Alginate based bio-adhesive for bookbinding application

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Abstract

Alginate-based adhesives were formulated by incorporating micro-cellulose fibers (MCF, 20 µm) at concentrations of 0.1, 0.5, 1, 2, and 3 wt%. Rheological measurements were conducted to assess viscosity behavior under varying shear rates, and pull-out tests were performed to determine adhesive strength. Increasing MCF concentrations resulted in higher viscosities, particularly at low shear rates. Pull-out strength exhibited a concentration-dependent trend, with 1 wt% MCF yielding the highest mean pull-out force of 3.41 N/cm². The results indicate that alginate-MCF systems offer potential as bio-based adhesives for bookbinding applications, although their mechanical performance remains below that of conventional petrochemical adhesives, highlighting the need for further optimization.

Introduction

Historically, adhesives were derived from biopolymers such as casein, starch, glutin, and hemoglobin. These biopolymers are biodegradable and do not pose environmental concerns after disposal. In contrast, synthetic adhesives, developed in the 1930s to meet the growing demands for improved adhesion on metals, glass, and other non-porous materials, are derived from petrochemicals. The development of synthetic adhesives was driven by three main factors: the need for enhanced adhesion properties, improved resistance to aging, and the facilitation of mass production (Industrieverband Klebstoffe e.V., 2020; Habenicht, 2009, pp. 141–147). However, the limited availability of petroleum resources and the non-biodegradability of petrochemical adhesives have raised increasing environmental concerns, particularly regarding their end-of-life impact and recycling challenges.

The bookbinding industry is a significant contributor to waste production, with large quantities of paper being wasted. In Germany alone, 19 million tons of paper waste were produced in 2021, with 6 million tons being used for graphical applications like books or magazines (NABU - Naturschutzbund Deutschland

Stuttgart Media University

e.V., 2024). Approximately 79 % of waste paper is recycled, which is beneficial for the environment. In 2021, 3.2% of the 967 000 tons of adhesive produced were utilized by the German paper industry. This equates to approximately 30 944 tons of adhesive being used (Industrieverband Klebstoffe e.V., 2023). The recycling of 15 million tons of paper produces approximately 24 430 tons of adhesive waste, which subsequently contaminates the recycling process. It is estimated that bookbinding alone generates approximately 6 514 tons of adhesive waste in recycling plants. This contamination leads to increased water consumption during flotation and greater water pollution during cellulose reactivation processes.

Moreover, non-biodegradable commercial adhesives have been detected in the environment as micro plastic contaminants resulting from wastewater emissions (Habenicht, 2009, pp. 763–764; Göttsching, 1999, pp. 205–206; Onusseit, 2006; Zhang et al., 2022).

Bio-based adhesives have been used in bookbinding for centuries. Traditionally, adhesives based on glutin derived from bones and slaughterhouse by-products enabled strong bonds when combined with thread-sewn structures, offering durable and flexible lay-flat properties. However, the complexity of these techniques led to the replacement of bio-based adhesives by simpler and cheaper petrochemical alternatives. Recently, there has been renewed interest in bio-based adhesives driven by growing awareness of sustainability and environmental responsibility (Arias et al., 2021).

One promising candidate is alginate, a biopolymer extracted from brown algae. Global demand for alginate is estimated at 26 million tons per year for various applications, including capsule production in the pharmaceutical sector, packaging materials, and cosmetics (Olatunji, 2024; Ching, Bansal & Bhandari, 2017).

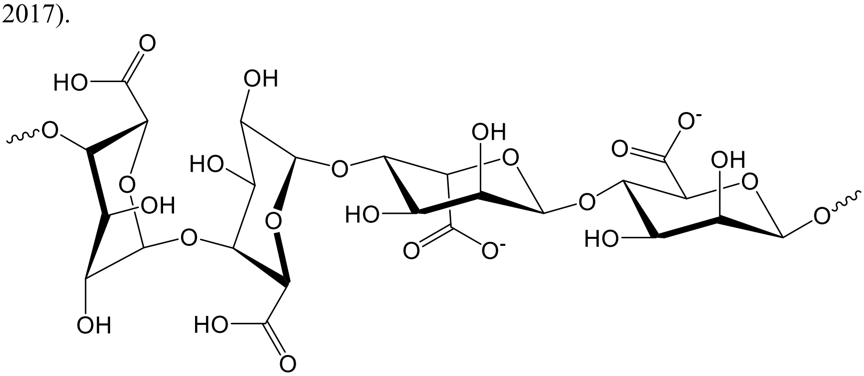

Figure 1: Chemical structure of the alginate blocks.

