Xiang, Wenchao; Preisig, Natalie; Laine, Christiane; Hjelt, Tuomo; Tardy, Blaise L.; Stubenrauch, Cosima; Rojas, Orlando J.

**Surface Activity and Foaming Capacity of Aggregates Formed between an Anionic Surfactant and Non-Cellulosics Leached from Wood Fibers**

*Published in:*
Biomacromolecules

*DOI:*
10.1021/acs.biomac.9b00243

*Published: 10/06/2019*

*Document Version*
Publisher's PDF, also known as Version of record

*Published under the following license:*
CC BY-NC-ND

*Please cite the original version:*

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
ABSTRACT: This study relates to the release of non-cellulosic components (cell wall heteropolysaccharides, lignin, and extractives) from swollen wood fibers in the presence of an anionic surfactant (sodium dodecyl sulfate, SDS) at submicellar concentrations. Highly surface-active aggregates form between SDS and the leached, non-cellulosic components, which otherwise do not occur in the presence of cationic or nonionic surfactants. The in situ and efficient generation of liquid foams in the presence of the leached species is demonstrated. The foaming capacity and foam stability, as well as the foam’s structure, are determined as a function of the composition of the aqueous suspension. The results indicate that naturally occurring components bound to wood fibers are extractable solely with aqueous solutions of the anionic surfactant. Moreover, they can form surface-active aggregates that have a high foaming capacity. The results further our understanding of residual cell wall components and their role in the generation of foams.

INTRODUCTION

The unique properties of foams fulfill a wide range of purposes in nature and industry, for example, for the protection of embryos, the dispersion of fibers in nonwoven manufacture, the assembly of functional materials via templating, the delivery of drugs, and the formulation of household and food products. In such applications, it is of critical importance to understand foam generation and stabilization. Air bubble generation in liquid media requires an energy input, which depends on the surface tension, γ, and the surface area of the generated air bubbles, ΔA. For the generation and stabilization of foams, surfactants are often used because they lower the surface tension thus facilitating the incorporation of bubbles. (Bio)polymers, including proteins and particles, are also used for foam generation and stabilization. Relevant for this study is the use of wood fibers and their main constituents for foam generation and stabilization. The main constituents in wood fibers refer to cellulose, which forms the structure of the cell walls and non-cellulosic components, mainly heteropolysaccharides (often termed as hemicelluloses), extractives, and lignin. These components have been incorporated in value-added materials including lightweight structures. Moreover, cellulotic nanomaterials have been proposed for the stabilization of aqueous foams.

Using the components of the fibers’ cell walls requires their isolation or fractionation with high energy and chemical costs. However, a different approach can be considered, namely, the treatment of fibers with surface-active agents, polymers, acid or base solutions by impregnation and diffusion. Therein, the interactions between non-cellulosics and cellulose depend on hydrogen bonding and hydrophobic effects. Typically, in neutral or weakly acidic conditions, non-cellulosics are negatively charged due to the presence of glucuronic acid and carbohydrate groups. Thus, surfactants (anionic, cationic, or nonionic) can alter their net charge, surface chemistry, and colloidal stability. Most studies in this area deal with the interaction between negatively charged fibers and cationic or nonionic surfactants. However, the interactions between
negatively charged fibers and anionic surfactants have been studied only to a limited extent. Wood impregnation with microemulsions containing sodium dodecyl sulfate (SDS) was found to improve fiber wetting and the capillary penetration of SDS by adsorption onto hydrophilic sites. It is thus reasonable to ask if an anionic surfactant enhances wood fiber accessibility, for example, by swelling and loosening its cell walls and if its interactions with non-cellulosic components lead to colloidal stable species or aggregates.

