NANOCRYSTALLINE CELLULOSE MODIFICATION WITH ACRYLIC ACID AND FURFURYL AMINE THROUGH DIELS-ALDER AND MICHAEL ADDITION REACTIONS

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In this work a novel method for chemical surface modification was created by grafting acrylic acid onto the surface of nanocrystalline cellulose (CNC). Furfuryl amine will then react with CNC through the Diels Alder and Michael addition reactions. This work aims to alter the CNC's surface so that it may be used with non-polar polymer matrices like PLA. Significant variations in the FT-IR spectra were detected in all samples. According to the TGA graph, CNC-AA has lower thermal stability than the neat CNC sample. According to the DSC results, modified CNC samples had lower T_{max} than neat CNC. The successful acrylic acid and furfuryl amine modification of CNC surfaces was validated by XPS spectroscopy also.

Keywords: Diels Alder, Michael Addition, Nanocrystalline cellulose, Acrylic acid, Furfuryl amine

1. Introduction

An essential structural element of plant cell walls, cellulose is the most abundant naturally occurring polymer on Earth [1]. The content of highly organized, crystalline regions and some disordered (amorphous) regions varies depending on the source of naturally occurring bulk cellulose [2]. Cellulose nanocrystals, or CNCs, are produced when the highly crystalline portions of the cellulose microfibrils are separated via mechanical, chemical, and enzymatic processes [3]. Due to the negative surface charges on its surface, CNC has strong

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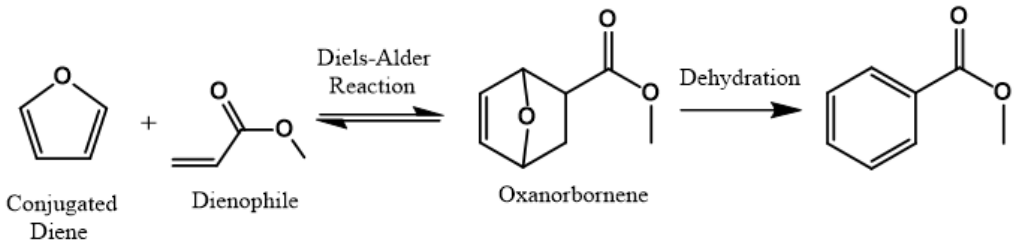
polarity and good dispersion in aqueous solutions but limited solubility in non-polar liquids [4]. As a result, surface modification and functionalization are necessary to improve CNC compatibility with non-polar environments [5].

Numerous modification methods, including physical adsorption, ion exchange of surfactants onto the CNC surface, and covalent attachment of molecules, have been employed to produce functionalized CNCs [6].

Researchers have recently become very interested in molecular covalent bonding to cellulosic nanomaterials because of the high number of hydroxyl groups on their surface, which can be involved in a variety of reactions, including amidation, urethanization, silylation, etherification, and esterification [7].

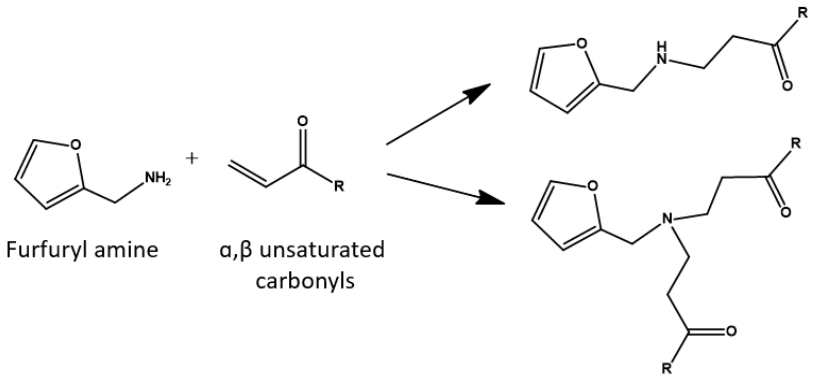
The Diels–Alder cycloaddition reaction (CNCs), which involves the interaction between an alkene and a conjugated diene leading to a cyclohexene molecule, is one of the most potent and promising methods for creating six-membered heterocyclic structures from cellulose nanocrystals.

A conjugated diene (furans or furan derivatives) and a dienophile (an alkene or an alkyne) combine to form cyclohexene by a [4+2] conjugate addition reaction. as presented in Scheme 1.



Scheme 1: Diels-Alder reaction of a conjugated diene and a dienophile [8].

