



Water Sorption and Surface Properties of Bathroom Tissues

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Bathroom tissues have characteristics that optimise their application to absorb water. Their surface topography enhances their elasticity and maximise their absorbance. These properties modify the surface heterogeneity. With the increasing awareness of the importance to protect the environment, manufacturing companies are developing more environmentally responsible blends of components to create their product. This study compares the surface chemistry of commercially available bathroom tissues and their water sorption uptakes.

Introduction

Bathroom tissues have characteristics that optimise their application to absorb water. Their surface topography enhances their elasticity and maximise their absorbance. These properties modify the surface heterogeneity. With the increasing awareness of the importance to protect the environment, manufacturing companies are developing more environmentally responsible blends of components to create their product. The main component of tissue paper is wood pulp fibres. To increase sustainability, the pulp can be blended with recycled paper or alternative fibres. Alternative fibres can include bamboo, sugar cane or agricultural waste. Blended composites increase tissue biodegradability and effects wettability, allowing the paper to break down quicker than its non-blended alternative.

The current Application Note is dedicated to the characterisation of four bathroom tissues: Commercial Cotton, UK Industrial, Asian Industrial and Recycled tissue, using iGC-SEA. This is a well-known technique for the characterisation of industrial and natural fibres. iGC-SEA provides the required sensitivity to study surface adsorption. The system can obtain measurements at infinite dilution where high energy sites of a heterogeneous surface interact with vapour molecules. This is useful to map out the heterogeneity of similar surfaces. Physicochemical parameters such as surface heterogeneity, wettability and adhesion with water, will give an insight to the differences between these tissue products.

Contact angle measurements are the most commonly used technique to calculate wettability and surface energy. Contact angle measurements employ the fundamentals of liquid dispersal to determine the surface





energy of a solid. However, these measurements are only representative of a specific part of the surface. It also requires the surface to be flat and homogeneous. Another problem of wettability method is the absorption of liquid in the bulk which would lead to an overestimation of the surface energy. For these reasons the techniques vary in reproducibility. The iGC-SEA technique overcomes these limitations by injecting a variety of different vapour phase probe molecules and has the added benefit in varying the temperature and relative humidity. The stronger the interaction between the probe and the surface, the longer the retention time and the greater the contribution to the surface energy. The high sensitivity of the technique allows measurements to be carried out at infinite dilution. At this low concentration range, probe molecules can interact with high energy surface sites reflecting subtle changes in energetic heterogeneity between samples. This makes the technique suitable for the investigation of batch-to-batch discrepancies, composite interactions and the adhesion with solids or with liquid like water.

Method

In the case of the iGC-SEA experiments small piece of paper sample was packed in a column with 30 cm length and a 3 mm ID. All iGC analyses were carried out using iGC Surface Energy Analyzer (SMS, Alperton, UK) and the data were analysed using advanced SEA Analysis Software. Samples were run at a series of surface coverages with alkanes and mono-polar probe molecules to determine the dispersive surface energy profile as well as the acid-base surface energy profile. For the analysis, the Dorris and Gray method was applied for the dispersive component [1]. The acid-base contribution was determined by first measuring the free energy of desorption based on the polarisation approach [2]. The specific surface energies were determined based on the van Oss methodology using the Della Volpe scale [3]. Each column was pre-conditioned for 2 hours at 30°C and 0% RH with helium carrier gas to remove any physisorbed water. All experiments were carried out at 30°C with 10sccm total flow rate of helium, using methane for dead volume corrections.

Dynamic Vapor Sorption (DVS) experiments were carried out using DVS Endeavor system (SMS, Allentown, USA). The instrument measures the uptake and loss of vapor gravimetrically using the SMS UltraBalance with a mass resolution of at least $\pm 0.1 \mu\text{g}$. The water sorption measurement was measured at 25°C using nitrogen carrier gas.



Results

Materials

Initial which is an industrial UK toilet tissue (2 ply), Super soft recycled toilet paper, Sainsbury's (2 ply) which is recycled tissues are made from 100% recycled paper and sustainably sourced. Classic Clean with a touch of cotton (Andrex-2 ply) and the Asian Industrial toilet paper (1 ply). All samples were commercially available.

