PROPERTIES OF RECYCLED PAPERS IMPORTANT FOR PRINTABLE ANTENNAS

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In this research work, recycled papers differing by the grammage and recycled fiber content were analysed. The research was focused on the properties of paper substrates, which are crucial for the functionality of printed antennas used in radio frequency identification (RFID) tags. Two commercially available printing inks with conductive silver particles were applied. The surface properties of coated and uncoated papers were analysed in connection with the conductivity of the printed ink layer. The thermal stability of the paper substrates was also evaluated as a function of various drying temperatures and processes. Another aspect of the investigation was the evaluation of the stability and print quality of the printed ink layer. The results have shown that recycled paper is an appropriate substrate for the printed electronic structures, such as RFID antennas, and could also be used for packaging applications.

Keywords: recycled paper, conductive ink, resistance of printed ink layer, print penetration

INTRODUCTION

The radio frequency identification (RFID) technology is one of the automatic technologies describing the system that transmits data about an object wirelessly using radio frequencies. The RFID system consists of one or more RFID tags, a reader and an antenna.[1] The use of an RFID system is on the increase in the supply chain management, especially for automatic identification of various packaging.[2] The RFID tag is composed of an antenna and a chip and can operate on different frequencies.[3] The antennas of RFID tags can be manufactured in different ways, conventionally by etching, hot stamping or by printing. Printed RFID antennas are becoming increasingly common due to the possibility of producing RFID tags more economically, ecologically and rapidly.[4] Various printing technologies enable printing on rigid as well as on flexible materials. Among printing technologies, screen printing,[4-9] inkjet,[10-12] flexography,[13] gravure[14] and pad printing[15] are used, the most common being screen printing and inkjet printing. Among flexible printing substrates, thermoplastic films and paper-based materials are mostly used for printed electronics.[7,16-23]

In our research, the possibility of printing RFID antennas on recycled papers using a semi-automatic screen printer was analysed. Recycled paper was chosen as a printing substrate because the use of recycled paper is constantly increasing and also the quality of recycled papers has improved substantially.[24] The main goal of the study was to find out if recycled paper is an appropriate substrate for printed electronics and which properties are most important for the functionality of printable RFID antennas.

EXPERIMENTAL

Materials

In this study, two types of conventional printing paper, coated and uncoated, were used as printing substrates. The papers differ by the grammage and content of recycled fibres, as seen from Table 1. The conductive layer was screen printed using the thermal drying silver conductive ink recommended for hand, semi-automatic or fully automatic screen printing machines. The two commercially available printing inks were applied: CRSN2442 SunTronic Silver 280 (SunChemical) and DuPont 5064H (DuPont). Printing was performed with the RokuPrint semi-automatic screen printing machine. A monofilament polyester plain weave mesh with 120 L/cm was applied (theoretical ink volume 16.3 cm^3/m^2).

The optimization of printed ink layer drying was achieved with a two stage drying process; hot zone drying in a tunnel followed by the heat-press process.[25] The optimal drying was determined as the point where the resistance of printed ink layer became constant.

The resistance of printed ink layer was measured with the digital multimeter DG-890G between two points. The nominal length (L) between two points was 22 mm and the width (W) 3 mm. The nominal number of squares $N_{sq} = L/W = 10.3$; the final sheet resistance (R_{sh}) of the conductive ink layer was calculated.

Methods

Paper substrates were tested under standard climate conditions (ISO 187). Among basic properties, the basic weight (ISO 536), thickness, bulk (ISO 534) and moisture content (ISO 287) were measured. Surface roughness was evaluated according to ISO 8791-2 with the Bendtsen tester and with the TR200 profilometer (ISO 4287). Optical properties were evaluated by the following standards: opacity (ISO 2471), ISO brightness (ISO 2470) and colour CIE L^*, a^*, b^* D65/10° (ISO 11475). The thermal stability of paper substrates at high temperature was measured by the colour difference (ΔE^*) of the paper substrate caused by the drying process according to Equation 1:

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (1)$$

where ΔL^* is difference in lightness/darkness value; Δa^* is difference on red/green axes; and Δb^* is difference on yellow/blue axis.