The amino group in furfuryl amine may also react with a double bond in acrylic acid, a reaction known as the Michael addition, which describes the addition of a nucleophile, such as an enolate anion (Michael donor), to an activated molecule containing α, β-unsaturated carbonyl (Michael acceptor), via base catalysis [9]. Enolate is the nucleophilic donor in a Michael reaction, whereas unsaturated carbonyl is the electrophilic acceptor. Furfuryl amine is a good candidate for Diels-Alder and Michael addition reactions with acrylate groups attached to the surface of CNCs because it possesses both an amino group and a conjugated diene.



Scheme 2: Michael addition reaction between furfuryl amine and unsaturated carbonyls

With the use of dimethylformamide (DMF) as an aprotic solvent, the current work suggests a novel method for chemically modifying CNC by grafting acrylic acid onto its surface through an esterification reaction between the hydroxyl groups of CNC and the carboxyl group of acrylic acid (AA) at high temperature. Diels-Alder and Michael addition reactions are used to react the acrylic acid-modified CNC with furfuryl amine because of having a surface carbonyl group (dienophile) and a double bond. Consequently, the product shows increased dispersion in organic solvents and enhanced hydrophobicity.

2. Materials and methods

2.1 Materials

Cellulose Nanocrystal (Nanocrystalline Cellulose, CNC) was purchased from Nanography, Germany (Average Particle Size: 300–900 nm in length, 10–20 nm in width, 1.49 g/cm3 density, Cellulose Crystallinity (XRD): 92%). Acrylic acid (AA) (d:1.051 g/ml), Sulfuric acid 96%, Furfuryl amine >99% (FA) and 99.8% anhydrous N, N-dimethylformamide (DMF) was supplied from Sigma Aldrich.

2.2 Methods

A Bruker VERTEX 70 spectrometer was used to perform Fourier Transform Infrared Spectroscopy (FT-IR) spectra. A Ge crystal was used in total attenuated reflection mode (ATR), and 32 scans were recorded per spectrum at a 4 cm^{-1} resolution in the 400–4000 cm^{-1} domain.

A Netzsch 204 F1 Phoenix device was used to record non-isothermal differential scanning calorimetry (DSC) thermograms. Aluminum crucibles containing 5 mg of each sample were heated at a rate of 10°C/min to 300°C while nitrogen flow was maintained at a rate of 20 mL/min.

Using a platinum/rhodium crucible, the samples were heated at a rate of 10°C/min from room temperature to 700°C under nitrogen atmosphere (20 mL/min) for thermogravimetric analyses (TGA) on a TG 209 F1 Libra apparatus.

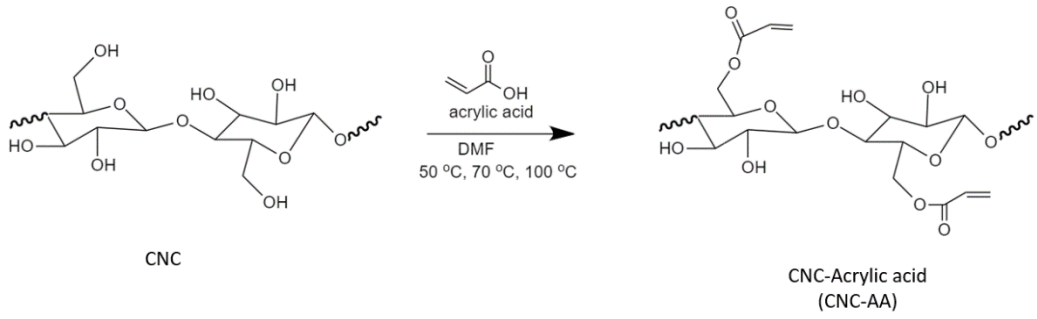
Using a monochromatic Al Ka source (1486.6 eV) and $2x10^{-9}$ mbar of pressure, X-ray photoelectron spectroscopy (XPS) analyses were carried out on a Thermo Scientific K-Alpha apparatus. By using the C1s peak at 284.8 eV as the internal standard, the binding energy was calibrated.

A HitachiTM4000plus II tabletop scanning electron microscope (SEM) (Spectral, Lidingo, Sweden) with a cooling stage and 15 kV operation was used to examine the morphological features of all the samples that were analyzed. A thin layer of electrically conductive gold was applied to the samples prior to SEM analysis in order to prevent "charging," lessen thermal damage, and enhance secondary electron emission.