BET Specific Surface Area

The BET Specific Surface Areas (BET-SSA) of all samples were determined with the physical adsorption of octane molecules by iGC-SEA. The results are presented in Table 1. The recycled super soft sample has the highest specific surface area, indicating higher surface roughness. It was expected based on the procedures applied during the recycling process and production of these types of products.

Table 1. Specific surface area determined from octane sorption isotherm used by Peak Max retention times

Sample	Sorption Constant	Monolayer Capacity [mMol/g]	BET Specific Surface Area [m ² /g]	R ²
Classic Clean	3.217	0.003	1.215	0.999
Initial UK	2.571	0.004	1.549	0.995
Japanese Industrial	3.009	0.003	1.251	0.999
Recycled Super Soft	3.010	0.004	1.698	0.999

Surface Energy Profiles

Dispersive (γ_s^D), acid-base (γ_{sab}) and total surface energy (γ_s^{AB}) profiles obtained directly from the iGC SEA for the samples. All profiles show that all samples are energetically heterogeneous – meaning the surface energy changes as a function of surface coverage. Based on the van Oss approach, the specific surface energies (γ_s^{AB}) of the samples were calculated using a pair of mono-functional acidic and basic probe molecules (dichloromethane - γ^+ : 124.58 mJ/m² and Ethyl acetate - γ^- : 475.67 mJ/m²) and the Della Volpe scale is employed. The combined plot of dispersive, specific (acid-base) and the total surface energy of the samples are presented in Figures 1a-c.