To address these questions, bleached pine fibers were used, which mainly consist of cellulose and small amounts of non-cellulosic components. The stability of the fibers suspended in water and in SDS solutions was studied, and the changes of the fiber’s chemical composition were determined. The interaction between SDS and the non-cellulosics was examined by surface tension measurements using MQ and SDS (0.7 mM) solution. Mixing for 1 min, the suspension was filtered through a capillary of 0.13 mm radius. SDS was used at three different concentrations, namely, 0.083 cmc_{SDS}, 1 cmc_{SDS}, and 8.3 cmc_{SDS}. The y_{dynamic} measurements were performed at 21.8 °C for 15–50 min until reaching a surface tension plateau as a function of bubble lifetime. The experimental time (15–50 min) is the time spent by the gas sensor in the tensiometer (a) to change gas flow, which is for generating bubbles with different lifetimes and (b) to establish the change interval between different gas flows. The bubble lifetime is the time interval from bubble generation to its hemispherical size. The surface tension was plotted as a function of bubble lifetime with 1 s resolution in this study. For comparison, the dynamic surface tension of MQ, Leachate_{BKP} and pure SDS solutions at different concentrations was also recorded. The y_{dynamic} of the leachate obtained from cationic (C_{12}TAB) and nonionic (β-C_{12}G_{2}) surfactant solutions at different concentrations was also measured. Only BKP fibers were utilized in the dynamic surface tension experiments.

UV–Vis Spectroscopy and Attenuated Total Reflection–Fourier Transform Infrared Spectroscopy (ATR–FT-IR). The presence of soluble lignin content in the leachates was examined by measuring the absorbance at wavelengths between 200 and 1000 nm using a UV–vis spectrophotometer (UV-2550, Shimadzu, Kyoto, Japan). The absorbance intensity at 205 nm was used to qualitatively compare the lignin content. Hemicelluloses were identified in freeze-dried leachates using infrared spectroscopy ( Nicolet 380 FT-IR) at 500–4000 cm⁻¹ with the single-reflection diamond attenuated total reflection (ATR) accessory (smart orbit). The background signal was collected before measurements by running 64 scans in air.

Sample Preparation for Foam Experiments. To study the role of SDS concentration on foam properties, in the presence or absence of fibers, the following samples were prepared: (1) SDS solutions at a concentration below, at, and above the cmc_{SDS} (0.7, 8.4, and 70 mM); (2) aqueous fiber dispersions (0.3 wt %) in the presence of 0.7, 8.4, and 70 mM SDS; and (3) suspensions of Leachate_{BKP} generated in situ from the respective samples in (2). Specifically, for the preparation of samples in (2), 70 mM of BKP fibers was dispersed in double-distilled water. Then, right before foam measurements, a certain volume of the SDS stock solution (315 mM) and double-distilled water were added to the suspension so that its final volume was 90 mL. The BKP fiber content was fixed at 0.3 wt %, while the SDS concentration was 0.7, 8.4, or 70 mM. Before the foam experiments, the given fiber dispersion in SDS was kept under gentle magnetic stirring for 1 min to ensure homogeneous mixing while avoiding bubble formation. For the preparation of samples (3), the Leachate_{BKP} was collected by filtering the respective system using a clean nylon membrane, as described before. Double-distilled water was used throughout the foam experiments, which are described in detail next.

Aqueous Foam Generation and Evaluation. Foam properties (foamability and foam stability) were followed by using a FoamScan unit (Teclic, France). The initial liquid volume was kept at 60 mL and nitrogen gas was injected from the bottom of the column at a rate of 84 mL/min using a porous fritted glass disc (average pore diameter in the 41–100 μm range). The foamability was evaluated by recording the time taken to reach a foam volume V_{f,90%} = 120 mL. Once the gas
Figure 1. Photographs of 0.3 wt % (BKP) fibers dispersed in (a) MQ water and (b) 0.7 mM SDS solution 0, 5, 10, 15, and 30 min after mixing. Note that the phase separation can be followed by observing the upper clear phase (i) that develops with time relative to the bottom phase (ii). Schematic illustrations of the time evolution of the fiber dispersions in MQ water and 0.7 mM SDS are included in (c,d), respectively (the legend for the different components in the bottom is not to scale).