Alginate is composed of α -1,4,guluronic acid (G) and β-D-mannuronic acid (M) units, arranged either randomly, in blocks, or alternately (Figure 1).

A key property utilized in packaging is the crosslinking of alginate chains via divalent ions such as Ca^{2+}, forming a stable, irreversible film through ionic interactions described by the "egg-box model" (Cao et al., 2020). This ionic crosslinking imparts strong cohesion; however, it simultaneously reduces the availability of polar groups required for adhesion, resulting in decreased adhesive strength.

As an alternative to ionic crosslinking, micro cellulose fibers (MCF) have been proposed to enhance alginate's cohesive properties without compromising adhesion.

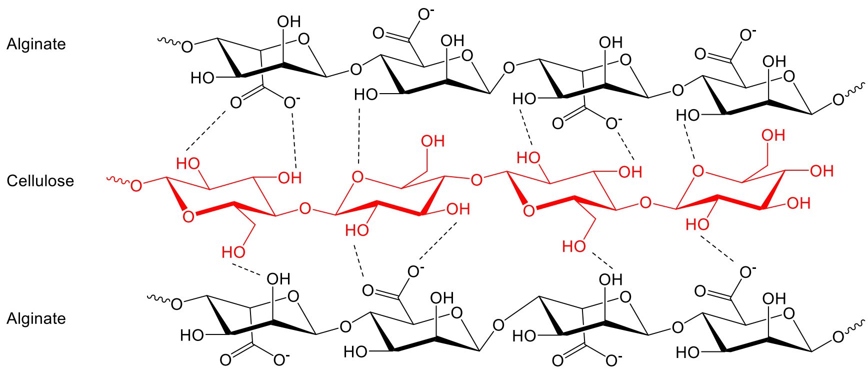

Figure 2: Interaction of alginate (black) with cellulose (red) via hydrogen bonds (dotted line)

MCF can interact with alginate chains via hydrogen bonding, preserving adhesion while improving cohesion. Additionally, the microcrystalline structure of MCF may enable mechanical interlocking at the paper edge, further enhancing adhesive performance (Sirviö et al., 2014).

In this study, alginate was combined with varying concentrations of micro cellulose fibers to investigate the effects on rheological behavior and pull-out strength, aiming to assess their suitability for sheet-edge bonding applications in bookbinding.

Experimental procedure

Materials

Sodium alginate (10000 – 600000 g/mol) was purchased from *AppliChem*. Glycerol and Micro Cellulose fibers (20 µm) were purchased from *SIGMA Aldrich.*

Preparation of sodium alginate/MCF based adhesive

Sodium alginate (3 wt%) was mixed with Glycerol (25 wt%) at 1000 rpm at room temperature to form an alginate solution. Subsequently, varying concentrations of MCF (0, 0.1, 0.5, 1, 2, 3 wt%) were added to the solution and were stirred at 5000 rpm. After one hour of stirring, the adhesive was obtained in the form of a white, viscous liquid.

Preparation of the test samples

In this study, A6-format books comprising 40 pages were produced as test samples, utilizing a *Ribler* Gecko 75. The adhesive was applied with a wet thickness of 1 mm. The experiment employed Amber Graphics 90 g/m² as test papers, provided by *Inapa Deutschland*

Rheology

The viscosity curves of the adhesive material were measured using a Physica MCR-300 rheometer, equipped with a 24.955 mm cone-plate. The dynamic viscosity was measured within a shear rate range of 10–1000 1/s at 293.15 K. The measurement of all samples was conducted on three occasions, following which the mean value was calculated. The standard deviation of these values was then determined. All rheological analysis was performed using the Python programming language.

Pull test

Pull test measurements were performed using a QLIBRO PPT Newton 451. One sample contains 10 books in A6 format with 40 pages each which were produced in the Gecko 75. Page 3, 8, 13, 18, 23, 28, 33 and 38 were pull out. For each page, the mean value and the standard deviation was calculated. All analysis was performed using the Python programming language.

Results and discussion

Rheology analysis

The dynamic viscosity of the samples with different MCF concentrations are shown in figure 3.

