

# Influence of Critical Synthesis Parameters and Precursor Stabilization on the Development of Adhesive Strength in Fructose–HMF–Amine Adhesives\*

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## Abstract

The synthesis of an adhesive composed of fructose, hydroxymethylfurfural (HMF), and bishexamethylene triamine was optimized. The intended application of the adhesive is the production of wood composites such as particleboard or medium-density fiberboard. Adhesives synthesized using HMF-rich precursors produced in continuous and batch systems were compared in regard to their tensile shear strength development; no significant differences could be found. The use of sodium dithionite for HMF stabilization during precursor production led to lower resin viscosities, whereas no significant influence on the adhesive strength development was measured. Variation of the critical synthesis parameters' reaction temperature and reaction atmosphere allowed the production of an adhesive with similar or even faster strength development than commercially used urea–formaldehyde adhesives. The ideal reaction temperature was found to be 60°C. Adhesive synthesis under nitrogen atmosphere shifts the curing reaction to lower temperatures, which was demonstrated by differential scanning calorimetry measurements, but did not improve the overall strength development of the adhesive system.

Particleboards and medium-density fiberboards are important wood composites for the furniture industry. They are composed of approximately 90 percent wood particles or fibers and 10 percent adhesive and are produced in vast

amounts. In 2019, the worldwide production of 95 million m<sup>3</sup> of particleboard (FAO 2020) required approximately 6–9 megatons of adhesive. The usually used urea–formaldehyde (UF) adhesive system is fossil based and formaldehyde was

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classified as cancerogenic (European Commission 2014). These disadvantages lead to investments in the development of bio-based binder systems and a high interest for new approaches for their production. Carbohydrate-based adhesives usually show low reactivity at industrially applied process conditions, which leads to high press factors during board production (Dunky 2021, Rosenfeld et al. 2022). The conversion of carbohydrates into reactive compounds and the use of reactive cross-linkers are therefore of interest for the development of such adhesive systems. One compound that has gained interest for its multiple possible applications is the platform chemical 5-hydroxymethylfurfural (HMF), which can be produced from carbohydrate sources via acidic dehydration utilizing various catalysts and reaction systems (van Putten et al. 2013, Yu and Tsang 2017, Zhao et al. 2021). Although the research interest is high, only one small plant for HMF production (< 300 t/yr) was established up until now (Rosenfeld et al. 2020). This makes approaches that use HMF-rich precursors produced directly in an in situ reaction system very interesting, since no cleanup or extraction steps to reach high purity are needed in the overall process.

The production of such HMF-rich precursor solutions with an approach that follows green chemistry principles was studied in earlier works (Sailer-Kronlachner et al. 2021; Sailer-Kronlachner et al. 2022). The study reported here was conducted to optimize the synthesis of adhesives on the basis of these precursors and the reactive amine cross-linker bishexamethylene triamine (BHT), which was found to be the best candidate as an amine cross-linker in an amine screening (Thoma et al. 2021). The influence of parameters such as reaction atmosphere (during precursor production and adhesive synthesis), reaction temperature, and the use of HMF-stabilizing compounds such as sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ; Gomes et al. 2018) on the adhesive performance and adhesive properties such as the viscosity of the final product, was studied. Also, the influence of the reaction system (batch vs. continuous) used in the precursor production was of interest. The aim of the study was to confirm the hypothesis that the optimization of the new adhesive system leads to similar or better performance in terms of strength development when compared with an industrially used adhesive system such as UF.

## Materials and Methods

Fructose, in the form of a sugar syrup containing 70.5 weight percent sugar (consisting of 95% fructose and 5% other sugars and sugar di- and trimers), was supplied by Cargill Deutschland GmbH (Krefeld, Germany) and diluted to the desired concentrations with deionized water. Sulfuric acid ( $\text{H}_2\text{SO}_4$ , 98% p.a.), sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ , EMPLURA®), and BHT (high purity) were purchased from Sigma-Aldrich (Merck Supelco, Darmstadt, Germany). Sodium hydroxide ( $\text{NaOH}$ ,  $\geq 99\%$ ) was purchased from Carl Roth GmbH + Co. KG (Karlsruhe, Germany). The reference UF resin was a core layer-E1 standard industrial resin provided by FRITZ EGGER GmbH & Co. OG (Unterradlberg, Austria).