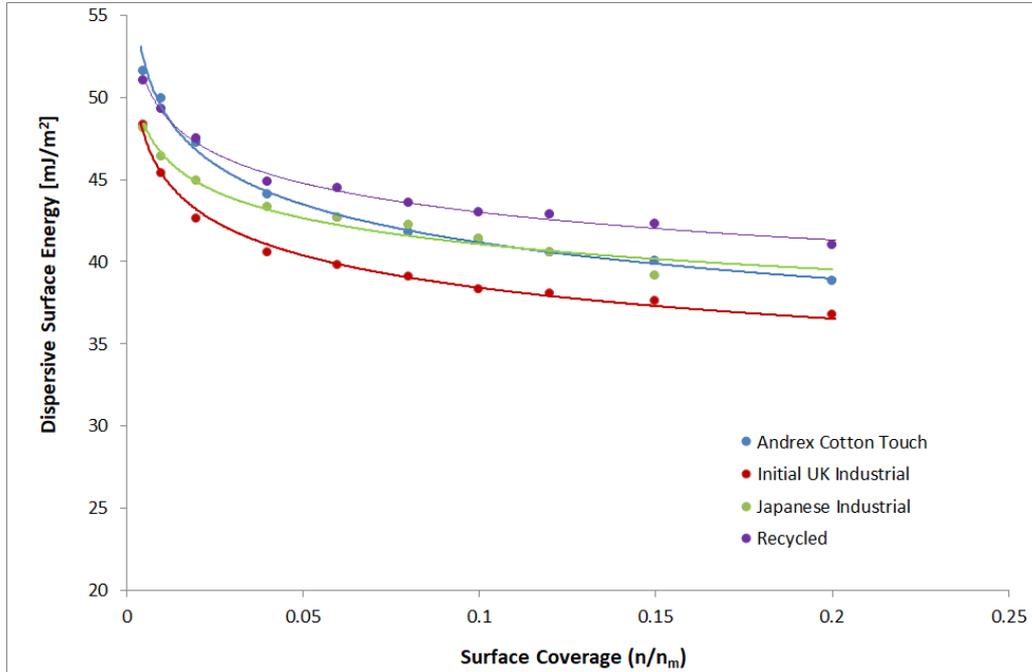


Figure 1a: Dispersive Surface Energy profile of the different paper samples

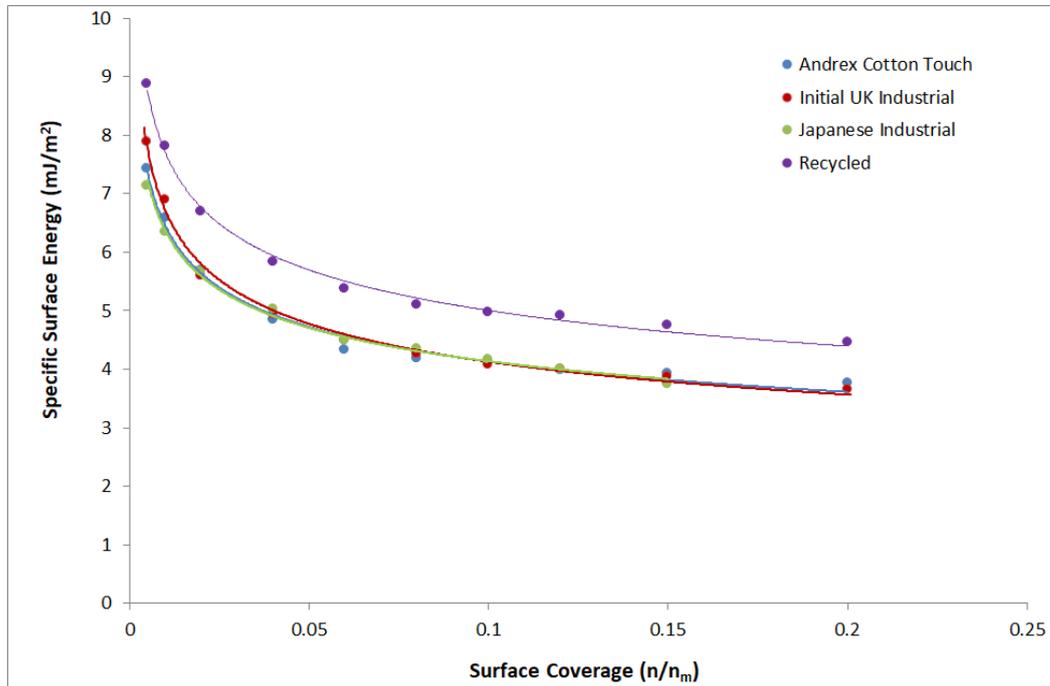


Figure 1b: Specific Surface Energy profile of the different paper samples

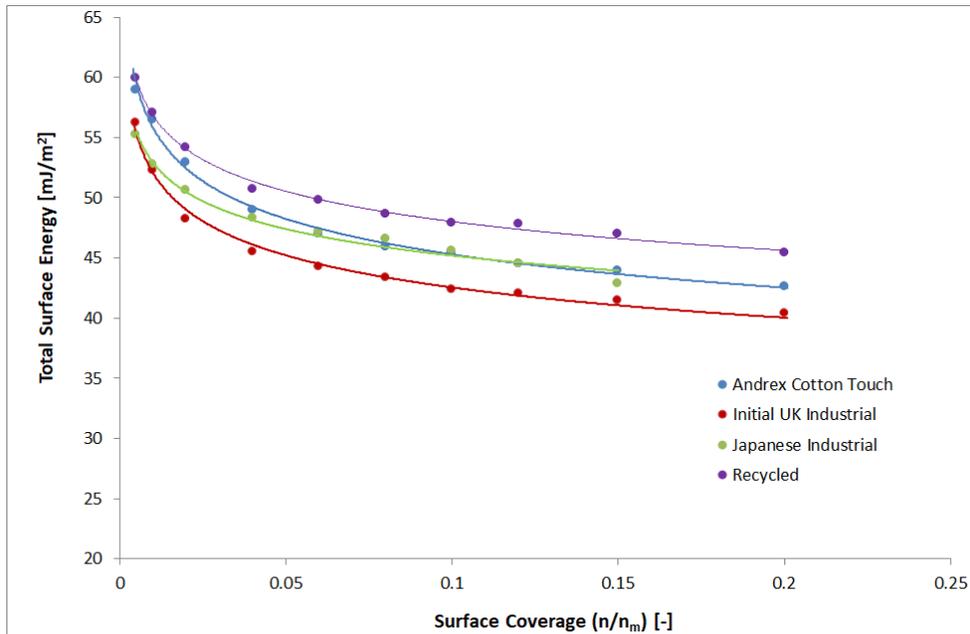


Figure 1c: Total Surface Energy of the different paper samples

During recycling the paper is treated, usually bleaching, in order to whiten it and to get aesthetically acceptable colour for its application and during production of recycled paper, the paper passes through certain stages where it is heated to high temperatures and so it is practically sterilised [4]. These treatments chemically modify the surface and creates polar functional groups on it. Due to this treatment the recycled paper has higher specific surface energy and more heterogenous specific surface energy profile. To further investigate the wetting behaviour of these materials, Dynamic Vapour Sorption (DVS) experiments were performed. Complete moisture sorption and desorption behaviour was investigated at 25 C. Figure 2 highlights the water sorption isotherms collected for each sample using DVS.

