Eco-friendliness of Inkjet Inks and a Novel Solution to Increase It

Anu Ilmonen, and Laura Kela; VTT Technical Research Centre of Finland; Espoo, Finland

Abstract

Eco-friendly inks have appeared also to digital printing area during last ten years, although every ink manufacture has slightly different determination for "eco-ink". One way to increase the eco-friendliness is to use bio-based ingredients instead of petroleum-based materials. The term "bio-based" describes a product that utilizes biological products, or renewable domestic agricultural or forestry materials. At the moment the bio-based materials of inkjet inks are mainly originating from soybean or other sources that are suitable also for food, which makes their use arguable. The water soluble wood hemicelluloses could offer a truly sustainable option for binder in water-based inks. Lately the paper industry has intensively started to study how to exploit the wood maximally in pulp making process and the isolation of hemicelluloses from pulp making waste waters has been recognized to be one of the promising ways to utilize the side streams.

Due to newness of eco-friendly inks, the terminology is still very fragmented. In this paper we consider the term eco-friendly ink and how it is used nowadays. The isolation methods of hemicelluloses and their properties and suitability for inkjet inks are discussed including some test results of hemicellulose-based ink.

Introduction

Ink suppliers have become more interested in developing eco-friendly (EF) inks due to increased customer interest. The area of EF inks is relatively new and therefore ink suppliers have very different justifications, when they use the term in their marketing. Often the justification comes from the comparison to the older similar product, for example some ingredient has been replaced or removed from the formula. Very rarely the ink manufacturer has proved the eco-friendliness by life cycle assessment (LCA).

The problem with EF inks is familiar from other sectors: consumers think "going green" is a good thing, but so far they have not been willing to pay any or very little premium for it [1]. Therefore the big steps in eco-friendliness of inks have commonly been enforced by changes in government regulation. Even at the moment many ink ingredients could be replaced by products coming from green sources (e.g. synthesized from bio-derived monomers), but it is too expensive as long as the oil price is low. From the cost and environmental impact point of view the best situation would be if the new EF ingredients would become as a by-product or waste product from existing biomaterial processes.

Eco-friendliness of inks

According to PIRA report [2], there are usually four areas considered when discussing EF inks:

- Reduction of volatile organic compounds (VOC's),
- Decreased energy usage,
- The use of renewable resources in ink formulation and
- Life cycle assessment (LCA)

This division is partially misleading, because the lifecycle analysis takes into account all the three previous areas, but also other factors influencing environmental impacts of the ink. Nevertheless, this division shows the areas ink suppliers are concentrating at the moment.

VOC's are both toxic for humans and they participate in climate change by producing photochemical oxidants. The VOC emissions of printing industry have decreased rapidly due to tightened legislation. In inkjet printing, the VOC's have been a problem in solvent ink printing, in which the drying occurs by evaporation of solvent. The new EF solvent inks have been sold as a mild-solvent, eco-solvent or bio-solvent inks. The difference of these terms is non-specific, but according to marketing materials, one interpretation could be that mild solvent inks contain less fast evaporating solvent, eco-solvent inks contain only mild solvents and in bio-solvent inks the solvents are plant-derived. Distinctly the terminology of EF solvent inks would need an industrial standard. In some contexts the UV inks have been brought out as eco-friendly option for solvent inks, although this presumption has been based only on the amounts of released VOC's at printing stage. To certify this presumption, LCA's of solvent and UV inks should be compared.

The energy usage refers in most cases to the power needed to dry the ink layer at the printing stage. This interpretation covers mainly UV inks and aqueous inks. UV inks need the UV lamps to be polymerized and often aqueous inks need to be dried by heat. On both sectors new more efficient drying equipment is available, like LED lamps and radio frequency drying [3, 4]. From ink chemistry point of view, the use of LED lamps in UV curing requires adding of photoinitiators responding at the same wavelength as LED lamps are radiating. Radio frequency drying does not need any changes in ink formula. However, when the energy usage is discussed, one should take into account also e.g. the energy needed in production of the ink ingredients as well as the ink itself and in waste management. For example the pigment grinding for inkjet purposes is very energy intensive stage.

The use of renewable resources in ink formulation is a hot topic in printing industry at the moment. This refers to replacing the petroleum-based chemicals by chemicals derivated from renewable resources. National Association of Printing Ink Manufacturers (NAPIM) launched the Bio Renewable Content (BRC) Index in 2009. This index certifies the amount of bio-renewable content in an ink formulation. Many ink manufacturers have adopted the index and utilize it in the marketing. At the moment the sources of bio-chemicals are often also suitable for food and this has aroused criticism against their industrial usage. Especially soy has been a popular food-plant origin for bio-derivated chemicals used in inks. When bio-based chemicals are discussed, another important point is the amount of modification and what kind of processes and chemicals has been used in it its production. The bio-based polymers can for example be modified by polymer synthesis with petroleum-based chemicals to enhance desired properties. This process step naturally increases the environmental impact of the product and the modification can also change biodegradability of the material.