### Adhesive synthesis procedure

The production of the HMF-containing precursor solution was discussed in detail in earlier works (Sailer-Kronlachner et al. 2021, 2022). Two types of precursor solution were used in this study: one was produced in a continuous reaction system with a subsequent concentration step and

the other type was produced utilizing a batch reaction system that was adjusted and optimized for the dehydration reaction. The two precursors were similar in composition but differed in HMF content (73 g/L batch vs. 65 g/L continuous), levulinic acid content (8 g/L batch vs. 5 g/L continuous), and formic acid content (3 g/L batch vs. 1.5 g/L continuous), which made adhesive synthesis with both variants necessary to investigate whether the precursor produced in batch can be used in the same way as the continuously produced precursor. The precursor solutions were neutralized with NaOH (50 weight percent) before use. Precursor solutions were produced with and without sodium dithionite addition in the batch reaction system to determine the influence of the stabilizer on the precursor production and on the adhesive properties. The precursor produced with the stabilizer had the same or even slightly higher HMF content but significantly lower side product formation, especially the formation of solid humin byproducts. This also means that the formation of HMF is slower, but the system is easier to control since unwanted solid residues can clog the reactor. The precursor is not stable for longer time periods; HMF levels drop by 0.2 percent within 1 week when the solution is neutralized with NaOH directly after production. Since levulinic acid levels remain the same, this points to HMF oligomerization. The oligomers are not expected to interfere with resin synthesis; nevertheless the precursors should not be stored for longer periods before usage. This is certainly an issue that needs to be examined further (Sailer-Kronlachner et al. 2022).

In a standard adhesive synthesis, fructose syrup and adhesive precursor were added to a three-neck flask, equipped with a thermoelement and a reflux condenser, in the desired quantities. The mixture was heated to the targeted reaction temperature (50, 60, or 70°C) with a hot-plate magnetic stirrer with Teflon coating. The first half of the molten BHT was added when the reaction temperature reached 40°C, which led to a quick rise in temperature due to the addition of 40–50°C warm BHT and first-occurring reactions. The reaction solution was kept at the targeted temperature for the desired reaction time. Reaction times varied for different experiments and depended on the reaction temperature and the viscosity increase. Reactions at 60°C were run for 45 min. Samples were taken to monitor the viscosity development of the resins. After the desired reaction time, the solution was cooled to room temperature. The second portion of the amine was always added directly before resin analysis or usage; the resin was stored without the second portion of amine. The target solid content after the second addition of amine was 55–58 weight percent. The molar ratio between carbohydrate, HMF, and amine was 3.7/0.2/1. Calculations for the synthesis are based on the HMF amount in the precursor; extra fructose was added to obtain the targeted molar ratios. The influence of the molar ratio on the adhesive was discussed in an earlier study (Rosenfeld et al., 2022).

### Tensile shear strength measurement

The strength development of the screened adhesive formulations was measured with an automated bonding evaluation system, as originally patented by Humphrey (1993). The tests were performed according to ASTM-D7998-15 (ASTM International 2015). Uniform, planar, and defect-free European beech veneers, 120 by 20 by 0.6 mm, were stored at a standardized climate of 20°C with 65 percent relative humidity before testing. On the basis of the

dry weight, 125 g/m<sup>2</sup> adhesive were applied to the overlapping area of the joint (20 by 5 mm). The samples were hot pressed at 120°C and the press time was varied between 60 and 600 seconds. A cooling phase (60 s) was used directly after hot pressing, as suggested in the standard to test below the relaxation temperature of the adhesive. After pressing, a tensile force was applied and the tensile shear strength of the joint was calculated.

### Thermal analysis

A Polyma 214 (Netzsch-Gerätebau GmbH, Selb, Germany) was used for the differential scanning calorimetry (DSC). Between 2 and 5 mg of the samples were measured in a closed, high-pressure steel crucible. The device was calibrated by measuring gallium, indium, tin, and bismuth at a heating rate of 5 K/min. Typical measurements were performed from 20 to 350°C. The data were analyzed using Netzsch Proteus® software (Netzsch-Gerätebau) and Origin 2016G (OriginLab Corporation, Northampton, Massachusetts, USA).

### Rheological measurements

The viscosity of the resins was measured directly after sampling during or after the synthesis using a rotational rheometer MCR 302 (Anton Paar, Austria). The mean value of the viscosity was calculated on the basis of 10 measurements at 23.0°C ± 0.2°C. A shear rate of 100/s was used. The disposable, parallel plate diameter was 25 mm and the gap size was 1 mm.

