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Novel use of biomass derived alkyl-xylosides in wetting agent for paper impregnation suitable for the wood-based industry

E. Papadopoulou · A. Hatjiissaak · B. Estrine · S. Marinkovic

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Abstract Today, papers impregnated with thermosetting resins like urea-formaldehyde and/or melamine-formaldehyde are broadly used as covers for wood-based panels like particleboards (PB) and medium density fibreboards (MDF), because they offer flexibility in surface decoration, mechanical endorsement and protection from emissions of Volatile Organic Compounds (VOCs) of the panel. The resin is enhanced with various additives, like hardeners, de-foaming agents, surfactants, wetting agents etc. that are traditionally derived from petroleum. In this study, CHIMAR Hellas tested for the first time biomass-derived surfactants, produced by ARD company, in resin mixtures suitable for paper impregnation. From a chemical point of view, these natural surfactants are alkyl xylosides and particularly amyl and butyl xylosides and proved to have performance equivalent to the petrochemical surfactants conventionally used in this industrial field. Although such surfactants have already been used successfully in other industrial fields, they had never been tested before in paper impregnation processes.

Neuartige Verwendung von aus Biomasse hergestellten Alkylxylosiden für Benetzungsmittel zur Papierimprägnierung in der Holzwerkstoffindustrie

Zusammenfassung Melaminharz- und/oder Harnstoffharz-imprägnierte Papiere werden heute vielfach zur Beschichtung von Holzwerkstoffen wie Span- oder Faserplatten eingesetzt. Sie bieten eine große Auswahl an Dekorpapieren, verbessern bestimmte Eigenschaften und tragen zur Reduzierung der VOC-Emissionen der beschichteten Platten bei.

Den duroplastischen Harzen werden zur Optimierung des Imprägnierprozesses diverse Additive wie Härter, Antischaummittel, Benetzungs- und Trennmittel etc. zugesetzt, die traditionell auf Ölbasis hergestellt werden. In dieser Forschungsarbeit hat CHIMAR Hellas zum ersten Mal aus Biomasse hergestellte grenzflächenaktive Substanzen der Firma ARD in Netzmittelformulierungen zur Papierimprägnierung eingesetzt. Diese Substanzen sind im Allgemeinen Alkylxyloside und insbesondere Amyl- und Butylxyloside, und ihre Wirkung entspricht derjenigen von ölbasierten Produkten. Sie werden schon seit Jahren erfolgreich in anderen industriellen Anwendungen eingesetzt. Ihre mögliche Verwendung zur Melaminpapierimprägnierung wurde bisher jedoch nicht untersucht.

1 Introduction

Wood-based panels like particleboard (PB), medium density fibreboard (MDF), plywood (PW), etc. find many applications in our everyday life products, like furniture, flooring, wall panelling and construction. However, the largest part of the particleboard and MDF production is consumed by the furniture industry that is by far the biggest sub-sector of the wood-working industries (EPF report 2007–2008). These panels are used neat or covered. The covering offers not only flexibility to surface decorative designs but also characteristic properties like smoothness and glazing (achieved with cost saving method), improved mechanical strength without significant additional weight (Norvydas and Minelga 2006), enhanced water repellence and protection of VOCs emissions. Covering materials may be enamel paints, veneers,

E. Papadopoulou (✉) · A. Hatjiissaak
CHIMAR Hellas S.A., Sofouli 88, 55131, Kalamaria, Thessaloniki, Greece
e-mail: papadopoulou@ari.gr

B. Estrine · S. Marinkovic
ARD (Agro-industrie Recherches et Développements), Route de Bazancourt, 51110 Pomacle, France

laminating plastics and impregnated paper while the manufacturing of most of them frequently requires sophisticated processes.