LCA is a research method developed for assessing the potential environmental impacts of a particular product. It takes into account the product's entire life cycle beginning with the sourcing of raw materials and including every stage of the product's life cycle from production to use and disposal. It is much wider than for example carbon footprint calculation, which tells only the total amount of greenhouse gases produced directly and indirectly through entire life cycle of the product. The LCA is a useful tool for examining and evaluating the potential environmental impacts of products and for identifying areas where improvement is needed. On the other hand LCA requires laborious calculations and assessments and the ink manufacturer need to get properly acquainted with the ingredients used in inks. Then again it can be considered as an only usable standardized method, if all the ecological impacts are truly wanted to be found out.

Aqueous inkjet inks are considered to be an environmental choice, since the water is the main component of them. Binders are used in waterborne inkjet inks to give e.g. gloss, adhesion to substrate, resistance to chemicals and environment. The amount of binders can vary from almost zero to 10% depending on the application [5]. Most of the binders used in aqueous inkjet inks are petroleum-based and therefore changing the binder to bio-based option offers a good way to decrease the ecological impact of aqueous inkjet ink.

Binders from wood

The hemicelluloses are one of the most abundant biopolymers in the plant kingdom: they are widely available in the form of waste from forest industry, energy crops, agricultural residues, straw and grass. Since they are renewable and biodegradable, there has aroused an interest to refine them and use them as environmental friendly polymers in different applications.

The forest industry has adopted the biorefinery concept and therefore the isolation methods of wood hemicelluloses, as well as modification methods have been developed exceedingly during last years. This matches well with the ideal situation of green thinking because the materials come as a by-product or waste product from existing biomaterial processes. There is considerable potential of waste and by-products since the forest industry companies convert annually huge amounts of wood.

In softwoods like spruce and pine, the dominating hemicellulose is non-ionic O-acetyl-galactoglucomannan, often referred as AcGGM (Figure 1). The amount of AcGGM in softwood is about 10- 20% of wood material [6].

AcGGM can be isolated either by filtration from the process water of thermomechanical pulping (TMP) [7], by pressurized hot water technique from saw meal [8] or by steam explosion method from wood chips [9]. When the filtration method was used, the reported yield was 5 kg AcGGM /ton pulp with 95% purity. This method was also tested in mill-scale resulting in less pure AcGGM [10]. The extraction technique and the process parameters affect the yield, purity, average molar mass and removal rate of acetyl groups, which enhance the water solubility. However, it is

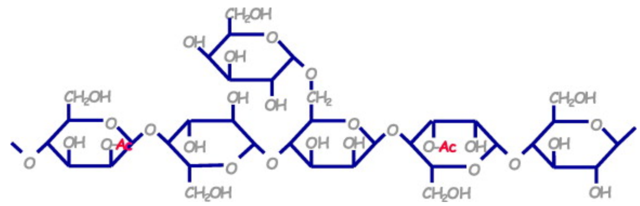

***Figure 1**. Structural features of Norway spruce water-soluble O-acetylgalactoglucomannans. [10]*

assumed that obtaining truly pure AcGGM without any aromatic structures or other polysaccharides attached to the backbone will be extremely difficult [10].

Whereas softwood is an excellent source of galactoglucomannan, the hardwoods, like birch and eucalyptus contain lot of O-acetyl-4-O-methyl-glucuronoxylan, often referred as glucuronoxylan, or simply xylan (Figure 2). For example birch contains circa 28 % and eucalyptus circa 20 % of xylan (structural substances in percent referred to extracted air-dry wood) [11].

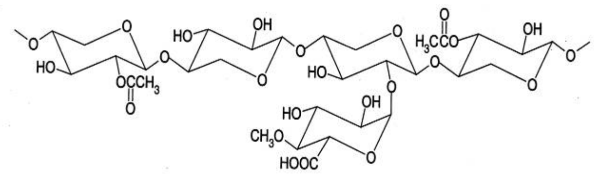

***Figure 2.** The structural features of O-acetyl-4-O-methyl-glucuronoxylan. [12].*

Several processes have been developed for isolation of hardwood xylan. For instance xylan can be extracted from bleached hardwood kraft pulp before papermaking [13] or it can be isolated from hardwood black liquor derived from cooking [14]. Also steam explosion method can be utilized for xylan extraction [9]. In most cases the acetyl groups are removed from the molecule during the extraction process resulting to poor water-solubility, but good alkaline solubility.

As pure components neither AcGGM or xylan suit perfectly for ink components, but both of them can be modified after isolation. The hydroxyl functional groups enable modifications, such as esterifications and etherifications [15]. For example the birch xylan has been etherified with benzyl chloride in aqueous alkali solution for other than ink purposes at VTT to attain hydrophobic and thermoplastic xylan derivative [15]. Another, so far unpublished xylan derivative has shown excellent film forming capability without external plasticizers and after drying it has formed a flexible, translucent and colorless film [16].