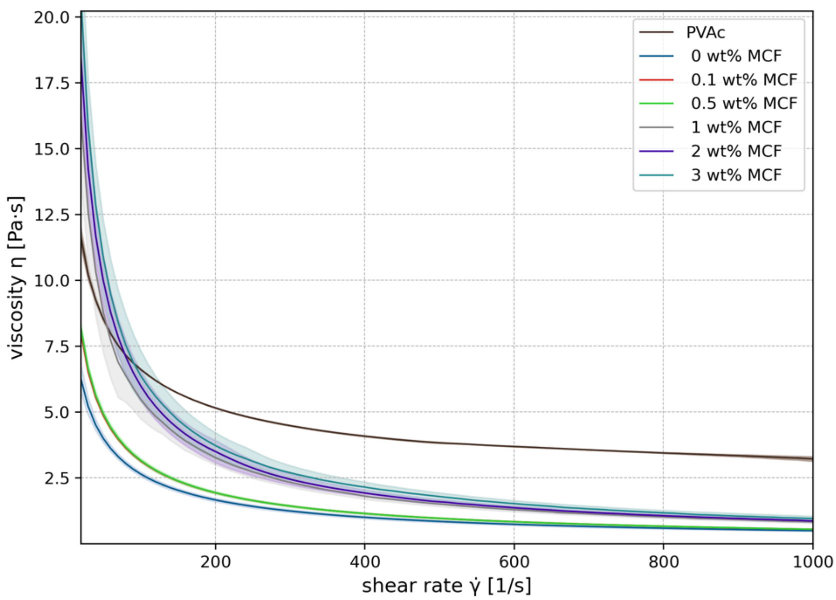

Figure 3 Mean dynamic viscosity curve of Alg/MCF adhesives with varying MCF concentrations, alongside their standard deviation (lighted out) and PVAc as a reference.

The addition of MCF to the adhesive formulation has a clear influence on its rheological behavior, particularly at low shear rates. At a shear rate of 100 s^{-1}, the sample without MCF exhibits a mean viscosity of approximately 2.644 Pa·s, while the sample containing 3 wt% MCF shows a significantly higher viscosity of about 6.579 Pa·s. This indicates that the MCF content substantially increases viscosity under low shear conditions.

As the shear rate increases, all samples display shear-thinning behavior, characterized by a decrease in viscosity. This results in a convergence of the viscosity curves, suggesting that at high shear rates, the influence of MCF concentration on the rheological properties diminishes and the formulations behave more similarly.

Polyvinyl acetate (PVAc), used as a reference material, demonstrates a higher viscosity than the 0, 0.1, and 0.5 wt% MCF samples at low shear rates. However, compared to formulations with higher MCF concentrations (1, 2, and 3 wt%), PVAc shows a relatively lower viscosity in this range. At high shear rates, PVAc maintains a higher mean viscosity than all MCF-containing samples, further supporting the shear-thinning behavior introduced by MCF.

Pull test

In order to investigate the effect of varying the MCF concentration on adhesion strength, different pages of the test book samples were torn out using the pull tester. The results obtained from the various pages are displayed in the subsequent bar chart.

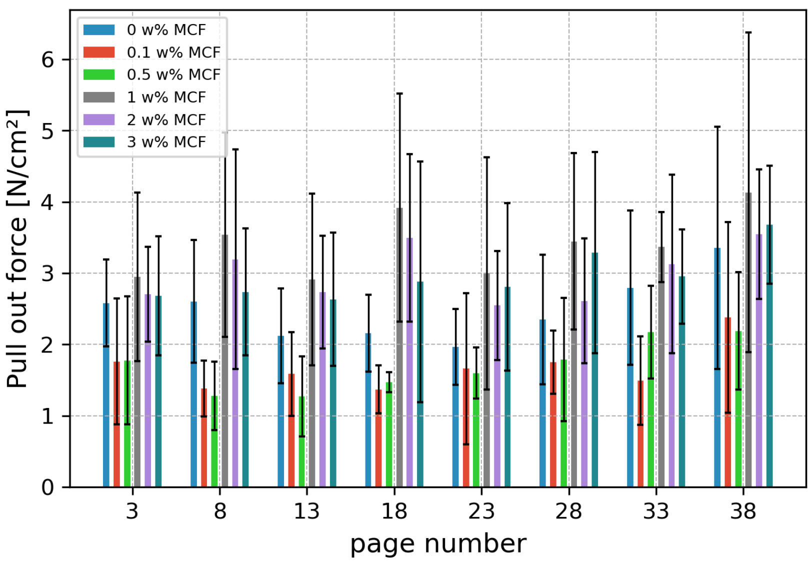

Figure 4: Mean pull-out force of Alg/MCF adhesives with varying MCF concentrations, along with their standard deviation, is presented on different pages.

The bar chart illustrates that the addition of low amounts of MCF (0.1 wt%, 0.5 wt%) leads to a significant decrease in pull-out force compared to pure alginate (0 wt%). However, when increasing the MCF concentration to 1 wt%, the pull-out force significantly increases, indicating improved adhesive strength. Further increasing the MCF content beyond 1 wt% again results in a decline in pull-out force, suggesting reduced adhesion.