Particularly in the case of impregnated papers that are used as self-bonded overlays, the manufacturing process consists of three steps. Initially a coloured or pre-printed paper of 60–120 g/m^2 weight is impregnated with a resin mixture. Next, the impregnated paper is dried in an oven where the resin is partially cured. Last, it is the lamination step where the impregnated paper is pressed under heat on a substrate of PB or MDF. At this final step of the process, the resin used for the impregnation cures completely. Typically, the resin mixture used for paper impregnation consists of a thermosetting urea-formaldehyde (UF) or/and melamine–formaldehyde (MF) resin and some additives, like fillers, hardeners, de-foaming agents, surfactants, wetting and glossy agents. These additives are necessary as to achieve a quick and defect free wetting of the paper and a coating surface with specific properties, like shelf life, non adhesion within the touching layers of the coated material during their storage and non sticking to the platens of the pressing machine at the step of the lamination. It is not easy to successfully prepare such a resin mixture because physical and chemical synergy among its ingredients is requested while the final product has to comply with specific properties. In particular, the additives used for the preparation of an impregnation mixture have to be of low colour or even colourless, environmentally friendly, able to reduce the foaming and promote wetting of the paper. Proper and quick wetting of the paper is considered likely to give surfaces without defects such as crawling, cratering, pinholing and orange peel, and shorten the impregnation time thus making the entire process more profitable for the manufacturers in this industrial field.

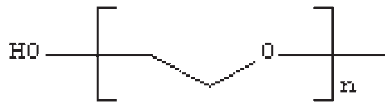
Nowadays, although there are many materials available on the market that are able to respond well to the needs of the paper impregnation industry, all of them are derived from petroleum.

In this study, biomass derived surfactants were tested for the first time in paper impregnation mixtures and a natural-based wetting agent was successfully developed for the same industrial field by CHIMAR Hellas, a Greek innovative research centre serving the wood-based industry.

2 Experimental part

2.1 General

The biomass-derived surfactants tested by CHIMAR Hellas were alkyl pentosides that belong to the category of non-ionic surfactants and are known to have excellent wetting and penetration properties. Such materials, although find



2005), they had never been used before in formulations for the wood-based industry.

The corresponding petrochemical non-ionic surfactants that are traditionally used in the paper impregnation industrial field are usually ethoxylated or prop-oxylated fatty alcohols or acids e.g. polyoxyethylene alcohols (Fig. 1) (Edwards 1998).

In this study, CHIMAR Hellas initially evaluated the performance of alkyl pentosides in blends consisting of a resin and the natural surfactants at ratio 100/03 (resin/surfactant). The resin was a urea-formaldehyde (UF) syrup prepared according to the know-how of CHIMAR Hellas.

Furthermore, CHIMAR Hellas tested the performance of these biomass-derived surfactants in the formulation of a proprietary wetting agent, with the scope of optimisation relative to foaming and wetting speed.

In total, five wetting agents (WA) were tested, whereby two of them were entirely petrochemical products available on the market. Namely, the commercially available WA 0397 and the WA1703 traded by CHIMAR. The other three wetting agents were prepared based on the recipe of the WA1703 of CHIMAR and by replacing petrochemical ingredients with each of the following biomass derived surfactants:

- Commercial available amyl-xyloside with code name: Radia Easy Surf 6505, provided by WHEATOLEO company, France.
- Experimental amyl xyloside with code name: ML09-008, provided by ARD company, France
- Experimental butyl xyloside, with code name: ML09-016, provided by ARD company, France.

All of the above alkyl pentosides were derived from fusel oil (fatal by-product of ethanol fermentation) and agricultural by-products.

Especially the experimental surfactants produced by ARD company were prepared during the EU Project Biosynergy starting from sugar sources derived from wheat straw (Fig. 2). Alkyl-xylosides with code name ML 09-008 and ML 09-016 were prepared following an optimised process adapted from the literature (Marinkovic et al. 2008).

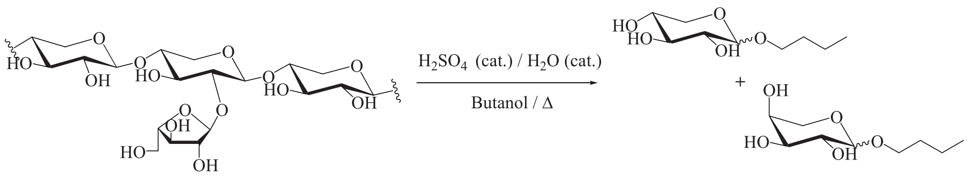


Fig. 2 Process for preparation of alkyl-xylosides from lignocellulosic sugars
Abb. 2 Verfahren zur Herstellung von Alkylxylosiden aus Lignocellulose-Zucker

2.2 Testing of resin blends

The resin blends prepared with the UF syrup and each of the natural-based surfactants were tested for their wetting efficiency via the following tests of surface tension and contact angle.

