Polyvinyl alcohol-composite films composed with modified cellulose nanowhiskers to enhancing its mechanical properties

Cristiane Spagnol[a], Elizângela. H. Fragal[a], Maria A. Witt[a], Heveline D. M. Follmann[a], Rafael Silva[a] and Adley F. Rubira[a]
[a]*Chemistry Department, State University of Maringá, Maringá, Brazil*
*afrubira@uem.br

Cellulose nanowhiskers (CWs) extracted from cotton fibers were successfully modified with distinct anhydrides structures and used as additives in poly (vinyl alcohol) (PVA) nanocomposite films. The surface modification of CWs was performed with maleic (MA), succinic (SA), acetic (AA) or phthalic (PA) anhydride to compare the interaction and action the carboxylic groups into PVA films and how these groups influence on the mechanical properties of the nanocomposites. The modified-CWs were named as CWMA, CWSA, CWAA and CWSA, according to the anhydride used (See Figure 1 to illustration).

CWs presented a high degree of crystallinity and good dispersion in water, with average length at the nanoscale. The addition of specific amounts (3, 6 and 9 wt.%) of modified-CWs increased up to 4.4 times the storage modulus (PVA88-CWSA 9 wt.% sample), as observed from dynamic mechanical analysis (DMA), compared to the bare PVA films. The significant increase in mechanical properties such as tensile strength, elastic modulus, and elongation at break showed a close relationship to the amount and chemical surface characteristics of CWs added, suggesting that these modified-CWs could be explored as reinforcement additives in PVA films.

In this way, an illustration scheme of PVA88 (88% of hydroxyl groups) composite films containing pre-determined amounts of the distinct nano-reinforcements (0, 3, 6 or 9 wt.% of modified-CWs) with the intention to improve final mechanical response is shown in Figure 1. Briefly, it has been reported that modified-CWs bearing groups such as hydroxyl (-OH) and/or carboxyl (-COOH) could increase cellulose hydrophilic character at the same time that these groups can react to each other to form covalent ester bonds, with no changes of the original CWs mechanical properties.[1]

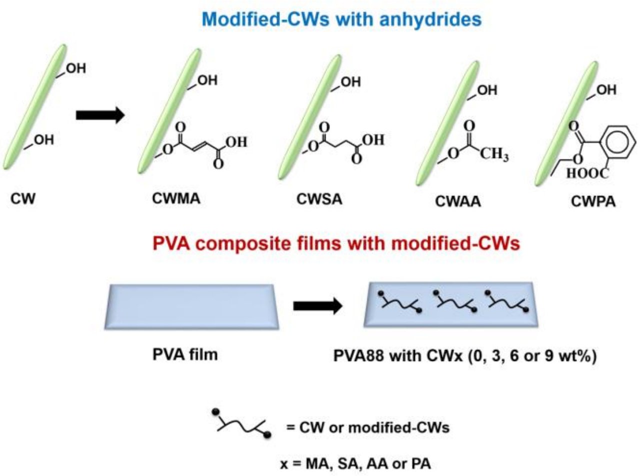

Figure 1. *Ilustration scheme of PVA88/modified-CWs nanocomposite films containing distinct amounts of cellulose additives.*

Considering the hydrophilic nature of PVA, specific chemical modification of originally insoluble CWs can improve interfacial compatibility between polymer matrix/modified-CWs enhancing mechanical properties of the final composite[2]. The CWs are extracted from cellulose fibers through hydrolysis using hydrochloric acid, which attacks the amorphous regions of cellulose keeping its crystalline regions. Such process does not accumulate/add surface charge over CWs, so –OH groups present on the cellulose chemical structure can react with anhydrides (MA, SA, AA or PA).

Mechanical analysis deals with tensile strength (kPa), elastic modulus (kPa) and elongation at break (%) of the nanocomposite films by using modified-CWs as nano-reinforcement are shown in Figure 2. The addition of 9 wt.% of CW, CWSA, and CWPA to the polymer matrix increased the tensile strength values up to 16.6, 25.8 and 20.5% with respect to the bare PVA88 films, respectively, and with addition of 6 wt. % of CWMA and CWAA increased tensile strength values up to 33.1 and 22.3%, proportionately. These results showed the influence of additive (CW) chemical modifications as well as their amount present in the PVA88 polymer matrix, providing films with higher tensile strength.

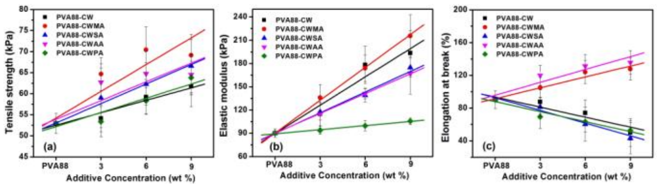

Figure 2. *(a) Tensile strength (kPa), (b) Elastic modulus (kPa) and (c) Elongation at break (%) of PVA88 nanocomposites films containing specific amounts of CW, CWMA, CWSA, CWAA, or CWPA additives (3, 6 and 9 wt. %). Note: In the X-axis, PVA88 have no additives.*

At 9 wt. % of additive, it was possible to verify an increase elastic modulus (kPa) of 114.9, 139.6, 94.1, 85.9 and 17.1% for CW, CWMA, CWSA, CWAA, CWPA, respectively.
Elongation at break (%) for CW, CWSA, and CWPA decreased down to 44.6, 52.3 and 41.6%, respectively, with the increase of bio-additive (9 wt. %), which can be the result of poor stress transfer from matrix polymer to filler resulting in stress concentration points and failure points. In short, these materials have promising applications as biodegradable composites, at the same time that modified-CWs could be explored as polymer matrices reinforcement.

References

1. M. Hakalahti et al (2015). Effect of interfibrillar PVA bridging on water stability and mechanical properties of TEMPO/NaClO2 oxidized cellulosic nanofibril films. *Carbohydr. Polym.*, 126, 78-82.
2. N. Rescignano et al (2014). PVA bio-nanocomposites: A new take-off using cellulose nanocrystals and PLGA nanoparticles. *Carbohydr. Polym.*, 99, 47-58.