The water absorption (Cobb method - ISO 535), porosity/air permeability (ISO 5636-3) and print penetration (IGT W24) were also measured. The reciprocal value of liquid absorption is called print penetration. Print penetration is unitless parameter determined as 1000/stain length of print, in mm. A large stain indicates a low roughness/absorption of the paper and gives also a low value of print penetration. SEM micrographs of the paper substrates and printed ink surface were taken by the scanning electron microscope (JSM-6060LV). The instrument was operated with 10 kV, at magnifications of 300-3000.

On the conductive printed ink layer, the line gain, print mottle and abrasiveness were analysed. Print uniformity (print mottle) and line gain were evaluated using ImageJ software. The print mottle was determined with the STFI method, by calculating the coefficient of variation ($CV = \sigma/R$), where σ is standard deviation of the grey values and R is the mean grey value. The line gain, $\Delta A(\%)$ was determined by measuring the area of 10 ideal lines $A_d\,(\%)$ – digital test element in comparison with the area of 10 printed lines $A_p(\%)$ using Equation 2:

$$\Delta A = (A_p - A_d) \quad (2)$$

The abrasion of the printed ink layer was assessed on the Param RT-01 Rub Tester (ASTM D5264). After 500 strokes, the surface of the receptor (uncoated plain paper) was examined for signs of transfer and the area covered with ink was evaluated in percentage by image analysis.

RESULTS AND DISCUSSION

Influence of drying conditions on the resistance of printed ink layer

It is known that the conductivity of the printing ink depends on the printing and drying conditions. Depending on the printing ink properties, at a certain temperature the resistance of the printed ink layer becomes constant. The small deviations in the measured resistance, which appear after the final drying point of the printed ink layer is reached, are the consequence of printing substrate characteristics, i.e. dielectic properties and moisture content, as well as environmental conditions (temperature, relative humidity), which affect the electrical properties of prints.

Because the resistance of the printed ink layer was still high after one stage drying, over 130 mΩ/sq for the SunChemical printing ink and over 2000 mΩ/sq for the DuPont printing ink, a two stage drying process was applied. For both printing inks, the drying in the hot zone tunnel was set at the temperature of 115 ºC for 90 seconds, whereas the temperature at the heat-press process was different for each printing ink (150 ºC for the SunChemical ink and 190 ºC for the DuPont ink). The results presented in Table 2 show that the optimal value of the resistance needs separate optimization of drying conditions for each printing ink. The average value of the sheet resistance on the prints made with the SunChemical ink was 87 mΩ/sq, and on the prints made with the DuPont ink 74 mΩ/sq.

Table 1
Description of paper substrates

Paper type	Grammage, g/m^2	Fibre composition	Surface treatment
C-R/M	80	Mainly recycled with added mechanical pulp	Coated
C-R	100	100% recycled pulp	Coated
UC-M/R	60	Mainly mechanical with added recycled pulp	Uncoated
UC-R/M	80	Mainly recycled with added mechanical pulp	Uncoated
UC-R	100	100% recycled pulp	Uncoated

Table 2
Sheet resistance of printed ink layer at different drying conditions and under standard climate (T = 23 ºC, RH = 50%) for printed paper substrates

Paper type	Sheet resistance (mΩ/sq)					
	SunChemical ink		DuPont ink		DuPont ink	
	Heat-press at 150 ºC	Standard climate	Heat-press at 150 ºC	Standard climate	Heat-press at 190 ºC	Standard climate
C-R/M	78	87	116	116	58	58
C-R	87	87	126	116	68	68
UC-M/R	87	87	214	233	78	87
UC-R/M	78	87	272	291	78	78
UC-R	78	87	194	204	78	78

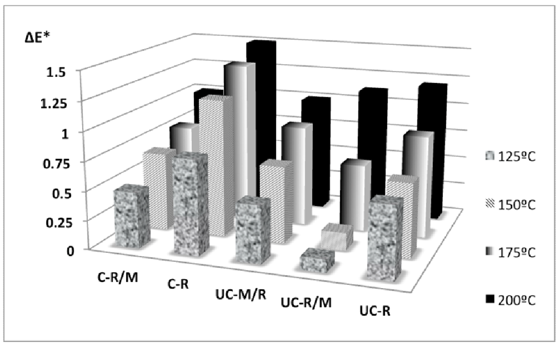


Figure 1: Colour change (ΔE*) of paper substrates at different drying temperatures