3. Results and discussion

3.1 Chemical modification of CNC with Acrylic acid (CNC-AA)

A two-necked flask with a magnetic stirrer and a nitrogen gas inlet was used to disperse 1 g of commercially available CNC in 60 ml of DMF. Further on, the reaction mixture was kept under nitrogen atmosphere for 20 minutes to remove any dissolved oxygen and avoid acrylic acid polymerization by free radicals. The next step involved adding 0.4 ml of acrylic acid and 2 ml of concentrated H_2SO_4 as catalyst under constant stirring. The reaction took place at 100ºC for 4 hours. Centrifugation was used to remove the CNC-Acrylate from the suspension after the reaction was complete and was further purified and dried at room temperature The obtained product will be further reffered as CNC-AA.

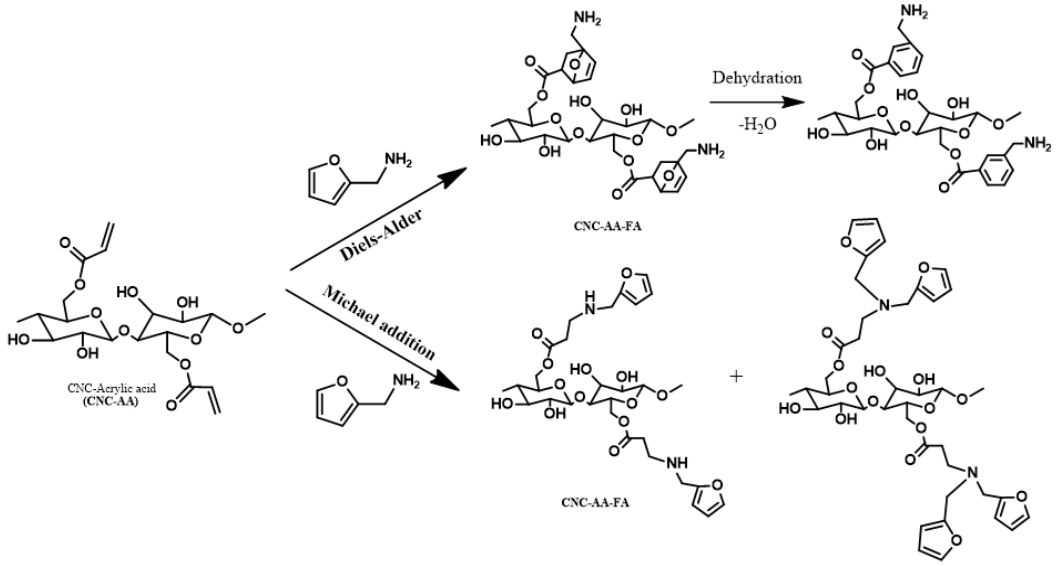


Scheme 3. Acryl acid-modified cellulose nanocrystal synthesis reaction pathway.

3.2 Reaction of CNC-AA with Furfuryl amine

Using a magnetic stirrer, 30 mL of DMF were mixed with 0.3 grams of previously synthesized CNC-AA. Further on, 0.5 g of furfuryl amine were added along with 0.1g of $AlCl_3$ as Lewis acid catalyst and the reaction was kept at 60ºC

for 4 hours. At the end of the synthesis, the CNC-Acrylic Acid-Furfuryl amine (CNC-AA-FA) product was separated from the reaction medium, washed for unreacted products removal and dried at room temperature. The final chemical structures are presented in Scheme 4.



Scheme 4. Reaction of CNC-Acrylic acid with furfuryl amine through Diels-Alder and Michael addition reactions

3.3. Fourier Transformed Infrared Spectrometry (FT-IR)

Fig. 1 shows the corresponding spectra of the FT-IR analysis of the chemical structure of cellulose nanocrystals (CNCs) and modified CNC samples. After modification with (AA) and (FA) significant changes in the spectra were observed within the region between 1200 and 1800 cm^{-1}.

Analyzing the spectra, all three samples present common peaks characteristic for cellulose chemical structure as follows: The OH's stretching and bending vibrations are responsible for the peaks between 3400 and 3300 cm^{-1}, while CH stretching is responsible for the peaks around 2900 and 2800 cm^{-1}, and CH_2 bending vibration is the cause of the peak around 1400 cm^{-1}. This absorption peak in that region is called crystalline band [10].

Regarding the CNC sample, the acetyl group of hemicellulose's -COO vibration is attributed to the peak at 1204 cm^{-1} [11]. Cellulose's stretching vibrations of C–O were identified as the source of the signals at 1057 cm^{-1} and 1162 cm^{-1} [12,13]. The saccharide structural unit's ring bending vibrations are detected at 1109 cm^{-1}, while C-O-C stretching is detected at 1034 cm^{-1} [14]. C-H

bending is responsible for the peak at about 1360 cm^{-1}, which also causes typical absorption at about 1280 and 1204 cm^{-1} [15].