flow was stopped, the foam stability was assessed by recording the changes of the foam volume ($V_{\text{furan}}$) and of the liquid fraction ($r$) as a function of time. For this purpose, a charge-coupled device (CCD) camera and electrodes located inside the FoamScan column, respectively, were used. The evolution of the bubble size was followed with a cell size analysis (CSA) camera positioned at the wall of the column. The maximum foaming and total experimental time were set at 2000 and 2200 s, respectively. At least two foaming tests were run for each sample. The images obtained from the CSA camera were analyzed with the freeware program ImageJ to obtain a water-free skeleton image after reducing the dark areas of the surface plateau borders into lines of one-pixel width. Then, the skeletonized images were analyzed using the CSA software of the FoamScan unit. The bubble size ($r$) and size distribution were determined in repeated experiments and the standard deviations are reported.

## RESULTS AND DISCUSSION

Fiber Leachate Caused by SDS. We first conducted very simple experiments to check whether SDS extracts non-cellullosics from the cell walls of wood fibers. As expected, BKP fibers dispersed in MQ water gradually separate into two phases, Figure 1a,c. The upper phase “i” contains non-cellullosics leached from fibers, while the lower phase “ii” contains fibers and traces of non-cellullosics dispersed in the entire aqueous medium. The composition in these two phases is confirmed further below. When SDS is added to the aqueous medium (at submicellar conditions, e.g., in the presence of SDS unimers), the amount of the top phase “i” (Figure 1b) is larger than that of the top phase “ii” without SDS (Figure 1a). To rule out the effect of ionic strength, we performed an experiment with 0.7 mM NaCl, which leads to the same results as the experiment with MQ water (images not shown). It is plausible that SDS causes the release of non-cellullosics by reducing the interfiber repulsion, leading to the formation of (a) a denser phase “ii”, which contains mainly fibers and traces of aggregates between non-cellullosics and SDS, that is Leachate$_{0.7\text{mM SDS}}$ as well as (b) phase “i” containing solely Leachate$_{0.7\text{mM SDS}}$ (Figure 1d). The release of non-cellullosics is suggested to be a consequence of three phenomena: (a) the adsorption of SDS onto fibers via hydrophobic interactions, possibly via ion/charge-dipole interactions. It is reasonable to expect that upon the leaching of charged non-cellullosics from fibers, an osmotic pressure gradient is generated between the interfiber cell walls and the dispersion medium, which may induce depletion flocculation of fibers. The complex nature and identity of the non-cellullosics remain as an unresolved challenge, which may require sophisticated analytical approaches. Instead, we focused our investigation on the consequences of the release of non-cellullosics induced by SDS and the formation of the respective aggregates. This is expected to provide grounds for further studies on the interaction between SDS and non-cellullosics and related phenomenological aspects.

To determine the composition of the leachate, we used ATR−Fourier transform infrared spectroscopy (FT-IR), UV−vis, and carbohydrate analyses. Negatively charged hemicelluloses, which are soluble in water, are expected to be one of the non-cellullosic components leached from the BKP fibers. To test this hypothesis, Leachate$_{\text{MQ}}$ and Leachate$_{0.7\text{mM SDS}}$ were obtained from the fibers after five dispersion/washing cycles, followed by freeze-drying and ATR−FT-IR characterization. By comparing the respective ATR−FT-IR spectra with those obtained from SDS and reference hemicelluloses, the characteristic peaks of hemicellulose are identified for both Leachate$_{\text{MQ}}$ and Leachate$_{0.7\text{mM SDS}}$. The absorbances of Leachate$_{\text{MQ}}$ and Leachate$_{0.7\text{mM SDS}}$ at 3355, 1040, and 897 cm$^{-1}$ (Figure 2a−c) are assigned to hemicelluloses. These characteristic peaks correspond to the O−H (3355 cm$^{-1}$) and the C−O (1040 cm$^{-1}$) bond stretching of the ether groups and the β-1,4 glycosidic bond stretching (897 cm$^{-1}$).42 Additionally, the peak at 1215 cm$^{-1}$ is assigned to the stretching of skeletal vibration of S−O in SDS, which is found in the spectra of neat SDS and Leachate$_{0.7\text{mM SDS}}$. The ATR−FT-IR results confirm the presence of hemicelluloses in Leachate$_{\text{MQ}}$ and Leachate$_{0.7\text{mM SDS}}$. However, released lignin in the leachate cannot be ruled out because hemicelluloses are associated with lignin forming lignin−carbohydrate complexes (LCC), which are difficult to separate into the individual components.43−49 In fact, the presence of lignin in Leachate$_{\text{MQ}}$ and Leachate$_{0.7\text{mM SDS}}$
Leachate and SDS, and leachate solutions. However, it is di (hemicellulose, lignin, and extractives) are present in the aggregates in comparison to the aggregates in leachate.