A comparison at page number 18 reveals that pure alginate exhibits a mean pull-out force of 2.157 N/cm², whereas the sample with 1 wt% MCF achieves a significantly higher mean pull-out force of 3.919 N/cm².

MCF likely acts as a network filler within the alginate matrix, contributing to its mechanical stabilization. At low MCF concentrations, the network may not be sufficiently stabilized, leading to weaker adhesion than pure alginate. Upon reaching 1 wt%, an optimal balance appears to be achieved, where the MCF both reinforces the matrix and enhances mechanical anchoring through its microscopic structure within the paper. Another contributing factor might be the distribution of MCF: at low concentrations, the filler may be inhomogeneously dispersed, while at around 1 wt% a more homogeneous distribution could be realized. Further increases in MCF content may again lead to aggregation and inhomogeneities.

Nevertheless, caution is required when interpreting these results due to the large standard deviations, as clearly visible in the bar chart.

In the following, the results for each concentration were averaged across all their pages to facilitate a more comprehensive overview. The following bar chart illustrates this.

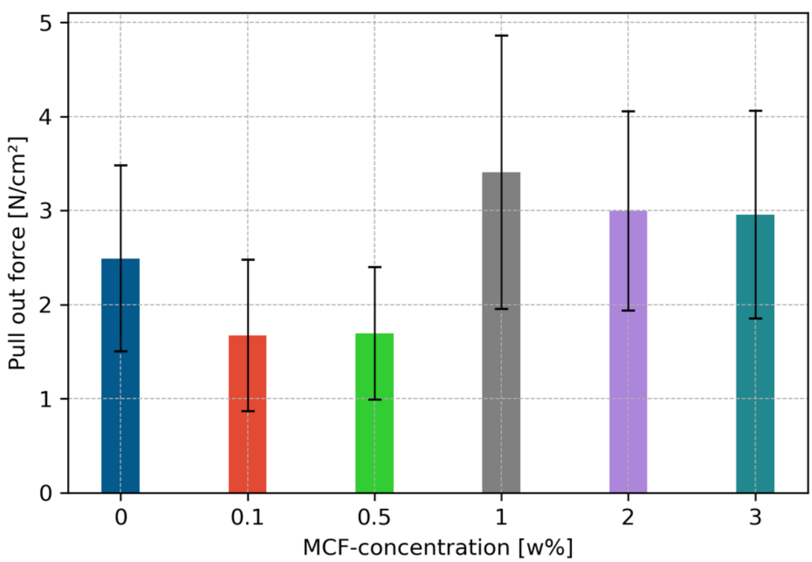

Figure 5: Mean pull-out force of Alg/MCF adhesives with varying MCF concentrations, along with their standard deviation across all pages.

Figure 5 shows the mean pull-out forces across all pages, averaged for each MCF concentration, along with the corresponding standard deviations. The trend clearly indicates that low concentrations of MCF (0.1 wt%, 0.5 wt%) result in significantly lower pull-out forces compared to pure alginate (0 wt%). In contrast, the addition of 1 wt% MCF leads to a pronounced increase in pull-out force. However, further increasing the MCF concentration beyond 1 wt% again results in a slight decrease.

Given the considerable standard deviations observed, a one-way ANOVA test followed by a Tukey post-hoc test was conducted to evaluate statistical significance. A significance level of 95 % ($\alpha = 0.05$) was applied. The ANOVA results are summarized below:

ANOVA	SS	df	MS	F	P-Value	F crit
Between the groups	208.5345	5	41.70691	38.11253	7.14×10^{-33}	2.233031

Table 1: one-way ANOVA test results

The subsequent Tukey HSD test yielded the following results:

Tukey test	Tukey HSD Q statistic	Tukey HSD p-value	Tukey HSD interference
0 wt% vs 0.1 wt%	6.9962	1.0053×10^{-3}	** p < 0.01
0 wt% vs 0.5 wt%	6.8177	1.0053×10^{-3}	** p < 0.01
0 wt% vs 1 wt%	7.8426	1.0053×10^{-3}	** p < 0.01
0 wt% vs 2 wt%	4.3168	2.8784×10^{-2}	* p < 0.5
0 wt% vs 3 wt%	3.9876	0.0561	Not significant
0.1 wt% vs 0.5 wt%	0.1785	0.8999	Not significant
0.1 wt% vs 1 wt%	14.8388	1.0053×10^{-3}	** p < 0.01
0.1 wt% vs 2 wt%	11.3129	1.0053×10^{-3}	** p < 0.01
0.1 wt% vs 3 wt%	10.9838	1.0053×10^{-3}	** p < 0.01
0.5 wt% vs 1 wt%	14.6603	1.0053×10^{-3}	** p < 0.01
0.5 wt% vs 2 wt%	11.1345	1.0053×10^{-3}	** p < 0.01
0.5 wt% vs 3 wt%	10.8053	1.0053×10^{-3}	** p < 0.01
1 wt% vs 2 wt%	3.5259	0.1277	Not significant
1 wt% vs 3 wt%	3.8551	0.7227	Not significant
2 wt% vs 3 wt%	0.3292	0.8999	Not significant

Table 2: Post hock Tukey test results

The results show that most sample comparisons are statistically significant. Notably, the 1 wt% MCF sample exhibits statistically significant differences compared to all other groups. This finding suggests that the observed increase in pull-out force at 1 wt% MCF is not due to random variation but is statistically meaningful.

Nevertheless, it should be noted that five pairwise comparisons did not yield significant differences. Thus, it is important to interpret these results with caution, particularly considering the relatively high standard deviations observed.

As 1 wt.% MCF produced the optimum result, a comparison is now made with a reference sample. In this instance, as in the rheometer study, a conventional PVAc adhesive is utilized as a reference. Furthermore, the alginate mixture without additive is also demonstrated in the bar chart below.

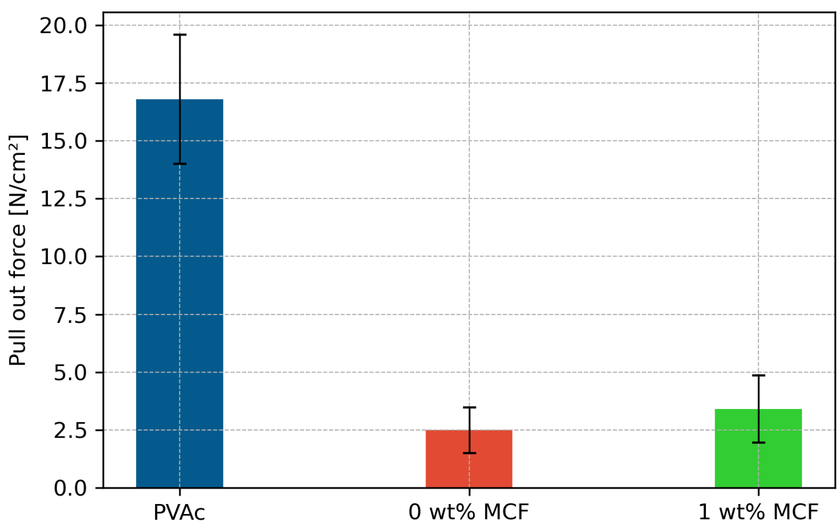

Figure 6: Mean pull-out force of PVAc (blue), Alginate with 0wt% (red) and Alg/MCF 1wt% (green) along with their standard deviation across all pages.

Figure 6 presents a comparison of the pull-out forces between PVAc, pure alginate (0 wt% MCF), and alginate with 1 wt% MCF. PVAc exhibits the highest mean pull-out force at 16.78 N/cm², followed by alginate with 1 wt% MCF at 3.41 N/cm², and pure alginate at 2.49 N/cm². These results clearly demonstrate that PVAc significantly outperforms the alginate-based adhesives in terms of adhesion strength.

However, the alginate-based systems still provide measurable adhesion, highlighting their potential for applications where renewable and biodegradable materials are preferred over synthetic adhesives.

Conclusions

In this study, the biopolymer alginate was combined with varying concentrations of micro cellulose fibers (MCF) to investigate its potential as a bio-based adhesive. Rheological characterization confirmed that increasing MCF concentrations led to higher viscosities. Pull-out tests demonstrated that the addition of MCF improved the adhesive performance of alginate, with 1 wt% MCF yielding the highest pull-out force.

Nevertheless, in direct comparison to a conventional petrochemical PVAc adhesive, the alginate-MCF formulations exhibited substantially lower adhesion strengths.

These findings suggest that while alginate-MCF adhesives currently do not match the performance of synthetic benchmarks, they offer a promising foundation for the development of renewable and biodegradable adhesive systems. Further research focusing on formulation optimization, dispersion strategies, and processing techniques is recommended to enhance their mechanical properties and broaden their potential application range, particularly in fields such as sustainable bookbinding.

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