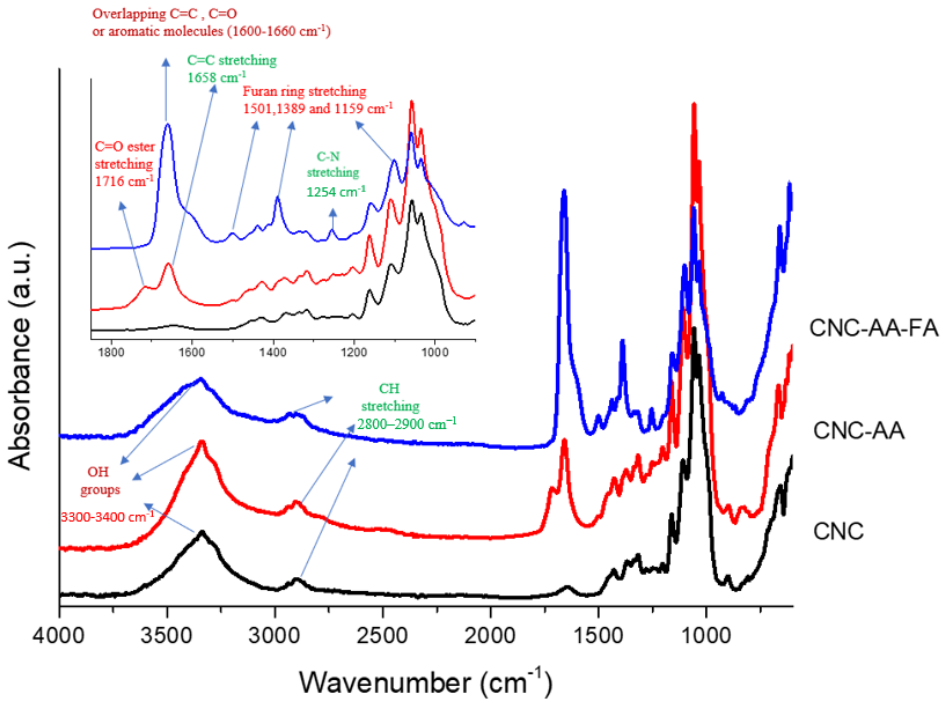


Fig. 1. FTIR spectra of neat CNC, CNC-AA and CNC-AA-FA samples

Major absorption peaks at 1716 cm^{-1} and 1658 cm^{-1}, respectively, resulting from C=O (carbonyl or ester stretching bond) and C=C stretching vibrations, are seen in the CNC-AA sample after the chemical modification, indicating the successful grafting of the AA on the CNC structure [16].

From the CNC-AA-FA spectrum is observed that the ester stretching from 1716 cm^{-1} is on longer present, but it may overlap with a strong peak around 1660 cm^{-1}. Furan ring stretching and –C–O–C–ether stretching for furan groups are represented by the peaks at 1501 cm^{-1} and 1159 cm^{-1}, respectively [17-18]. The five-member heteroaromatic ring with double bonds exhibits characteristic signals for bending and stretching around 1600-1660 cm^{-1}, 1500 cm^{-1}, and 1389 cm^{-1} [19]. The high intensity signals from 1650 to 1600 cm^{-1} may be attributed to double bonds or aromatic molecules [20]. The stretching vibrations of C-N are linked to the peak at approximately 1254 cm^{-1} [21]. These peaks characteristic for furan rings remained intact on the surface of CNC, indicating that some of furfuryl amine molecules reacted through Michael addition reaction.

In the case of the Diels-Alder reaction that took place on the surface of the CNC, we would get two distinct peaks in the 3400-3300 and 3330-3250 cm^{-1} ranges, showing the presence of the primary amine group. However, the presence of a significant number of -OH groups on the surface of cellulose molecules may result in overlap and cause the disappearance of N-H peaks in the 3400-3250 cm^{-1} area.

3.4 X-ray Photoelectron Spectroscopy (XPS)

The elemental composition analysis of the CNC/CNC-AA and CNC-AA-FA samples using XPS research verified the successful acrylic acid and furfuryl amine modification on CNC surfaces. As indicated in the Table 1, the fraction of C atoms increases from 61 to 62 while the percentage of oxygen atoms slightly decreases from 39% to 38%, suggesting that acrylic acid effectively reacts with the OH groups and it is uniformly attached on the surface of CNC.