## Results and Discussion

### Influence of the reaction temperature

Reaction temperatures of 50, 60, and 70 °C were tested in the synthesis optimization process; experiments were conducted with precursors produced in the batch system. As expected, a higher reaction temperature led to a faster rise in resin viscosity as displayed in Figure 1 (left side).

At 70°C reaction temperature, the polymerization runs fast and is hard to control, easily leading to overcondensation and an unusable resin (thick paste or gumlike solid). Although the reaction is easy to control at 50°C, the lower reaction temperature led to significantly lower adhesion strength during tensile shear strength testing. Prolonging the synthesis time to 80 minutes did not improve the tensile shear strength of the adhesive synthesized at 50°C. This is an interesting finding as similar viscosities were reached for the adhesive synthesized at 50°C for 80 minutes and the one synthesized at 60°C for 45 minutes. This suggests that there are some reactions only occurring at higher temperatures (60°C) that are essential for strength development. The strength development after reaction at 50 or 60°C is depicted in Figure 1 (right side).

This effect can be explained by the multiple possible reactions during the adhesive synthesis. The adhesive is most likely a complex mixture of multiple oligomers. These are formed by reaction of HMF with itself and levulinic acid to form huminlike structures, reaction of HMF with BHT, HMF with fructose, and fructose and BHT. The reactions between sugars and amines are generally known as Maillard reactions and these already lead to highly complex mixtures. Adding HMF to this system leads to reactions with higher activation energy that do not occur when HMF is not present. Expected reactions comprise Schiff base formation, aromatic substitution reactions on furanic cores, and reactions between amines and methylol groups. Main reactions are triggered at 60°C or above and lead to improved tensile strength formation. Nuclear magnetic resonance and Fourier transform infrared spectra show that furanic cores remain while aldehyde groups are consumed. Detailed analysis of the spectra is elaborate because of low HMF content and many possible reaction products in the adhesive. Moreover, fructose and BHT overlay most signals involving new bond formations (Rosenfeld et al., 2022). Experiments with the pure compounds and maybe isotope labeling would be needed to gain more information.

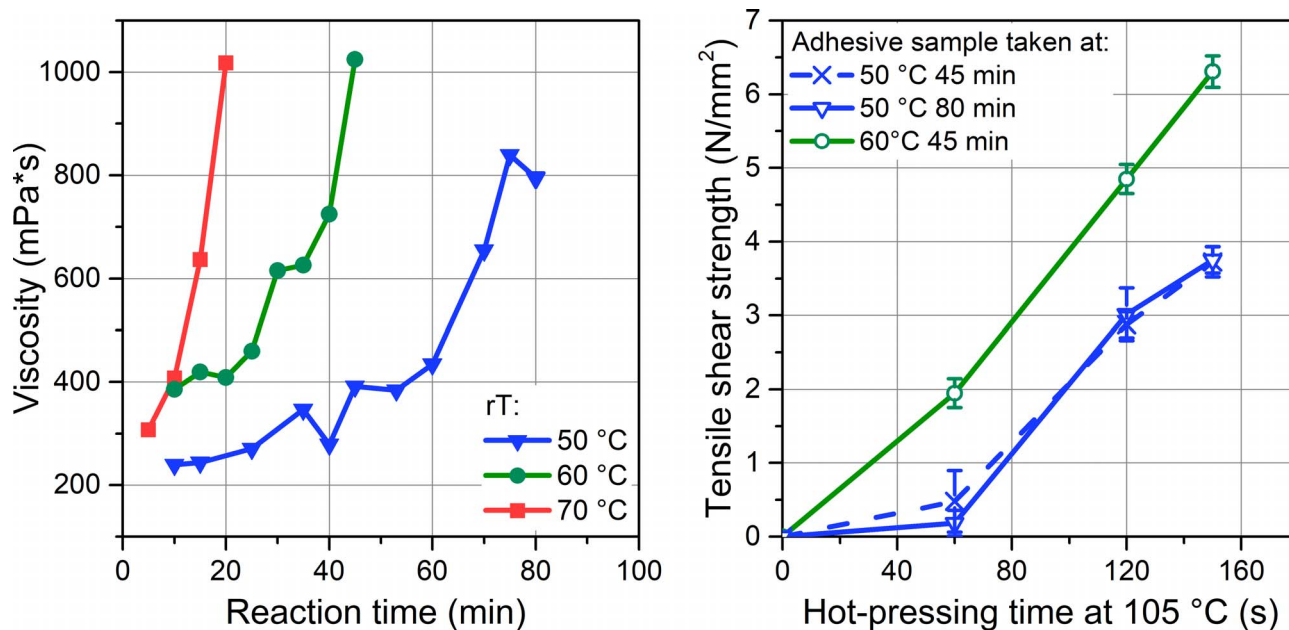


Figure 1.—(left) Reaction viscosity profiles at different reaction temperatures. (right) Comparison of tensile shear strength development after reaction at 50 and 60°C.