2.2.1 Surface tension

Surface tension measurements were carried out for the resin blends and the pure UF syrup, for comparison reasons. The surface tension measurements were carried out with a KRÜSS Processor tensiometer (K100) following the Wilhelmy method (KSV, Finland) where a platinum plate sensor in a jacketed cell was used. The temperature was controlled using a Julabo thermocontroler with an accuracy of $25 \pm 0.5°C$. The resin blends were stirred and allowed to stand for equilibrium at the set temperature before measuring the surface tension. The surface tension of the blends was obtained as a mean value of ten measurements.

2.2.2 Contact angle

Contact angle measurements were carried out to compare the surface tension of the various resin blends and the pure UF syrup. The measurements were based on goniometry (optical tensiometry), which involves the observation of a sessile drop of test liquid on a solid substrate. In this study, these measurements were carried out with the KRÜSS G10 contact angle measuring system (optical tensiometer), using glass as substrate. The basic elements of this contact angle meter included a light source, sample stage and lens. A drop of the tested liquid was placed on the glass and the contact angle was assessed directly by measuring the angle formed between the glassy substrate and the tangent to the drop surface.

2.3 Testing of wetting agents

Both the petrochemical and natural–based wetting agents were subjected to tests as to compare their effectiveness in wetting and foaming creation/persistence. These tests were:

2.3.1 Critical micelle concentration and surface tension

The surface tension measurements were carried out with a KRÜSS Processor tensiometer (K100) following the Wilhelmy method (KSV, Finland) where a platinum plate sensor in a jacketed cell was used. The temperature was controlled using a Julabo thermocontroler with an accuracy of $25 \pm 0.5°C$. The surfactant solutions were stirred and allowed to stand for equilibrium at the set temperature before measuring the surface tension. The surface tension of the solutions was obtained as a mean value of ten measurements.

The surfactant concentration at which micellization starts is known as the critical micelle concentration (CMC). This value is one of the most important properties of surfactant solutions, because the micelle formation affects both the surface or interfacial tension reduction and the properties of the surfactants such as the solubilization and detergency. The critical micelle concentration was graphically determined at the break of the curve of the surface tension measured versus the concentration of surfactants in solution (Hiemenz and Rajagopalan 1997).

The efficiency of a surfactant in reducing surface tension was also measured by CMC 20 value, which is the surfactant concentration necessary to reduce the surface tension by $20\ mN\ m^{-1}$ (Rosen 2004).

The effectiveness of the surfactant was also measured by the surface tension at the CMC.

2.3.2 Wetting properties

The ability of a surfactant to wet rapidly is a key performance property in many applications. The Draves Wetting test (Draves and Clarkson 1931) is a widely regarded laboratory procedure for ranking the relative wetting efficiencies of surfactants. This test is a timed determination for the wetting of a cotton skein by dilute surfactant solutions, where short wetting times are indicative of excellent wetting efficiencies. A 0.1% active solution in deionized water of each composition was tested using standard cotton disc from Empa Materials.

2.3.3 Foaming and colour performance

The coating resin mixture is usually colourless or white and thus any additives used have not to yield colour changes. More, the even impregnation of paper necessitates the use of low-foaming resin systems.

In this study, the foaming properties of the wetting agent containing Radia Easy Surf 6505 was evaluated against the

Table 1 Surface tension measurements
Tab. 1 Messungen der Oberflächenspannung

Material	Surface tension, mN/m	Temperature, °C
UF syrup	62.29	24.5
UF syrup with Radia easy surf 6505	51.112	24.5
UF syrup with Amyl xyloside ML09-008	51.505	24.5
UF syrup with Butyl xyloside ML09-016	59.911	24.5

Table 2 Contact angle measurements
Tab. 2 Kontaktwinkelmessungen

Resin mixture	Contact angle
UF syrup	33
UF syrup with Radia easy surf 6505	22
UF syrup with Amyl xyloside ML09-008	23
UF syrup with Butyl xyloside ML09-016	24