When furfuryl amine is reacted with CNC-AA sample, the percentage of C and O elements decreases, due to the presence of the N atoms from the furfuryl amine structure, which is a very strong indicator that the furfuryl amine reacted with the acrylic group on the surface of CNC via Diels-Alder or Michael Addition reactions.

The XPS spectrum of CNC-AA-FA, as illustrated in Fig. 2(d), clearly reveals the presence of C1s, O1s, and N1s peaks, whereas the XPS spectra of CNC and CNC-AA only demonstrate C1s and O1s peaks. The successful modification of the furfuryl amine on CNC-AA is indicated by the appearance of the N1s peak. Furthermore, the deconvolution of CNC-AA-FA's high resolution C1s spectrum reveals three peaks at 288.0, 286.5, 284.8, and 284.5 eV, which stand for C=N/C=O, C-O/C-N, C-C/C-H, and C=C, respectively [22].

Two peaks that correspond to C=O (530.98 eV) and C–O–H/C–O–C (531.08 eV) can be seen in the deconvolution of the O1s peak (Fig. 2f) [23]. In addition, the high resolution N1s spectrum of CNC-AA-FA (Fig. 4e) demonstrates the presence of primary amines (–N = 399.5 eV) and tertiary amines (–N-C3, 401.7 eV) [24]. The presence of primary, secondary, or tertiary amines in the CNC-AA-FA sample is associated with the Diels Alder and Michael addition products. When CNC-AA reacts with furfuryl amine via the Diels-Alder reaction, the result is primary amine; however, when the reaction proceeds by the Michael Addition pathway, the products are secondary and tertiary amine rather than primary amine. Because XPS confirmed the appearance of primary and tertiary products, it may be concluded that both Diels Alder and Michael addition reactions happened.

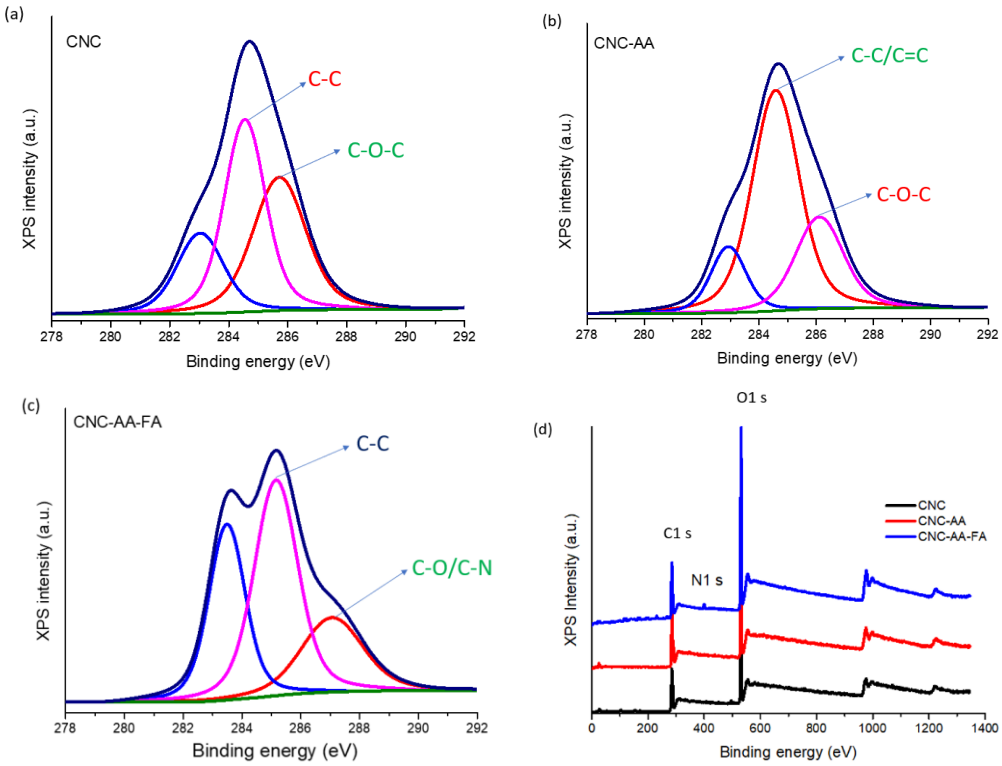
By examining the intensity of primary (4748.81 counts/s) and tertiary amines (3940.89 counts/s) in XPS data, we can estimate the fraction of the products. Thus, it was observed that the Diels-Alder: Michael addition ratio product formation is 1:2, which means that about 54.5% of the product is obtained through

Diels-Alder reaction and 45.5% is a Michael addition product. All these results have demonstrated that both acrylic acid and furfuryl amine have been used successfully to modify the surface of CNC.