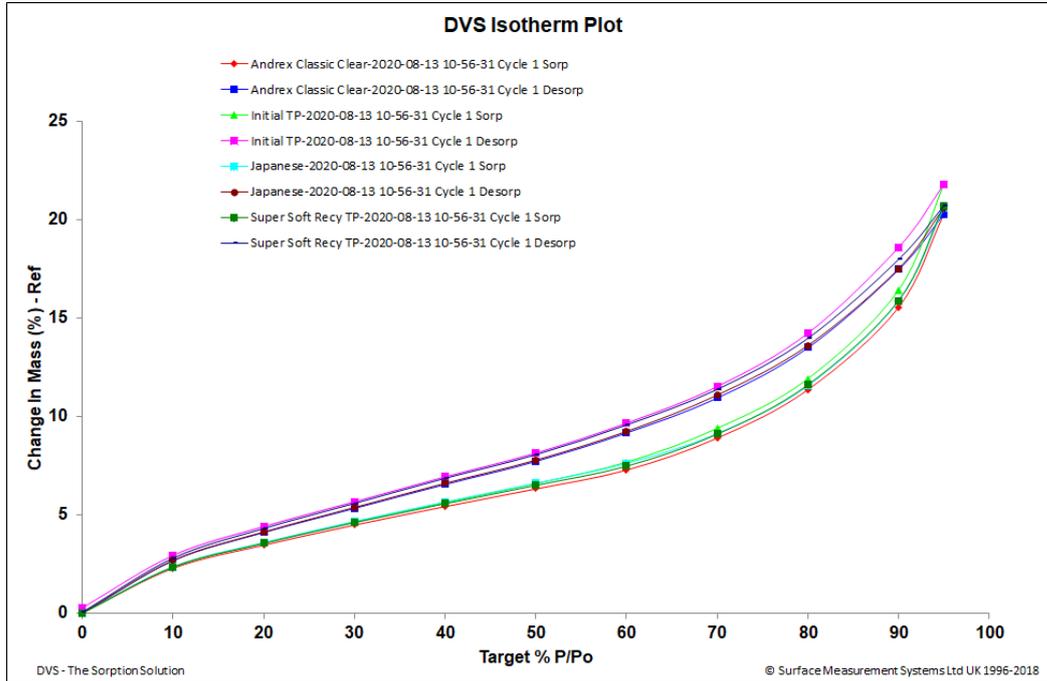


Figure 2: Overlap of the isotherm plots of water sorption of the paper samples collected on a DVS

As expected for this type of material, all the samples have particularly high and similar water uptake (over 20% mass change at 95% RH). This similarity in shape and height of the isotherm plot can be associated with the identical general structure of the samples, which are composed of cellulose. The difference in surface chemistry between the 4 samples, which were highlighted by the iGC-SEA data, does not affect the overall and equilibrium water sorption performance. Moreover, the data collected using DVS are mainly indicates the presence of bulk sorption, which is also re-enforced by the presence of a consistent hysteresis gap across the entire relative humidity range. iGC-SEA is more sensitive to differences in surface chemistry compared with DVS.

Conclusion

During iGC analysis the probe molecules only screen the surface and it is very sensitive to quantify of subtle differences in surface chemistry. While during DVS measurement the bulk become more dominant against the surface especially at this such a high uptake. iGC-SEA highlighted the differences between the different cellulose tissue samples and the data collected using DVS are mainly indicates the



presence of bulk sorption, which is also re-enforced by the presence of a consistent hysteresis gap. iGC-SEA is more sensitive to differences in surface chemistry compared with DVS.

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