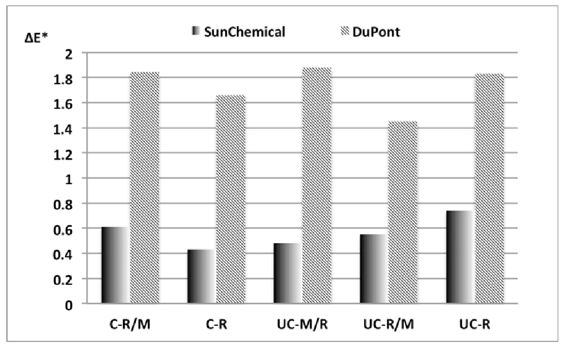


Figure 2: Colour change (ΔE*) of printed paper substrates

The different behaviour of printing inks could be the consequence of different size of conductive particles in the printing ink. It is also evident that the moisture in the paper substrates had some effect on the resistivity of the printed ink layer. The resistance measured immediately after drying was a bit lower than that measured on the samples exposed to the standard climate conditions (temperature = 23 ºC, relative humidity = 50%), when the paper substrates also contained some percentage of moisture (2.6 to 3.6), which influenced the conductivity of the printed ink layer.

In the case of prints made with the SunChemical ink, the substrate had no influence on the conductivity of the printed ink layer, whereas some minor influence could be seen for prints made with the DuPont ink. The reason could be the differences in the porosity and absorptiveness of the printing substrates.

Thermal stability of paper substrates

The thermal stability of paper after crossing the hot zone tunnel at high temperatures was evaluated by assessing colour difference (ΔE*) and ISO brightness. The critical drying temperature was set at the colour difference higher than 1, because the difference above 1 is already visually detectable. As seen from Figure 1, the critical drying temperature is 200 ºC, when all tested papers reached a colour difference of 1 or above 1. Only for the coated paper made from 100% recycled pulp (C-R), the thermal stability is lower, as a noticeable change in colour is already reached at the temperature of 150 ºC.

In the second step, the thermal stability of paper substrates was analysed at printing conditions set for both printing inks. In this case, two different drying processes and two different temperatures were applied. As seen from Figure 2, printing with the SunChemical ink gives a colour difference below 1 for all paper substrates, whereas for DuPont ink it is above 1. In this case, the colour change is higher because the temperature at the heat-press process was higher, i.e. 190 ºC. Higher colour differences than those obtained for drying in the hot zone tunnel at different temperatures (Figure 1) are the consequence of a longer exposure of paper substrates to the temperature (two step process) and the action of the pressure at the second drying stage. However, the colour differences between paper substrates are relatively small.

Beside colour difference, the change in ISO brightness of paper substrates was also analysed (Figure 3). After exposing the paper substrates to the drying temperature, ISO brightness decreased up to 3 units (%) for printing with the SunChemical ink and up to 5 units (%) for printing with the DuPont ink. Similarly to colour change, the grammage and paper composition, i.e. recycled pulp content, had only a minor influence on the change in ISO brightness.

Resistance of printed ink layer in connection with the properties of paper substrates

Tested papers differ by the grammage and thickness, ranging from 58.9 to 97.9 g/m^2 and from 72 to 110 µm. Uncoated papers are bulky, the highest bulk being for the paper made from a mixture of recycled and mechanical pulp. The difference in optical properties between papers of different composition was below 5%, as seen from Table 3.

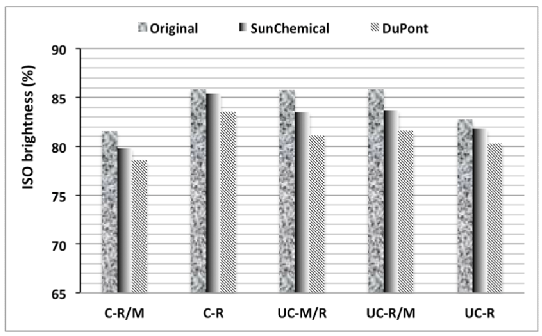


Figure 3: ISO brightness of printed paper substrates

Table 3
Characteristics of coated (C) and uncoated (UC) papers made from 100% recycled pulp (C-R, UC-R) and with mechanical pulp (C-R/M, UC-R/M)