Figure 2. (a) ATR–FTIR spectra (500–4000 cm⁻¹) of a reference hemicellulose, pure SDS, LeachateMQ and Leachate0.7mM SDS obtained from BKP fibers. (b) Characteristic peaks at 3355 cm⁻¹ for the reference hemicellulose and LeachateMQ are magnified 3x, while those assigned to SDS and Leachate0.7mM SDS are magnified 10x. (c) Characteristic peak at 897 cm⁻¹ for the reference hemicellulose and LeachateMQ (magnified 5x) and for SDS and Leachate0.7mM SDS (magnified 10x). The peak of Leachate0.7mM SDS was deconvoluted (dash lines) to highlight the peak at 897 cm⁻¹. (d) Bar plot corresponding to the absorbance intensity (205 nm) from the UV–vis spectra corresponding to LeachateMQ (filled bars) and Leachate0.7mM SDS (patterned bars) obtained from BKP fibers after the different dispersion cycle.

obtained from BKP fibers over five dispersion cycles is confirmed by the UV–vis absorbance data (205 nm), Figure 2d. Because residual extractives, such as fatty acids and sterols, may also be present in LCC, the presence of extractives in leachate was examined using carbohydrate analyses, for example, by comparing the composition of fibers before and after removing leachate. From the data in Table S1, it is clear that the leachate from the BKP fibers contained hemicellulose, lignin, and extractives.

After five dispersion cycles, using either MQ water or 0.7 mM SDS solution, a reduction in the amount of residual extractives in the solid phase (the BKP fibers) was observed, in agreement with the presence of extractives in LeachateMQ and Leachate0.7mM SDS, as previously hypothesized. The aggregates present in LeachateMQ and Leachate0.7mM SDS were further studied with dynamic light scattering (see the autocorrelation functions in Figure S1a). The longer decay time for Leachate0.7mM SDS indicates a larger hydrodynamic size compared to the aggregates in LeachateMQ (Figure S1b). In conclusion, the results clearly show that non-cellulosics (hemicellulose, lignin, and extractives) are present in the leachate solutions. However, it is difficult to determine whether lignin and the extractives in the leachate are solubilized as single components or bound to hemicelluloses. Carboxylic and other groups in lignin are very likely engaged in the formation of LCC. Similarly, the extractives are poorly soluble in water, and it is possible that they also bind to the hemicelluloses in the leachate.

The results discussed so far suggest that SDS extracts non-cellulosic components from the BKP fibers, which form aggregates with the surfactant in the aqueous medium. However, several questions exist, such as (a) the nature of the interactions between SDS and non-cellulosics; (b) the structure of the aggregates and their composition in the molar ratio, for example, SDS unimers versus non-cellulosics; and (c) the role of sodium counterions and the hydrocarbon groups of SDS. These points remain open for further studies. Here, we want to exploit the non-cellulosics in general and the surfactant/non-cellulosics aggregates in particular as foaming agents. For this purpose, we expand our studies by comparing the surface activity, the foaming capacity, and the foam stability of suspensions containing fiber and leachate, or leachate alone, with those of the respective SDS solutions.