Table 3 Surface properties of the wetting agent compositions
Tab. 3 Oberflächeneigenschaften der verschiedenen Benetzungsmittel

Reference	CMC ($mg\,l^{-1}$)	CMC 20 ($mg\,l^{-1}$)	γ_{cmc} ($mN\,m^{-1}$)	Wetting time (s)
Wetting agent 397	28	5	30.6	98
Wetting agent CHIMAR	80	3	30.9	38
WA CHIMAR with Radia 6505	230	4	29.2	82
WA CHIMAR with butyl xyloside ML09-016	194	4	29.3	82
WA CHIMAR with amyl xyloside ML09-008	206	4	29.4	95

two petrochemical wetting agents (WA1703 of Chimar and WA0397) following an adapted test from Ross Miles method (AFNOR NFT). The mixtures were prepared at room temperature (25°C). Rigorous stirring was applied and the foam generation as well as its stability after 3 minutes was measured.

3 Results and discussion

3.1 Results of the measurements of the resin blends

The following Tables 1 and 2 present the results of testing the resin blends with each of the biomass-derived alkyl xylosides as well as the pure UF syrup, for comparison reasons.

From the results of the surface tension measurements it is obvious that all natural surfactants reduce the surface tension of the UF syrup. The highest reduction is observed when amyl xylosides are used with the mixture prepared with the commercial surfactant Radia Easy Surf 6505. The lower surface tension is an indication of faster and smooth wetting of the paper. This performance is confirmed by the contact angle measurements where the resin mixture with Radia Easy Surf 6505 promotes significantly the spreading of the UF syrup improving thus its wetting power.

3.2 Results of the measurements of the wetting agents

The following Tables 3 and 4 as well as Figs. 3, 4 and 5 present the results of the tests the wetting agents of this study were subjected to as to evaluate their performance in colour and transparency, foaming and wetting efficiency.

Within the formulae studied, the WA 0397 possesses the lowest CMC with 28 $mg\,l^{-1}$. It means that this formula remains efficient at lower concentration than the other wetting agents. Nevertheless, when CMC 20 is considered, the performance variations are reduced and all formulae seem equally efficient (values between 3 and 5 $mg\,l^{-1}$). In fact, when the concentration required to lower the surface tension of 20 $mN\,m^{-1}$ is considered all the tested solutions seem comparable as the differences between C20 are not significant when method accuracy is considered.

In the case of surface tension measurements, the solutions containing xylose based surfactants show a lower γ_{cmc} with a difference of about 1.2–1.7 $mN\,m^{-1}$ that means slightly higher effectiveness in wetting.

Concerning the wetting power, at the concentration tested (0.1%wt.), the best solution is the WA1707 of CHIMAR Hellas (38 s) followed by the wetting agents with Radia Easy Surf 6505 and butyl xyloside (82 s), while the wetting agents with the experimental amyl xyloside (95 s) and the petrochemical WA0397 (98 s) are last. These latter two formulae

Table 4 Colour and foaming properties of the wetting agents compositions
Tab. 4 Farbe und Schäumverhalten der verschiedenen Benetzungsmittel

Wetting agents	WA0397	WA 1703 of CHIMAR with Radia Easy Surf 6505	WA 1703 of CHIMAR
Code name	WA 1	WA 2	WA 3
Colour [intension of yellowish colour: low (1) → high (4)]	1	2	No colour
Transparency	yes	yes	yes
Foam generation/stability: low (1) → (4)	2/2	3/3	4/4