Further, it was observed that small (<100 μm) particles formed during the adhesive synthesis at 60°C. This particle formation was not observed in adhesives made at 50°C or fructose/BHT reference adhesives without HMF (also synthesized at 60°C). Therefore, it can be speculated that the particle formation and increased tensile shear strength development of adhesive synthesized at 60°C is due to the HMF present in the system. Overall, the reaction at 60°C gave the best results of the tested conditions. Therefore, all further reactions were carried out at 60°C. Gel permeation chromatography data of the different adhesives can be found in another study by our group (Rosenfeld et al., 2022). As for storage stability, this is an issue that still needs to be improved. The resin is stable for longer periods when it is frozen or stored at low temperatures. If it is stored at room temperature or above, viscosity rises quite fast.

### Influence of the reactor used in precursor production

Two different reaction systems were used for precursor production, a continuous mesoreactor and a modified batch reactor. The reaction systems are described in detail in two previous works (Sailer-Kronlachner et al. 2021, 2022). Since the precursor solutions produced in both reaction systems had slightly different compositions (as described in the Materials and Methods section), the effect of precursor production on the adhesive system had to be tested. Another reason for these experiments was that the precursor production in the continuous reaction system involved an additional concentration step that could have led to precondensation of the precursor. If the precursor is concentrated too much or for too long, formation of first oligomeric humin structures is observed. Details on the structure of the formed humins can be found in another study of this working group (Sailer-Kronlachner et al., 2022).

As can be seen in Figure 2 (left side), only minor differences in strength development were found in typical

examples of resins from both variants, although there was no difference in the ultimate strength level reached after 150 seconds of press time. The slightly reduced shear strength for the batch curve at the longest press times can be explained by wood failure in the measurements, which occurred at the long pressing times.

### Influence of the reaction atmosphere

Since the reducing agent sodium dithionite showed an influence during precursor production, it was hypothesized that oxidation processes can have an influence on the reaction. Precursor solutions were produced in the batch reaction system under air and under inert N<sub>2</sub> atmosphere, all containing the stabilizer. Also, resin synthesis was carried out in both atmospheric conditions and the same reaction parameters using both precursor variants, which led to four different adhesives (Table 1). Standard work procedures for working under an inert atmosphere were followed.

No significant differences between the adhesives were found regarding the tensile shear strength reached after 150 seconds of pressing and only minor differences were found regarding strength development (Fig. 2, right side). However, when the adhesives are compared with DSC (Fig. 3), the variants synthesized under N<sub>2</sub> atmosphere miss a reaction peak at higher temperatures (150°C). This indicates that reactions at higher temperatures do not occur during the hardening process,

Table 1.—Adhesives produced under different reaction atmospheres.

Adhesive	Atmosphere precursor production	Atmosphere adhesive synthesis
ATM_1	Air	Air
ATM_2	Air	N <sub>2</sub>
ATM_3	N <sub>2</sub>	Air
ATM_4	N <sub>2</sub>	N <sub>2</sub>