Table 1

Elemental composition of CNC and its derivatives

Sample	C at. %	O at. %	N at. %
CNC	61	39	-
CNC-AA	62	38	-
CNC-AA-FA	57	35	8



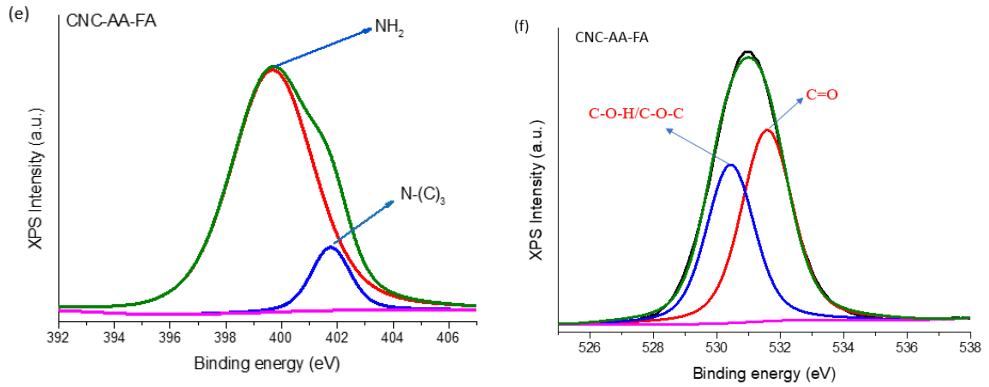


Fig. 2. High-resolution C1s spectral deconvolution from XPS of a) neat pure CNC b) CNC-AA c) CNC-AA-FA derivatives and d) full range of XPS spectra of all samples e) The deconvolution of N1s spectra of CNC-AA-FA f) The deconvolution of O1s spectra of CNC-AA-FA

3.5 Thermogravimetric analysis (TGA)

The TGA curves and the derivative thermogravimetric curves (DTG) of every CNC product that was examined in the 25 °C to 600 °C range are reported in Fig. 2, while the primary thermal parameters from thermogravimetric investigations are listed in Table 2.

Table 2

Thermal parameters for CNC and its derivatives

Sample	$T_{d3\%}$ (°C)	$T_{d5\%}$ (°C)	$T_{d10\%}$ (°C)	$T_{d30\%}$ (°C)	T_{max} (°C) (from DTG)	Residual mass (%)
CNC	273.1	284.2	291.7	303.4	305.8	20.65
CNC-AA	71.6	93.8	202.6	257.3	258.2	22.14
CNF-AA-FA	55.2	64.3	81.4	215.3	263.7	25.02

All three samples (CNC, CNC-AA, and CNF-AA-FA) have unique thermal properties, as can be seen from the thermograms shown in Fig. 3. With regard to the CNC sample, the initial 3% weight loss was most likely caused by thermal disintegration of the amorphous phase, which occurs just before the crystalline phase degrades at 273°C [25], the onset degradation temperature ($T_{d10\%}$) is at around 292°C and the maximum degradation temperature at approximately 306°C. The residue at 800°C of the CNC samples was around 21%.

In the case of the CNC-AA sample the onset degradation temperature ($T_{d10\%}$) is at around 203°C and the maximum degradation temperature at approximately 258°C. Compared with neat CNC, CNC-AA displays decreased

thermal stability. This result is related to the presence of acrylate group on the surface of CNC, which might accelerate the degradation of cellulose nanocrystal.

Since the TGA and derivate thermogravimetric analysis curves for CNC-AA only show one peak, this is a strong proof that the AA is covalently linked to the CNCs and no other by products are found in the intermediary compound. The onset of thermal degradation has decreased from 292°C for neat CNCs to 203°C for the CNC-AA.

CNC-AA-FA exhibits two phases of thermal loss: the breakdown of FA is linked to the first weight loss (approximately 90°C), while the degradation of acrylic acid is linked to the second weight loss (approximately 260°C).