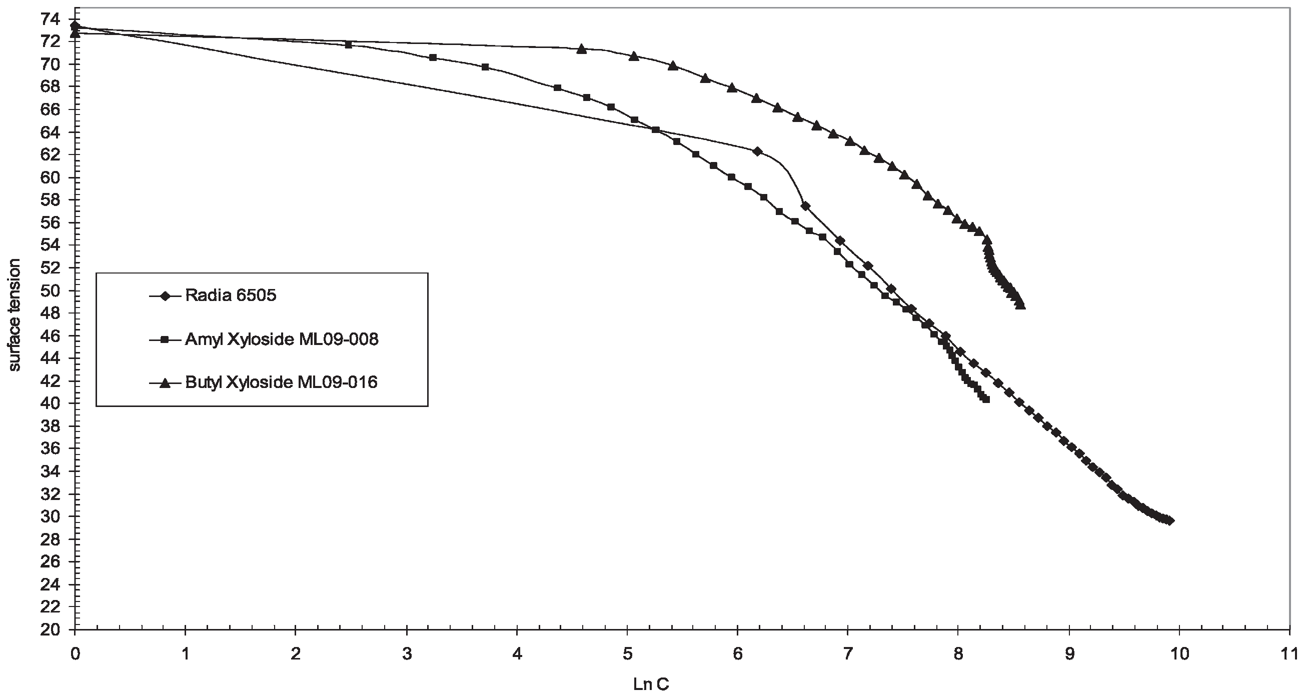


Fig. 3 Surface properties of biomass derived surfactants
Abb. 3 Oberflächenspannung der aus Biomasse hergestellten grenzflächenaktiven Substanzen

are the less efficient ones in terms of wetting. The differences in the wetting power between the wetting agents with amyl xylosides namely the traded product Radia Easy Surf 6505 and the experimental amyl-xyloside may be attributed to impurities of electrolytes produced during the bleaching process (Marinkovic et al. 2008). The presence of electrolyte is known to affect greatly the wetting performance of non ionic surfactants (Rosen 2004).

The WA1703 of CHIMAR Hellas is the solution with the highest clarity since it is transparent and of no colour. Next comes the WA0397 and last the modification of WA1703 with Radia Easy Surf 6505. Nevertheless, it is obvious that this surfactant improves significantly the foaming performance of the petrochemical wetting agent WA1703. The lower foaming performance is attributed to the presence of multi-hydrophilic groups causing a considerable increase in area per molecule and creating less cohesive force on the surface (Wang and Chen 2006).

4 Conclusion

The biomass-derived alkyl xylosides proved to be effective surfactants in UF syrups, a type of resin suitable for paper impregnation, as they testified to be able to decrease the surface tension and contact angle of the neat resin.

Moreover, these natural non-ionic surfactants were tested as components of a petrochemical wetting agent proprietary of CHIMAR Hellas and proved to be able to improve its performance relative to surface tension and foaming. Further, these natural-based wetting agents demonstrated reduced wetting time when compared with another entirely