Surface Activity of LeachateSDS. Figure 3a compares the surface tension isotherm of SDS solutions (filled symbols) with that of LeachateSDS after having the BKP fibers exposed to SDS solutions of the corresponding concentration (open, gray symbols). The surface tension isotherm of SDS solutions at 22.1 °C is in line with those reported in the literature. The solutions of LeachateSDS obtained after being exposed to SDS at submicellar concentrations have lower surface tension values than those of the respective pure SDS solution (Figure 3a). The enhanced surface activity of leachate is more apparent in the presence of SDS (Figure 3b, pattern-filled bars) than in MQ water (Figure 3b, filled bars). By increasing the number of dispersing cycles, one can see that the surface tension difference between leachate and the corresponding solutions (SDS or MQ water) decreases (Figure 3b). This observation indicates that the amount of non-cellulosics extracted from fibers exhausts progressively over dispersing cycles. Given the extremely low concentrations, our gravimetric and carbohydrate analyses were not sensitive enough to quantify the concentration of non-cellulosics in the leachates (Table S1). However, their presence is clearly evidenced from the surface tension isotherms of LeachateMQ and Leachate0.7mM SDS obtained after a given number of dispersion cycles, as discussed above.

Fibers other than BKP, namely, “dissolving grade” (DP) and TMP fibers, which widely differ in their composition (Tables S2 and S3), were used to further elucidate the effect of leached non-cellulosics obtained over five dispersion cycles (LeachateMQ and Leachate0.7mM SDS) on aggregate formation and surface activity (Figures S2 and S3). Detailed discussions can be found in the Supporting Information.

Taken all together, there is a clear evidence of the presence of non-cellulosics that interact with the anionic surfactant and increase the air/water interfacial activity of LeachateSDS. This conclusion is relevant for the application of natural components released in situ from fibers via a simple surfactant treatment, such as their use for the generation of liquid foams as will be shown further below.

In addition to the static surface tension, we also measured the dynamic surface tension of SDS solutions at three concentrations, namely, 0.7 mM = 0.083 cm/sSDS, 8.4 mM = cm/sSDS, and 70 mM = 8.3 cm/sSDS. Because γdynamic is time-dependent and relates to the diffusion and adsorption rates in the system, we also evaluated the efficiency of the respective
leachates in reducing the surface tension. We investigated whether SDS unimers diffuse faster to the air/water interface than the surface-active aggregates in Leachate_{SDS} (see Figure 3c for the γ_{dynamic} of SDS (filled symbols) and Leachate_{SDS} (empty, gray symbols) as a function of bubble lifetime). At a SDS concentration < cmc_{SDS} (Figure 3c, circles), SDS unimers reach an equilibrium in γ_{dynamic} (γ_{dynamic,eq}) very rapidly (∼0.05 s). In contrast, Leachate_{0.7 mM SDS} takes longer time (∼1 s) to reach γ_{dynamic,eq}. The shorter diffusion time of Leachate_{0.7 mM SDS} is expected owing to the hydrodynamic size of the aggregates compared to SDS unimers (Figure S1). The γ_{dynamic,eq} of Leachate_{0.7 mM SDS} is similar to that obtained from static measurements (Figure 3a). Upon increasing SDS concentration to the cmc_{SDS} and above (8.3 cmc_{SDS}), the γ_{dynamic} of both SDS and Leachate_{SDS} present a similar trend, indicating that SDS dominates the measured surface tension (an observation i.e., corroborated later from foam experiments). Additionally, γ_{dynamic,eq} at high SDS concentrations is reached rapidly as a result of the readily available SDS unimers in the system. We note that the surface tensions of Leachate_{SDS} at SDS concentrations of 0.7, 8.4 and 70 mM (Figure 3a) are similar to those in the presence of BKP fibers (Table S4), indicating that the leaching of non-cellulosics mainly depends on SDS concentration (Figure 3b) and less on the contacting time.