Characteristics	C-R/M	C-R	UC-M/R	UC-R/M	UC-R
Grammage, g/m^2	80.2	97.9	58.9	79.9	97.3
Bulk, m^3/g	0.935	0.950	1.222	1.377	1.088
Moisture content, %	2.8	2.6	3.6	2.8	3.1
Opacity, %	99.4	98.4	94.4	99.1	96.9
ISO brightness, %	81.5	85.8	85.7	85.8	84.0
Colour L*/a*/b*	88.7/0.64/-2.15	92.2/-0.22/-0.07	92.1/-0.01/1.34	89.7/1.11/-2.12	91.1/0.06/0.28
Roughness Bd, mL/min	60	73	764	1009	203
Roughness Ra, µm	2.08	3.36	5.71	5.48	3.6
Air permeability, mL/min	7	11	381	200	311
Water absorpton, g/m^2	58.5	62.3	/	14.8	20.9
Print penetration	9.8	11.5	23.4	23.7	22.6

Large differences between the coated and uncoated papers can be observed in the surface properties. Uncoated papers (samples UC-M/R, UC-R/M, UC-R), with high surface roughness, high air permeability and low water absorptiveness have given higher values of print penetration, comparatively with coated papers (samples C-R/M, C-R). Print penetration is a measure of the velocity of ink penetration into the printing substrate. The amount of ink absorbed by the surface of paper is given by the absorption of liquid in the surface recesses (roughness) and into the pores at paper surface. A higher value of print penetration means a higher penetration velocity, which is the result of higher roughness and higher porosity of the paper surface. Print penetration could be correlated also with the thickness of the printed ink layer. In the case of a higher penetration velocity, a higher amount of ink is transferred to the paper substrate in the process of screen printing. The thinnest layer of printed ink was obtained for the two paper substrates with a low print penetration, i.e. samples C-R/M and C-R, as seen in Figure 4. Uncoated paper made from 100% recycled pulp with the highest penetration velocity, followed closely by the other two uncoated papers, had a thicker printed ink layer compared to the prints made on uncoated papers. In the case of DuPont printing ink, a thicker layer resulted also in a higher sheet resistance, as seen from Figure 5.

The differences in printed ink layer thickness are also related to differences in surface roughness, micro- and macro-porosity of the paper substrates. The surface roughness (macro-roughness) was determined with an apparatus based on the contact air-leak principle, measuring the airflow across the surface. The micro-roughness was detected with a contact profilometer, measuring the movement of the stylus caused by the irregularities.[26] As seen from Table 3, both methods reveal a similar trend, the roughness of coated papers is much smaller than the roughness of uncoated paper substrates. A good correlation between the surface roughness, thickness of the printed ink layer and sheet resistance is remarked for the DuPont ink. The lowest value of sheet resistance was obtained for prints on coated papers, meaning that the silver particles in the ink, which are responsible for conductivity, are aligned and well connected on a smooth paper surface. The alignment of conductive particles also depends on the porosity of paper substrates. In the case of coated papers, a very low value of air permeability in relation to microporosity is connected to the absorptivity and penetration of low viscosity components from printing ink. Macroporosity refers to the surface pores, which are larger than 2 µm and are responsible for bonding solid ink parts on the surface. It is important that the macropores are not larger than the silver particles in the printing ink, because they have to stay on the surface in high concentration. The size of the conductive particles in the SunChemical printing ink was between 0.2 to 10 μm^2, with an average of 3.3 μm^2, and in the DuPont printing ink between 1 to 5 μm^2, with an average of 3.7 μm^2. The size of the pores on the surface of coated papers was also evaluated from the SEM micrographs. The measured pores are small, with an average size of 0.37 μm^2, meaning that the conductive particles of printing inks are much larger and stay on the surface. Besides pore size, surface uniformity is an important issue in obtaining a uniform ink layer with mutual well-connected conductive particles. The captured SEM micrographs of paper surface topography at 2500 magnification for coated papers and 300 magnification for uncoated papers are presented in Figure 6. The differences between samples were clearly visible. The visual estimation confirmed the higher smoothness and more uniform surface of the coated papers. As the conductive particles are non-uniform in size and shape, their uniform spreading on the surface of uncoated papers, which are non-homogenous materials with non-uniform surface, was more difficult. Regardless of the paper substrate used, the two stage drying allowed achieving a uniform ink layer and well-connected conductive particles in the ink layer, as seen in Figure 7.

