.m\(^{-2}\), of uncoated papers 44.5-56.9 mJ.m\(^{-2}\). Printing roughness of coated papers was 0.7-2.0 µm and of uncoated papers 5.3-6.2 µm. Deionized water (surface tension 72.1 mN.m\(^{-1}\)) and 16 % water solution of isopropyl alcohol (surface tension 39.0 mN.m\(^{-1}\)) was used for paper surface quality measurements. Isopropyl alcohol IPA (min. 99.7 %) was obtained from CentralChem, Slovakia. For determination of paper surface energy thiodiglycol (2,2’-Thiodiethanol) from Sigma-Aldrich, (min. 99 %), diiodomethane and ethylene glycol (min. 99 %) from Merck, Slovakia was used.

Measurements of dynamics penetration

Intensity of transmitted high-frequency low-energy ultrasonic signals with a fixed frequency of 2 MHz were measured 35 ms after contact of paper surface with a liquid in the measuring cell of the PDA instrument (EMTEC, Germany) for a 60 second period. The ultrasound of transmittance of paper is changing with absorption of liquids and is influenced by several mechanisms. Increase of scanned ultrasound is a result of decreased reflection on the interface of liquid-paper during wetting. Decrease of scanned ultrasound is a result of increased scattering caused by trapped air in isolated points of paper structure in course of uneven penetration. Increase of scanned signal is a result of increased absorption of ultrasound caused by total filling of pores and capillaries by liquid. A decreased signal is a result of decreasing transmittance of ultrasound caused by decreasing elasticity of fibers when the paper is moistened by vapor of transporting water (in case aqueous testing liquids are used). The maximum value transmitted signal intensity was 138 %.

Measurements of roughness of paper

Roughness of paper was characterized by air flow measurements according the Parker Print Surf method (ISO 8791-4: 2007) and by measuring distribution of light and shadow on an obliquely illuminated paper surface in machine (MD) and cross direction (CD) with application of photoclinometry (Muinonen et al. 1989, 1990) and with the Coolpix E4500 digital camera and Image J software. A result of paper surface image processing is OVS (Optical Variability of Surface) parameter (Gigac et al. 2006).

Measurements of intake of printing ink and print density of printed surface

Print quality is expressed by sharpness of image, color, tone, gloss, print density, legibility and the uniformity of these properties. In printability studies following instruments and methods were used:

For print density measurement 0.5-9.0 g.m\(^{-2}\) IGT testing ink was applied on surface of papers by a metal disc under 20 kN.m\(^{-1}\) pressure using the Prüfbau Print Tester (Dürner, Germany). Print density was measured after 24 hours by a Macbeth RD-514 densitometer. For evaluation of the relationship between print density of printed surface and amount of printing ink the Tolenaar equation (Tolenaar and Ernst 1961) was used:

\[
D = D_{\text{max}} (1 - e^{-MX})
\]

where: \(D\) is the determined print density, \(X\) is weight of ink applied to the paper (g.m\(^{-2}\)). \(D_{\text{max}}\) is saturation value of print density.

The product of \(D_{\text{max}}\) and \(M\) is steepness of the density curve in the point \(X = 0\).
If parameter $M$ increases than suitability of paper in given conditions increases. Print quality of evaluated papers was characterized by two parameters - print density $D_{\text{opt}}$ and specific print density $(D/X)_{\text{opt}}$ related to a unit of applied printing ink. Both parameters were determined at the point of the density curve at which the tangent to the density curve has a magnitude 0.05. The larger are the values of print density $D_{\text{opt}}$ and specific print density $(D/X)_{\text{opt}}$, the more suitable is the paper for printing.

**Measurement of surface tension, contact angle and surface energy of paper**

Surface tension of water and of 16 % IPA solution was determined by the pendant drop method. Surface free energy of papers including polar and dispersion components was measured by the Owens-Wendt method using the OCA 35 tensiometer (DataPhysics Instrument, Germany). Surface free energy was determined using three testing liquids (diiodomethane, ethylene glycol and thioglycol).