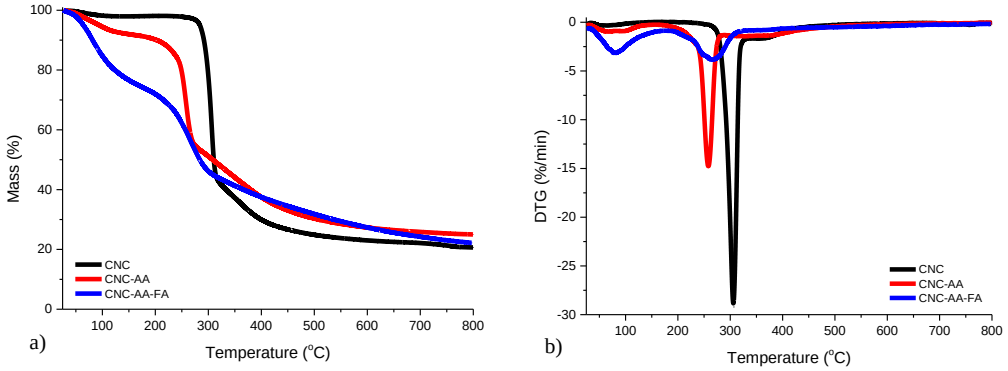


Fig. 3. a) TGA curves and b) the derivative thermogravimetric curves (DTG) of each CNC samples in the range of 25°C - 600°C

3.6 Differential Scanning Calorimetry (DSC)

In addition to TGA, the heat degradation of cellulose can also be examined using the DSC curves, as shown in Fig. 4, and Table 3 reports the DSC data for all CNC samples. All of the examined samples' broad endothermic signals, which range from 60 to 90°C, show how heat is absorbed during the evaporation of water.

The transition temperature displayed by the DSC spectrum must be considered when deciding whether a material will lose its structure after heating [26].

This demonstrates that neat CNC sample has the greatest degradation temperature which is 304.1°C among all samples. On the other hand, CNC-AA-FA sample (T_{max2} = 287°C) has a greater degradation temperature than the CNC-AA sample, which has a T_{max2} of 277.4°C.

The covalently linked molecules on the surface of modified CNCs induce lower transition temperatures than neat CNCs. Different melting enthalpy values of the samples demonstrate chemical modification.

The thermal degradation shown in the DSC graph between 200 and 300°C are correlated with the TGA values as well.

Table 3

DSC data of CNC and its derivatives

Sample	ΔH_1 (J/g)	T_{max1} (°C)	ΔH_2 (J/g)	T_{max2} (°C)
CNC	147.9	60.5	313.0	304.1
CNC-AA	175.4	75.6	240.5	277.4
CNF-AA-FA	210.9	78.0	227.8	287.0

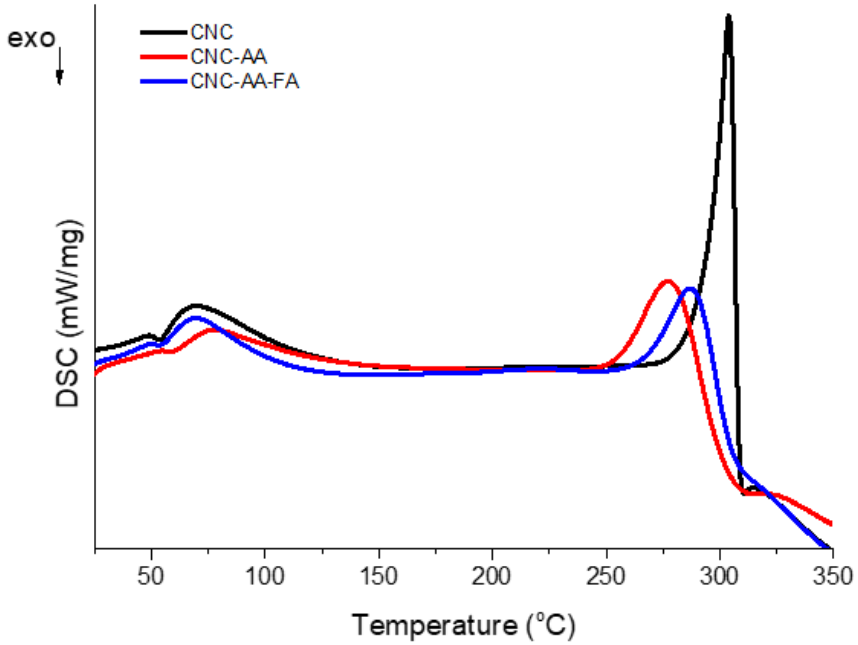


Fig. 4. DSC curves of all samples.

3.7 Scanning Electron Microscopy (SEM)

CNC morphology was examined using SEM both before and after modification. Fig. 5 illustrates the morphology of the neat CNC, CNC-AA, and CNC-AA-FA samples.