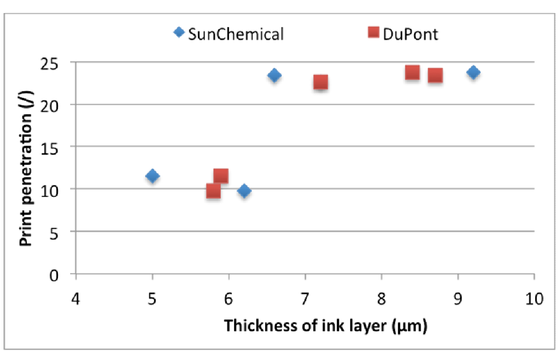


Figure 4: Relationship between print penetration and ink layer thickness

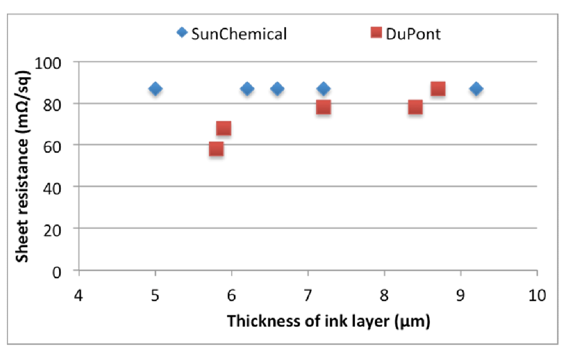
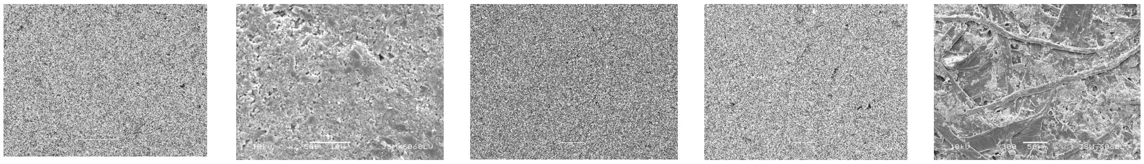
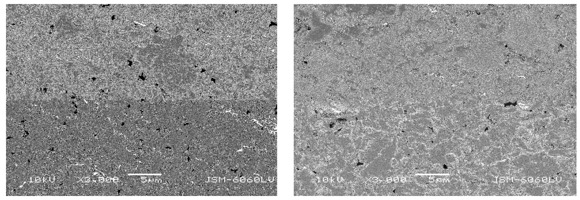


Figure 5: Relationship between sheet resistance and ink layer thickness



C-R/M C-R UC-M/R UC-R/M UC-R

Figure 6: SEM micrographs of paper substrates surface topography



SunChemical ink DuPont ink

Figure 7: SEM micrographs of printed ink layer

Table 4
Abrasion, print mottle and line gain of printed papers

Paper	Abrasion (%)		Print mottle (%)		Line gain (%)	
type	SunChemical	DuPont	SunChemical	DuPont	SunChemical	DuPont
C-R/M	2.9	5.2	2.3	4.3	8.0	8.0
C-R	1.5	7.2	2.2	4.1	4.8	4.8
UC-M/R	8.5	21.4	4.7	7.9	6.4	6.4
UC-R/M	17.0	34.5	5.0	8.7	4.8	6.4
UC-R	5.7	18.1	3.7	6.0	11.1	9.5