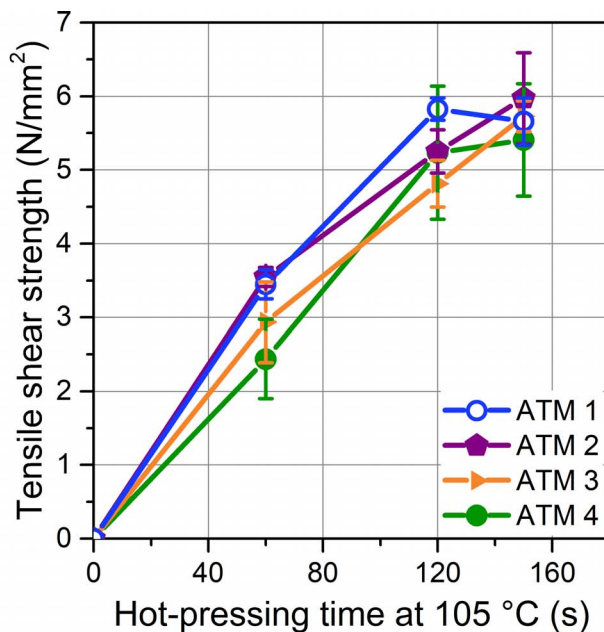
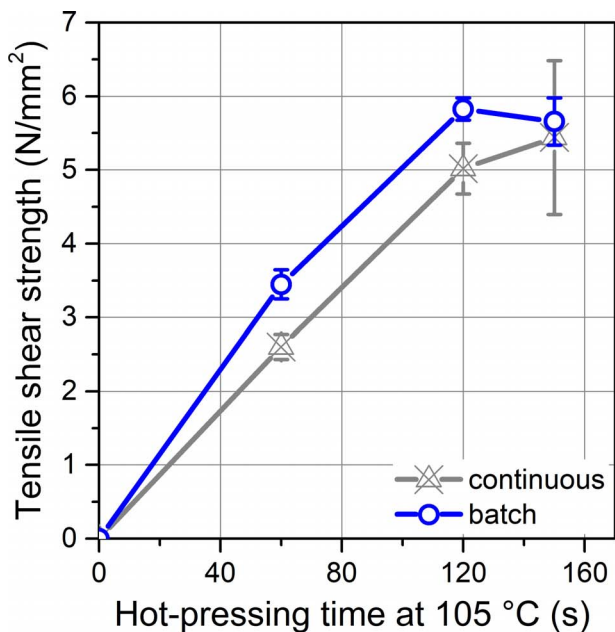


Figure 2.—(left) Influence of the precursor production system on tensile shear strength development; (right) influence of the reaction atmosphere (Table 1) on tensile shear strength development.