**RESULTS AND DISCUSSION**

**Water penetration**

Fig. 1 shows intensity of received ultrasound signal during water contact with surface of coated (1-5) and uncoated (6-10) papers. In case of uncoated papers with a printing roughness $PPS$ 5.3-6.2 µm a sharp increase of ultrasound signal was observed after overcoming the thin air film between water and paper that corresponds to wetting. Slow penetration of water into structure of sized paper further increased intensity of ultrasound signal. As the rear side of the paper sample is closed and compressed air in the paper structure causes dispersion a reduced increase of ultrasound signal was observed. The time increasing the intensity of the ultrasound signal of uncoated papers 6, 8 and 9 to the maximum value was in the range 600-1500 ms depending on paper sizing degree; this indicated start of fiber swelling. During the water penetration phase decrease of ultrasound signal was observed caused by decrease of elasticity of swelled fibers and by pressing the retained air into the largest pores of the paper structure. In case of uncoated papers 7 and 10 the signal gradually decreased after 2-3 seconds only. In case of coated papers 1-5 of printing roughness $PPS$ 0.8-2.0 µm the air after the contact with water was immediately displaced and the coating soaked. When water is used the intensity of ultrasound signal and time to reach its maximum characterizes surface roughness and contains information about condition of the surface regarding hydrophilicity or hydrophobicity respectively.
Penetration of IPA water solution

Fig. 2 shows the time record of received ultrasound intensity changes at contact of 16 % IPA water solution with surface of coated (1-5) and uncoated (6-10) papers. The course of ultrasound signal intensity at application of 16 % IPA water solution of 39.0 mN.m$^{-1}$ surface tension is totally different when compared with water application shown on Fig. 1. In case of uncoated papers of higher roughness (6-10) penetration of IPA water solution occurs immediately (Fig. 2); time of 95 % decrease of signal was 50-200 ms. The liquid displaced air from pores and paper was saturated in 2-3 seconds. Similarly air was slowly displaced by IPA water solution from pores of coated papers (1-5). The time period of ultrasound signal decrease by 95 % was 3.2-14.8 seconds. The different course of liquid penetration into coated papers when compared with uncoated papers is caused by high content of fine pores in the coating.

Fig. 2: Ultrasound intensity – time dependence diagram of coated (1-5) and uncoated (6-10) offset papers, measured with 16 % IPA water solution.
Fig. 3 shows intensity of the scanned ultrasound signal $USI70$ in a time 70 ms after the first contact with water compared with the time after which the ultrasound signal intensity scanned at contact of paper with 16 % IPA water solution decreased to 95 %. Intensity of $USI70$ ultrasound signal expressing surface roughness is shown on x-axis. Time $t95$ on y-axis expresses amount of fine pores. The relationship between parameters of uncoated and coated paper sets can be described by an exponential equation with a good correlation ($r = 0.934$).

In Tab. 1 surface roughness determination $USI70$ and content of fine pores $t95$ is compared with conventional method of surface roughness determination $PPS$, with $OVS$ measurement of optical surface roughness, with measurement of print density $D_{opt}$ and specific print density $(D/X)_{opt}$ of paper surface printed with the Prüfbau Print Tester. The correlation coefficients of compared methods relationships were in the range 0.890-0.956.

**Tab.1: Comparison of coated and uncoated papers surface roughness determination (PDA ultrasound method, PPS flow-through method, optical (photoclinometric) method OVS, printing method using Prüfbau Print Tester).**

<table>
<thead>
<tr>
<th>Correlation coefficients between methods</th>
<th>Flow-through $PPS$</th>
<th>Optical $OVS$</th>
<th>Printing $D_{opt}$</th>
<th>Printing $(D/X)_{opt}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrasound roughness $USI70$</td>
<td>0.952</td>
<td>0.928</td>
<td>0.943</td>
<td>0.890</td>
</tr>
<tr>
<td>Ultrasound fine pores content $t95$</td>
<td>0.943</td>
<td>0.950</td>
<td>0.956</td>
<td>0.891</td>
</tr>
</tbody>
</table>

*X is weight of ink applied (g.m$^{-2}$)
CONCLUSIONS

Penetration of liquid and surface roughness of paper was quantified by measurement of ultrasound signal intensity during contact of water and 16 % isopropyl alcohol water solution with paper.

Absorption of Newtonian swelling liquids was quantified with regard to wetting, fine pores content and surface roughness of coated and uncoated offset papers used for sheet printing.

Surface roughness \textit{USI70} and content of fine pores \textit{t95} were in correlation with printing roughness \textit{PPS}, optical roughness \textit{OVS}, print density \textit{D_{opt}} and specific print density \((D/X)_{opt}\). The respective correlation coefficients are presented in Tab. 1. The importance of ultrasound method in studying liquids transfer in the process of penetration was confirmed.

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REFERENCES