The development targets for both AcGGM and xylan are to improve film forming properties and increase water resistance after drying to meet better the demands set for aqueous ink binder. By applicable modifications these targets are possible.

The suitability of unmodified AcGGM for inkjet purposes was preliminarily tested with AcGGM extracted from the process water of thermomechanical pulping. The tested AcGGM had a very wide molar mass distribution and it contained impurities, including other polysaccharides and lignin. However the inks consisting 2-4% AcGGM provided relatively good jetting properties and adhesion. Then again the water resistance was poor.

Discussion

The encouraging results of preliminary test gave reason to believe that hemicelluloses can be utilized in aqueous inkjet inks as well as in other inks. Tight molar mass distribution, more advanced purification methods for raw hemicellulose and appropriate chemical modifications will be the important factors, when the hemicelluloses are considered for inkjet ink purposes. In addition to aqueous inks, we presume that proper modifications can be found also for UV inks. VTT has a long experience on hemicellulose chemistry and different modification methods. This gives a good starting point also for EF ink development. The best results would be obtained by continuing the development work together with ink manufacturer. Future work will cover e.g. the testing of different hemicellulose modifications, economic analysis and environmental evaluation of the concept.

Replacing conventional binders with bio-based binders is one step towards more ecological ink. The next big possible step could be replacing the pigments with bio-based products.

References

[1] M. Adams, Sustainable Packaging Trends: Consumer Perspectives and Product Opportunities. Datamonitor Report. (2009).

[2] L. Casatelli, The Future of Environmentally Friendly Inks, Market Forecasts to 2014. (Pira International Ltd, Leatherhead, 2009).

[3] A. Lockwood, The Practical Relevance of Solid State UV LED's for the Curing of Inks in Contemporary Ink Jet Applications, Proc. NIP22, pg. 54. (2006)

[4] A. Saad, Environmental pollution reduction by using VOC-free water-based gravure inks and drying them with a new drying system based on dielectric heating, PhD thesis (2007)

[5] C. Schmid, Formulation and Properties of Waterborne Inkjet Inks, In: S. Magdassi (ed.), The Chemistry of Inkjet Inks (World Scientific Publishing Co.Pte. Ltd., 2009), pg. 123-140

[6] S. Willför, A. Sundberg, J. Hemming, B. Holmbom, "Polysaccharides in some industrially important softwood species," Wood Sci Technol. 39, 245 (2005).

[7] S. Willfor, P. Rehn, A. Sundberg, K. Sundberg, B. Holmbom, "Recovery of water-soluble acetylgalactoglucomannans from mechanical pulp of spruce," Tappi Journal 2, 27 (2003).

[8] K. Leppänen, P. Spetz, A. Pranovich, K. Hartonen, V. Kitunen, H. Ilvesniemi, "Pressurized hot water extraction of Norway spruce hemicelluloses using a flow-through system," Wood Sci Technol., 45 223 (2011).

[9] K. Jedvert, A. Saltberg, M. Lindström, H. Theliander, Extraction of Hemicelluloses after Chemical Pretreatment Combined with Mild Steam Explosion, Proc. 16th ISWFPC, pg. 869. (2011)

[10] S. Willför, M. Tenkanen, K. Sundberg, B. Holmbom, "Spruce-derived mannans – A potential raw material for hydrocolloids and novel advanced natural materials," Carbohydrate Polymers, 72, 197 (2007)

[11] R. Patt, O. Kordsachia, J. Fehr. "European hardwoods versus Eucalyptus globulus as a raw material," Wood Sci Technol. 40, 39 (2006)

[12] T. Timell, "Recent progress in the Chemistry of Wood Hemicelluloses," Wood Sci. and Technol., 1, 45 (1967).

[13] B. Krogerus, A. Fuhrmann, Isolation of Xylan and Use as Wet-end and Binder Chemical, Proc. 15th ISWFPC, (2009).

[14] O. Dahlman, A. Jensen, D. Tormund, J. Östlund. Processing xylan from hardwood spent cooking liquors, Proc. NWBC 2008, pg. 114. (2008).

[15] R. Talja, J. Shan, M. Vähä-Nissi, A. King, I. Kilpeläinen, K. Poppius-Levlin, A New Birch Xylan Derivative by Aqueous Benzylation, Proc. 11th EWLP, pg. 403. (2010).

[16] R. Talja, K. Poppius-Levlin, Xylan From Wood Biorefinery – A Novel Approach, FlexPakRenew Workshop, 2011. From: http://www.flexpakrenew.eu/docs/filesProject/1/C1A5127A-188B-310B-B8EB8F5C212F9D42.pdf

Author Biography

Anu Ilmonen is a Senior Scientist in Digital Printing and Fabrication group at VTT, Espoo, Finland. She received her M.Sc. degree in graphic arts from Helsinki University of Technology in 2005. Since graduation she has worked at KCL and VTT in several research projects concerning digital and conventional printing, focusing on ink chemistry and interactions between ink and paper.