The effect of surfactants in extracting non-cellulosics from wood fibers was tested by comparing γ_{dynamic} of solutions containing the pure surfactant and those obtained after contact with the fibers. The surfactants chosen had nonpolar groups of the same length as SDS, namely, the cationic surfactant C_{12}TAB and the nonionic surfactant β-C_{12}G_{2}, which were tested at concentrations below, at, and above the respective cmc of each surfactant.
cmc (Figure 4). We noted no reduction in the surface tension of the leachate solutions obtained from C_{12}TAB or β-C_{12}G_{2}. This observation highlights the unique role of the anionic surfactant, which supports our hypothesis on leachate formation, as discussed earlier. Namely, SDS-induced fiber swelling due to hydrophobic effects{superscript}{30,31} and interactions with the polar group of SDS{superscript}{58} that increase the accessibility of non-cellulosics and their release from fibers{superscript}{39,40}. Such effects may not be relevant when cationic or nonionic surfactants are applied at submicellar concentration. In these cases, favorable electrostatic and hydrogen bonding interactions may exist, and the overall effect is that leaching does not occur or cannot be quantified. To the best of our knowledge, the role of SDS in leaching non-cellulosics from wood fibers and the subsequent formation of surface-active aggregates is reported here for the first time.

**Effect of Leachate_{SDS} on Foam Properties.** Substances with low surface tension and fast adsorption dynamics at the air/water interface are usually good foaming agents.{superscript}{52,53} Given the lower surface tension and fast diffusion (though Leachate_{0.7mM SDS} is slower than SDS unimers) of Leachate_{SDS} compared to those of pure SDS (Figure 3c), it is interesting to test whether Leachate_{SDS} influences the foaming properties. To elucidate whether the shape-anisotropic and relatively flexible fibers affect the foam properties, the foamability and the foam stability of BKP fiber dispersions in the presence of SDS (0.7, 8.4, and 70 mM) are compared to those of corresponding pure SDS solutions or Leachate_{SDS} prepared at the given SDS concentrations.

Figure 5a shows a typical FoamScan experiment, including foam generation (time up to 0 s, Figure 5a,I) and foam (de)stabilization (time >0 s, Figure 5a,II). The time required for generating 120 mL foam was used to determine the foamability, while the time evolution of V_{foam} was used as a measure for foam stability. As can be seen from Figure 5b–d, fiber-loaded foams in the presence of SDS and Leachate_{SDS} exhibit similar foamability and foam stability at the SDS concentrations studied. The enhanced foam stability of fiber-loaded foams compared to foams produced from Leachate_{0.7mM SDS} or 0.7 mM SDS is caused by an artifact in imaging, as can be seen in Figure S4. Thus, the presence of fibers does not change the foamability of pure SDS solutions or Leachate_{SDS} alone.

The foamability of Leachate_{SDS} is found to be SDS concentration-dependent. At a SDS concentration lower than cmc_{SDS} (c < cmc_{SDS}), the foamability of Leachate_{0.7mM SDS} and fiber-loaded SDS solution (0.7 mM) appear to be higher than those observed for the pure SDS solution at 0.7 mM (Figure 5b). The shortest time to reach V_{foam} = 120 mL (foaming time) is measured for Leachate_{0.7mM SDS} (159 s) (Video S1), followed by the foaming time of fiber-loaded SDS 0.7 mM (217 s) and that of the pure 0.7 mM SDS solution (734 s) (Video S2). Together with the surface tension data (Figure 3a,c), the results reveal possible synergies between SDS with non-cellulosics in Leachate_{0.7mM SDS} as well as their generation in situ from the dispersions containing the fibers in SDS solution.

Because of the low concentration of the surface-active aggregates in Leachate_{0.7mM SDS}, the newly created air/liquid interfaces are not stable enough to support the capillary suction against drainage. Therefore, once the gas flow stops, the foam volume collapses rapidly. Evidently, compared to those observed at a submicellar concentration, at a high-enough concentration of SDS (c ≥ cmc_{SDS}), the foamability and foam stability are higher for all the systems, including the pure SDS solutions, the fiber-loaded SDS dispersions, and the Leachate_{SDS} (Figure 5c,d). The results indicate the requirement of a sufficient amount of the surface-active agent to achieve fast foaming and good foam stability. Figure 5c,d show no substantial differences in the foamability and foam stability of SDS solutions, fiber-loaded SDS dispersions, and Leachate_{SDS} suggesting the dominant role of SDS in foam properties at c ≥ cmc_{SDS}.