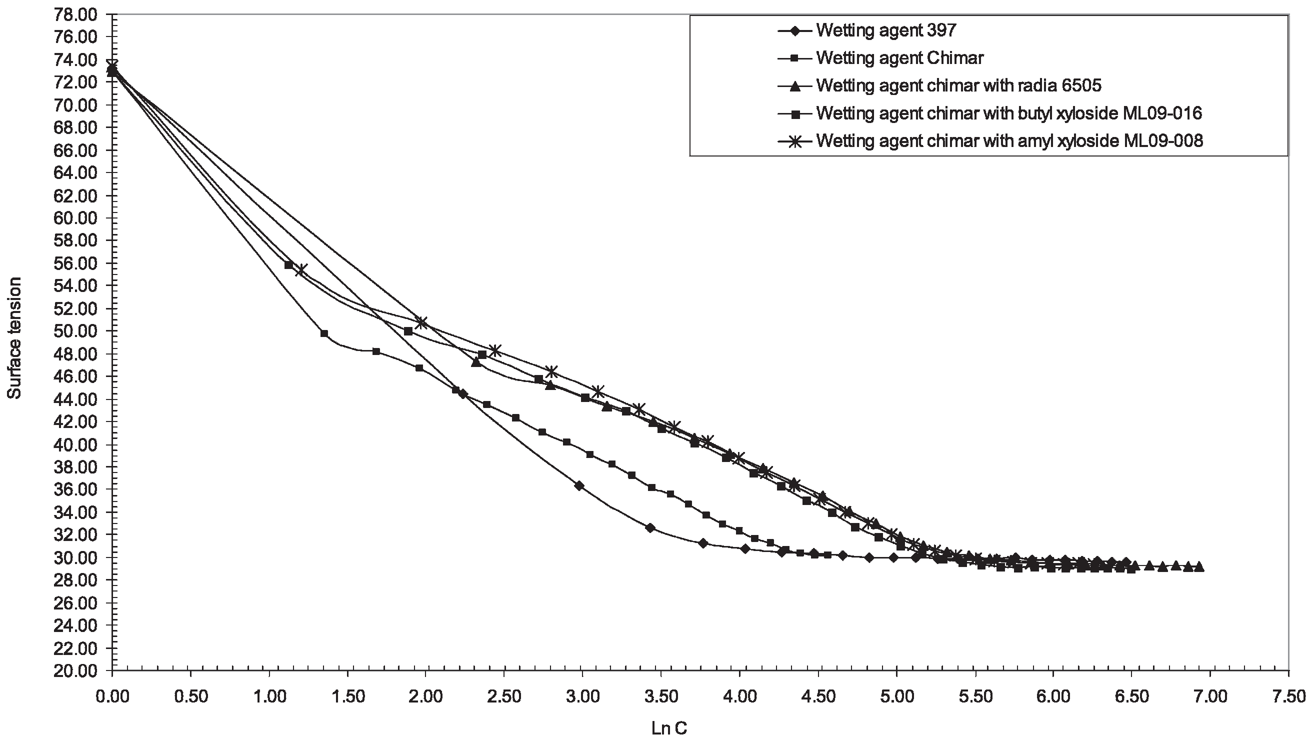


Fig. 4 Surface properties of wetting agents
Abb. 4 Oberflächenspannung der Benetzungsmittel

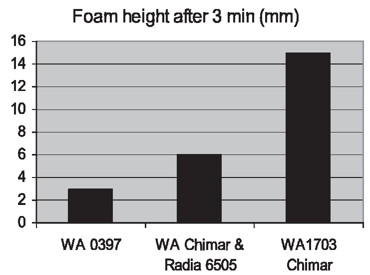


Fig. 5 Foam performance of wetting agents 3 minutes after their preparation
Abb. 5 Schäumverhalten der Benetzungsmittel 3 Minuten nach dem Einbringen

petrochemical wetting agent available on the market. Although the new natural-based wetting agents have a yellowish colour which is a disadvantage compared to the colorless petrochemical products, this property is not that significant considering the improvements they render to the foaming reduction and wetting efficiency, because they are added in very few quantity in the resin mixture and hence no notably colour alterations are observed overall.

Among the various alkyl xylosides tested in this study, the amyl xyloside with trade name Radia Easy Surf 6505 performed best both in resin blends and wetting agent formulations.

This development in the synthesis of wetting agents for the paper impregnation industry affords a reduction in the use of fossil fuel derived materials and allows the synthesis of products that are friendlier to the environment and less toxic for the human health, while they are not inferior in performance compared to their petrochemical counterparts.

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