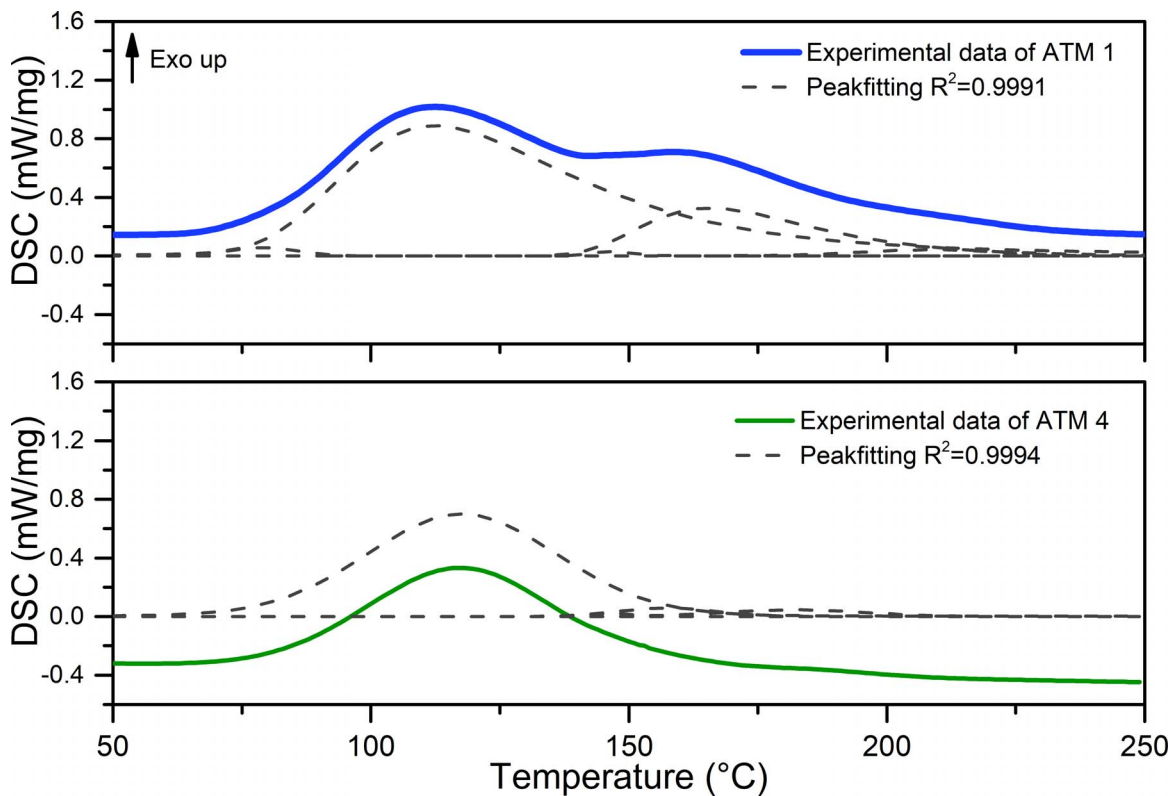


Figure 3.—Comparison of differential scanning calorimetry (DSC) curves measured with the adhesives ATM\_1 and ATM\_4 (Table 1).

which might be beneficial for the hardening of the adhesive, since only temperatures of 105–110°C are reached in the core layers of a particleboard during the production process (Solt et al. 2019). The reactions involved during the hardening process should therefore finish faster and without reaching the higher temperatures.

### Influence of the use of HMF stabilizing sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ )

The stabilizing influence of sodium dithionite on the HMF precursor production process was demonstrated in an earlier study (Sailer-Kronlachner et al., 2022). To this point, the mechanism for the stabilizing effect remains speculative. Sodium dithionite is a strong reducing agent, which points to the involvement of impeded oxidation processes. Another possibility is the discrimination of follow-up reactions leading to oligomerization or decomposition. The influence on sodium dithionite during adhesive synthesis was tested by synthesizing resins (60°C, 45-min reaction time) using precursors produced with and without sodium dithionite. Whereas the viscosity of the resin with sodium dithionite was significantly lower (Fig. 4, left side), no influence on tensile shear strength development was found (Fig. 4, right side).

The lower viscosity of the stabilizer containing resin is an advantage from an application perspective. Adhesive systems with lower viscosity are easier to handle in regard to spraying and adhesive distribution during the production process. Furthermore, lower resin viscosities are needed in the production of fiberboards, another class of composite in the production of which this adhesive system will be tested. The use of sodium dithionite as stabilizer can lead to sulfonation

in the adhesive system. It is possible that this can have a negative influence on the performance of the adhesive regarding hydrolyzation stability and board thickness swelling. This certainly needs to be investigated in the future. Besides sulfonation, the same effects that lead to HMF stabilization might lead to the lower viscosities, e.g., by hindering certain condensation or polymerization reactions.

### Comparison of optimization results with reference system

The optimized adhesive was compared with a UF reference system used in today's particleboard production. The fructose–HMF–BHT adhesive system is one of the very few bio-based and formaldehyde-free adhesive systems developed so far (Solt et al. 2019) that reach the same tensile shear strength values as a commercial UF system, but in even shorter time (Fig. 5). Regarding the raw material availability, the used main component fructose syrup is available from European biorefineries in surplus amounts. However, the amine cross-linker BHT, or polyamine compounds in general, are not readily available, though produced in large amounts. There already are bio-based ways to produce these compounds, but the main sources for these amine cross-linkers are still fossil resources. Therefore, the development of a bio-based amine cross-linker should be part of the next development steps toward a completely bio-based adhesive system.

The results allowed us to proceed to the next step in the testing of the adhesive system. Particleboards were produced in a first test series; the results will be published in a follow-up publication (Rosenfeld et al., submitted for publication).

