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## COMPOSITE OF CELLULOSE-NANOFIBER-REINFORCED CELLULOSE ACETATE BUTYRATE: IMPROVEMENT OF MECHANICAL STRENGTH BY CROSS-LINKING OF HYDROXYL GROUPS

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**Abstract.** Today, biocomposites produced from a bio-based filler and bio-based matrix are a great attraction, which can present desired functionalities at a reasonable cost. In this study, cellulose laminates were prepared by using CNF as a filler and cellulose acetate butyrate (CAB) as the polymer matrix. Cellulose composite material was manufactured by sandwiching CNF reinforcement filler between CAB matrices using the hot-press technique. The cross-linking agent polyisocyanurate D376N (STABio™) was applied to improve the adhesion between the matrix and filler. The optimal manufacturing conditions (cross-linker amount, hot-press pressure, and time) were investigated. When 14.3 wt. % of the cross-linking agent to the total weight of CNF and CAB was added, the tensile strength and flexural strength were improved by 72.4% and 16.3%, respectively, compared with neat CAB. It was concluded that this increase in strength is a result of both: cross-linking between the CNF sheets as well as the cross-linking occurring at the CNF/CAB interface.

**Key words:** composite material, CAB, CNF, mechanical strength, cross-linking, urethane bond.

### Results and discussion

First, the authors prepared a laminated material by combining an acetone treated CNF (A-CNF) sheet and a CAB matrix. To increase the strength of the final material, biomass-derived cross-linking agent polyisocyanurate (D376N) was added (Fig. 1).

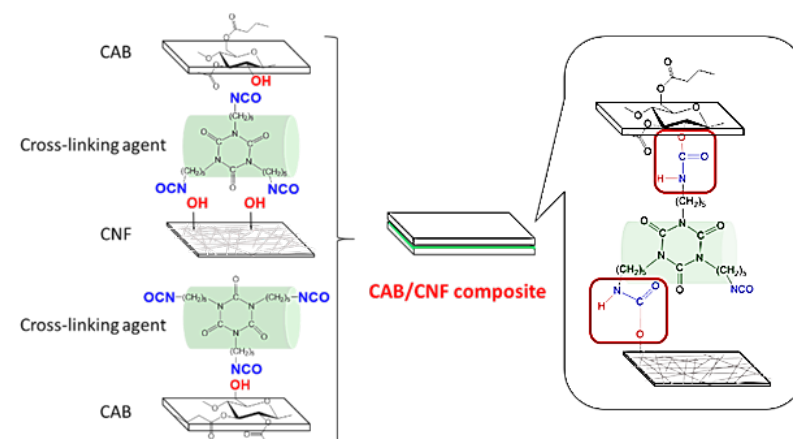


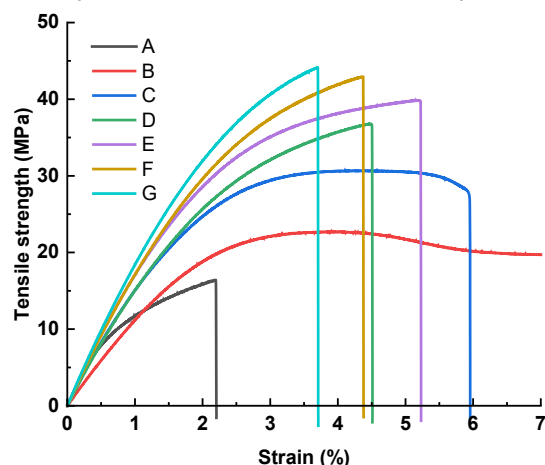
Figure 1 – CAB/A-CNF composite material development

The mechanical strength was measured to determine the appropriate cross-linking material amount and molding process conditions. The mechanical strength of the laminate was first investigated by varying the amount of crosslinking agent. Stress-strain curves obtained from tensile tests are shown in Fig. 2.

The tensile strength increased as the amount of cross-linker increased, and at 14.3 wt. % of D376N, the tensile strength was 43.1 MPa, which is 72.4% higher than for neat CAB. The tensile strength remained constant at approximately 43 MPa even when 14.3 wt. % or more of D376N was added. Cross-linking agent D376N contains three isocyanate groups. Although it can form a cyclic structure with hydroxyl groups on the same surface of CNF, remaining isocyanate groups can cross-link with other CNF surface hydroxyl groups and residual hydroxyl groups in CAB. The elastic modulus also showed a similar trend. From this experiment, it was found that 14.3 wt. % of cross-linking material is the most optimal amount for developing a high-strength laminate.

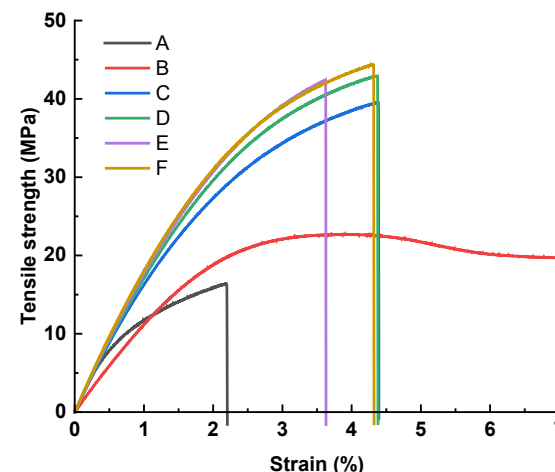
Next, the effect of varying the hot-press time was subsequently investigated: the amount of D376N was 14.3 wt. %, as determined in the previous experiment, and the hot-press pressure was 20 kN.