The decay of foam volume is not the only a measure for foam stability. Major factors influencing foam stabilization include gravity-driven drainage, coalescence due to film rupture, and coarsening via gas diffusion. Drainage is measured by monitoring the foam’s liquid fraction, ε_{f}, over time, as shown in Figure 6a,b. The results for foams generated with 0.7 mM SDS are not included in the following discussion due to limitations in the statistical analysis of the air bubbles captured by the CCD camera, Figure S4. At t < 400 s, the liquid fraction is about the same and decays at the same rate for the SDS solution, fiber-loaded SDS dispersion, and the Leachate_{SDS} (Figure 6a,b). The presence of fibers in the SDS solution does not inhibit drainage. Upon drainage, the foam films...
become thinner and large air bubbles form as a result of coalescence (Figures S5 and S6). The increased number of large air bubbles during this period leads to a higher bubble size polydispersity index (PDI) while \(\langle r \rangle\) remains constant (Figure 6c,d). However, as a result of further thinning, film rupture occurs due to the insufficient elasticity of the foam film. Figure 6c,d shows an increase in both \(\langle r \rangle_{t>400s}\) and PDI_{t>400s} which is correlated to the transition points for \(\varepsilon\) at \(t > 400 s\) (\(\varepsilon_{t=400s}\)), whereby a faster decrease of the liquid fraction is observed due to coalescence, while the foam volume remains the same (Figure 6c,d). The effect of SDS concentration on \(\varepsilon\), \(\langle r \rangle\), and PDI of the given foams (from SDS solutions, fiber dispersions in SDS, and Leachate_{SDS}) is not significant at SDS concentrations above the cmc_{SDS}. The PDI was recorded until 800 s because of the small number of bubbles in the CSA, given their larger bubble size (Figures S5 and S6 at 1600 s). Therefore, the PDI derived from images at 1600 s are not meaningful.

**CONCLUSIONS**

The anionic surfactant (SDS) releases non-cellulosic components from wood fibers, including lignin, extractives, and possibly hemicellulose-bound species. The release of the non-cellulosics is speculated to be facilitated by fiber swelling, an effect that is not observed when cationic or nonionic surfactants are used. Our experimental results confirm the generation of surface-active aggregates, Leachate_{0.7mM SDS} which are formed between non-cellulosics and SDS unimers via nonelectrostatic interactions. While the nature of the involved interactions and the formation of the leached aggregates are still open questions, it is interesting to note their distinctive effects in terms of surface activity. For instance, Leachate displays faster foamability compared to pure SDS solutions and fiber-loaded SDS solutions. Hence, for any given prospective application, we propose the use of anionic surfactants, or the respective leachate, to generate foams carrying suspended wood fibers. Such effects seem to be more evident in the case of mechanical or thermomechanical fibers (TMP), a subject that was also introduced in this study.

**ASSOCIATED CONTENT**

- Supporting Information
  - The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.9b00243.
  - Carbohydrates and extractive analysis; hydrodynamic size via dynamic light scattering; and surface activity of Leachate_{0.7mM SDS} from other fiber sources (PDF)
  - Foam volume changes of Leachate_{0.7mM SDS} from BKP fibers (AVI)
  - Foam volume changes of Leachate_{0.7mM SDS} from 0.7 mM SDS over time (AVI)

**AUTHOR INFORMATION**

*Corresponding Authors
  *E-mail: cosima.stubenrauch@ipc.uni-stuttgart.de (C.S.).
  *E-mail: orlando.rojas@aalto.fi (O.J.R.).

**ORCID**

Wenchao Xiang: 0000-0003-4281-3109
The authors declare no competing financial interest.

Acknowledgments

The H2020-ERC-2017-Advanced Grant “BioELCell” (788489) is acknowledged for funding support (O.J.R.). We are also thankful to the CLIC Innovation Ltd New Fibre Products project (https://clicinnovation.fi/projects/new-fiber-products/).

References