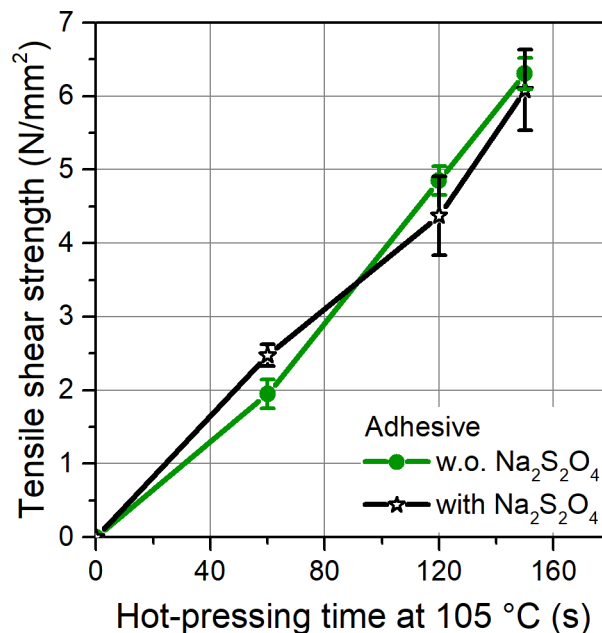
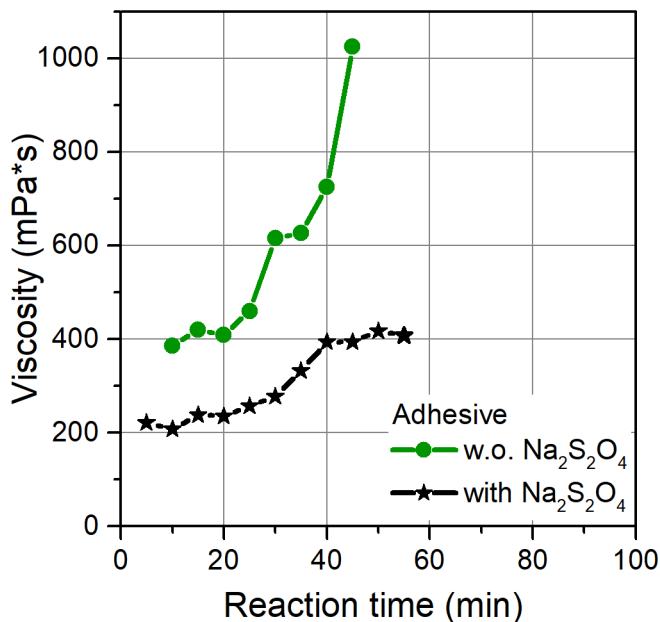


Figure 4.—(left) Viscosity development during synthesis of adhesives with and without (w.o.) sodium dithionite; (right) tensile shear strength development of adhesives produced with and without sodium dithionite.

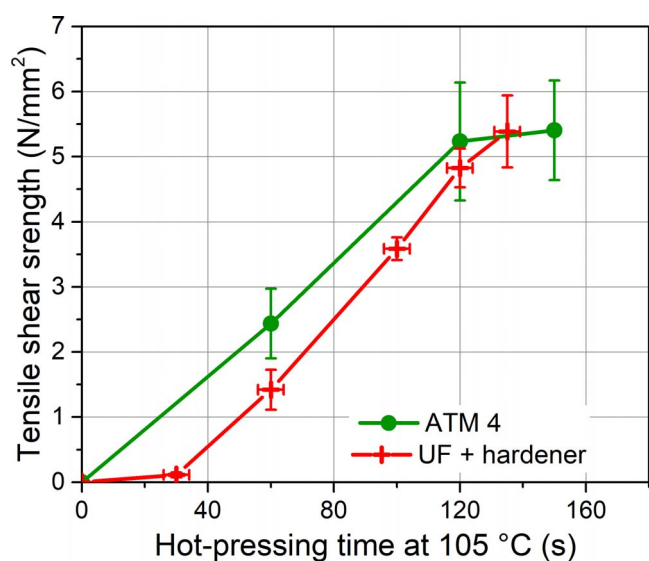


Figure 5.—Comparison of tensile shear strength development of the fructose-5-hydroxymethylfurfural-bis-hexamethylene triamine adhesive ATM\_4 with a reference urea-formaldehyde adhesive ( $\text{NH}_4\text{NO}_3$ ; 2.3% solid/solid as hardener).

### Conclusion and Outlook

The hypothesis that the fructose-HMF-BHT adhesive system can be successfully optimized by reaction temperature and reaction atmosphere variation was confirmed. The optimal reaction temperature was found to be 60°C. Adhesive synthesis under nitrogen atmosphere shifts the curing reaction to lower temperatures, which was demonstrated by DSC measurements, but did not improve the overall strength development of the adhesive system. The influence of the reaction precursor production system was tested and found to be not significant regarding the tensile

shear strength development, although adhesives produced with precursors out of the batch system seem to develop the same strength levels slightly faster. The presence of the HMF stabilizer sodium dithionite in the precursor leads to a lower viscosity of the final adhesive, which is beneficial from an application perspective. No significant influence of the stabilizer on the tensile shear strength development was found. The optimized system reaches similar or better performance regarding the tensile shear strength development when compared with an industrial UF reference adhesive, which allowed the testing of the system in first particleboard trials.

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