The obtained stress-strain curve is shown in Fig. 3. The tensile strength was slightly lower for the hot-press time of 5 min, but the values for 15 min and longer were close. The same trend was observed for the elastic modulus. From the above, the authors conclude that 15 min of hot-press time is sufficient. In the literature, the reaction time between cellulose and different isocyanates varies largely depending on the type of isocyanate and the reaction solvent system [1].

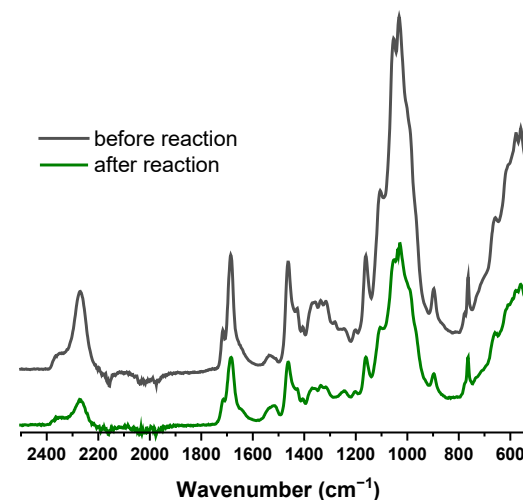


**Figure 2** – Tensile strength-strain behavior of laminated CAB/CNF with different amounts of cross-linker D376N. Samples: (A) A-CNF; (B) CAB500-5; (C) CAB/A-CNF/D376N (0 wt. %); (D) CAB/A-CNF/D376N (3.9 wt. %); (E) CAB/A-CNF/D376N (7.7 wt. %); (F) CAB/A-CNF/D376N (14.3 wt. %); (G) CAB/A-CNF/D376N (24.5 wt. %)

We investigated whether the addition of a cross-linking agent causes cross-linking between CNFs. FTIR spectra were measured to confirm the formation of urethane bonds. The results of the FTIR measurements are shown in Fig. 4. For both samples (before and after the reaction),  $\text{CH}_2$  angular vibration at  $764\text{ cm}^{-1}$ , amide II at  $1570\text{ cm}^{-1}$ , and NCO stretching vibration at  $2,248\text{ cm}^{-1}$  were observed. The intensity ratio of NCO to  $\text{CH}_2$  after the reaction



**Figure 3** – Tensile strength-strain behavior of laminated CAB/CNF/D376N for different hot-press time. Samples: (A) A-CNF; (B) CAB500-5; (C) CAB/A-CNF/D376N 5 min; (D) CAB/A-CNF/D376N 15 min; (E) CAB/A-CNF/D376N 25 min; (F) CAB/A-CNF/D376N 35 min



**Figure 4** – FTIR spectra before and after the reaction of A-CNF/D376N

decreased compared with that before the reaction, while the intensity ratio of amide II increase, confirming the formation of a urethane bond between the A-CNF/cross-linker. This is in good agreement with previously published data on cellulose cross-linking with isocyanate reagents [2].

Furthermore, the results of the tensile test (Fig. 5) show that the tensile strength of the A-CNF sheet alone was 16.5 MPa, while that of the A-CNF/D376N was 36.2 MPa, an improvement of 119%. The elastic modulus was also improved by 40.4%, from 1.93 GPa to 2.71 GPa, which confirms the reaction between the cross-linker and A-CNF surface.

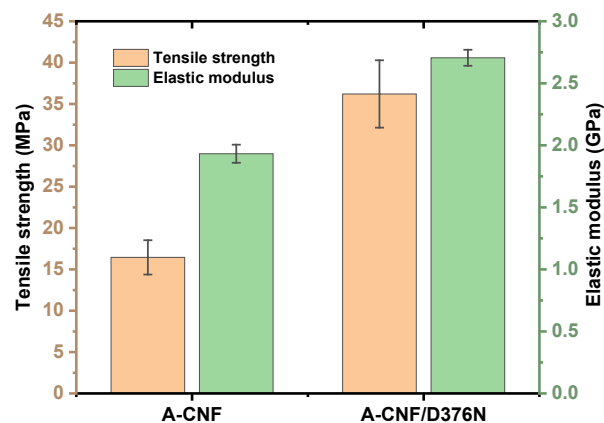


Figure 5 – Tensile strength and elastic modulus of A-CNF and A-CNF/D376N

### CONCLUSIONS

In this study, we developed cellulose composite material by sandwiching CNF reinforcement filler between CAB matrices using the hot-press technique. The optimal amount (14.3 wt. %) of cross-linking agent polyisocyanurate D376N (STABio™) was applied to improve the adhesion between the matrix and filler. The obtained composite material exhibits improved mechanical properties (tensile strength) compared with neat CAB. Finally, it was shown that

the improved mechanical properties of the CAB/A-CNF composite are due to cross-linking between A-CNF fibers as well as a reaction at the interface of CAB and A-CNF.

### References

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## ЕНЕРГЕТИЧНИЙ СТАН ПОВЕРХНІ ДИСПЕРСНИХ ОКСИДІВ

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**Анотація.** Ефективність застосування дисперсних оксидів в складі композиційних матеріалів різного функціонального призначення в значній мірі визначається фізико-хімічними властивостями їх поверхні. Не менш важливим фактором являється і стабільність останніх в процесі експлуатації. Однак дані відносно таких особливостей дуже обмежені, тому метою статті є кількісна оцінка складу, енергетичного стану та адсорбційної здатності ряду оксидів II–IV груп періодичної системи, що використовуються в якості наповнювачів або слугують складовими компонентами різних композитів.

Методами, що базуються на різних фізичних принципах (змочуваності полярними і неполярними рідинами, діелектричними властивостями, ІЧ-спектроскопія, комплексний термічний аналіз) оцінений енергетичний стан поверхні дисперсних оксидів та його зміни в процесі дії вологого середовища з мікроорганізмами.