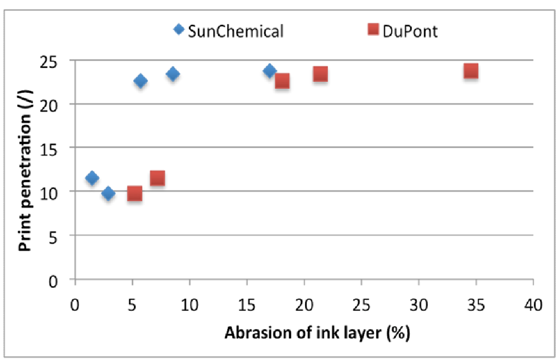


Figure 8: Print penetration in relation to abrasion of ink layer

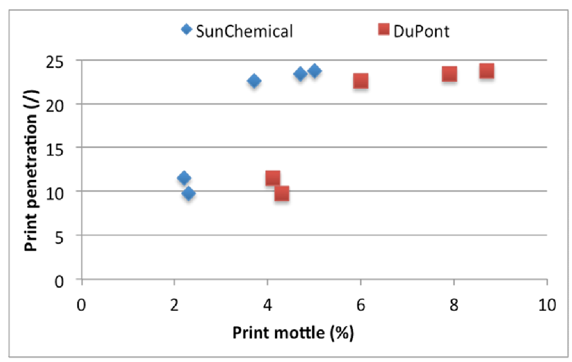


Figure 9: Print penetration in relation to print mottle

Stability and print quality of printed ink layer

The surface abrasion of the printed ink layer is a measure of the mechanical stability of the print. In printed electronics, high stability is needed to ensure conductivity for a longer period. If the stabilization of the printing ink occurs too quickly, then the low viscosity components of ink penetrate too fast into the paper substrate and the conductive particles remain unbounded on the surface and are easily removed from it. The abrasion is also high when the stabilization of printing ink is too slow, and the binder and conductive particles are not tightly bonded into the paper substrate. On uncoated paper substrates, the binder penetrates more quickly and deeply into the substrate, and the greater part of conductive particles remains unbounded on the surface, giving high abrasion. Moreover, the uncoated papers have high surface roughness, which also led to a high abrasion. In Figure 8, the correlation between print penetration and the abrasion of the printed ink layer is clearly seen. From Table 4, it is also evident that the printed ink layer made with DuPont ink has high abrasion, meaning that when rubbed, more particles remained on the receptor (unprinted paper). Comparatively with SunChemical ink, the DuPont ink has slower print penetration and is also less stable to abrasion.

The results of print mottle and line gain are presented in Table 4. The print mottle is a printing defect consisting in non-uniformity of the printed layer. It is the result of an uneven ink layer in connection with an irregular and uneven absorption of printing ink across the printing substrate. The higher roughness, porosity and print penetration of uncoated papers resulted also in the higher print mottle. The print penetration in relation to the print mottle is presented in Figure 9. The difference between the two printing inks is also obvious, the DuPont printing ink having a slightly higher non-uniformity.

Print quality does not concern only visual appearance, it is also important for the final antenna performance, which depends on print uniformity and line gain. If the antenna is printed onto a highly absorbent, porous substrate with a rough surface, the conductive silver particles in the ink cannot be well connected and the final conductivity is questionable. In our case, line gain was relatively low and independent of the printing substrate or printing ink used, whereas the print mottle was lower for the coated papers and the SunChemical printing ink, comparatively with uncoated papers and DuPont ink.

CONCLUSION

In this research, the suitability of recycled papers as substrates for printed electronics was studied. The conductive layer was screen printed using thermal drying silver conductive ink. The optimization of printed ink layer drying was achieved with a two stage drying process, which involved hot zone drying in a tunnel followed by a heat-press process. The surface properties of coated and uncoated papers were analysed in connection to the conductivity of the printed ink layer.

The results have shown that the coated papers have a lower value of print penetration because of lower roughness and porosity, comparatively with uncoated papers. This low value of print penetration results in a thin printed conductive ink layer and low sheet resistance. In the case of uncoated papers, the rough surface and high porosity lead to quick penetration of the ink, which results in low abrasion resistance of the printed ink layer and higher print non-uniformity.

It was found out that the selection of the conductive ink is very important and special consideration should be given to the size of conductive particles. For good conductivity and low sheet resistance, particles must be bound on the paper surface, which is more difficult to achieve on uncoated papers.

The comparison between the papers made only from recycled pulp and those made with the addition of mechanical pulp, did not reveal any significant differences in their functionality. Therefore, it was proved that, with the optimization of the drying process according to the printed ink used, recycled papers are suitable for the production of printed electronic structures, such as RFID antennas.

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