The morphology of the neat CNC samples is shown in Fig. 5a and b. The micrographs show that the commercial CNC sample has a spherical shape rather than rod like structure. Figs. 5c and d show that when CNC is treated with acrylic acid, the spherical CNC structures agglomerate and tend to form a more stiff and dense structure. Agglomeration may occur when particles are brought near together during solvent evaporation [27]. Fig. 5e and f show the further modification of CNC-Acrylic acid samples with Furfuryl amine.

Fig. 5c and 5e show that the agglomerated structure of CNC-AA is reduced by the reaction of furfuryl amine and produced more irregular and ununiform structure.

We may conclude that CNC samples agglomerate during the acrylic acid reaction, and that the subsequent reaction with furfuryl amine decreased agglomeration due to the hydrophobic interactions on the surface of CNC samples.

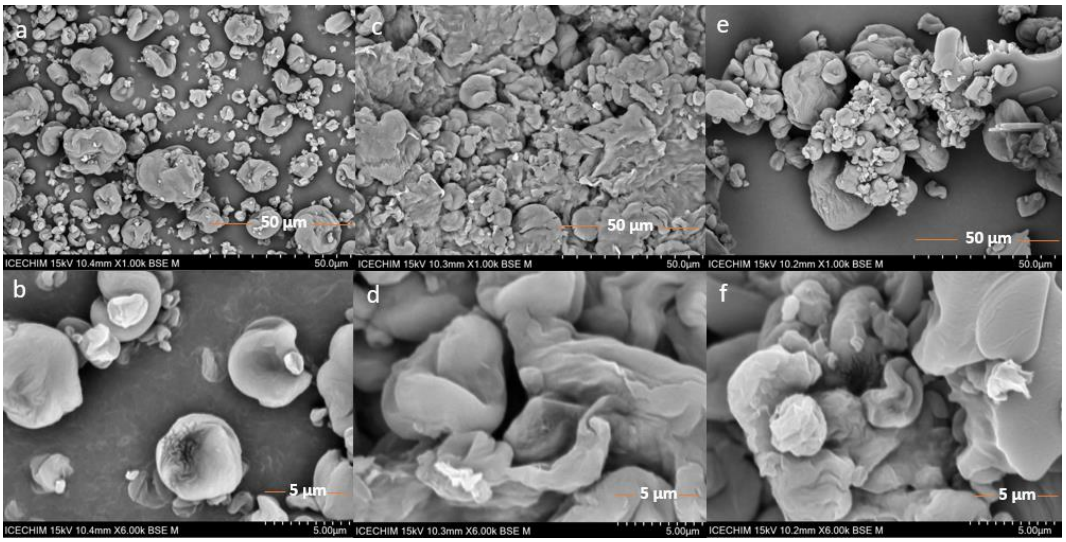


Fig. 5. SEM samples of a,b) neat CNC c,d) CNC-AA e,f) CNC-AA-FA

4. Conclusions

1. After CNC is modified with acrylic acid (AA) and Furfuryl amine (FA) significant changes in the FT-IR spectra were observed within 1200 cm^{-1} and 1800 cm^{-1}. The significant absorption peaks that corresponded to the new C=O (carbonyl double or ester stretching bond) and C=C stretching vibrations demonstrated the formation of CNC-AA. CNC-AA-FA modification was demonstrated by the vibrations observed at around 1600-1660 cm^{-1}, 1500 $cm^{-1}$and 1389 cm^{-1} which are the characteristic bands and stretches of furan ring.

2. Comparing CNC-AA to the neat CNC sample, the TGA graph showed that CNC-AA had less thermal stability. The acrylate group that is present on the surface of the CNC may be responsible for this result by accelerating the cellulose nanocrystal's degradation. CNC-AA-FA showed two weight losses, around 90°C and 260°C associated with the degradation of furfuryl amine and acrylic acid respectively.

3. According to the DSC graph, modified CNC samples had lower T_{max} than neat CNC, but covalent attachment should increase the T_{max}. This might be

attributed to an increase in the ratio of amorphous composition following the chemical modification compared to CNC, which is more crystalline.

4. The elemental composition analysis of three samples using XPS spectroscopy confirmed the successful acrylic acid and furfuryl amine modification on CNC surfaces. Because XPS confirmed the existence of primary and tertiary amine products, we may conclude that both Diels Alder and Michael addition reactions occurred.

5. SEM examination of the samples demonstrates that the surface uniformity of CNC has been altered because of the functional groups linked to the surface of CNC.

R E F E R E N C E S

[1] George, J., & Sabapathi, S. N. (2015). Cellulose nanocrystals: synthesis, functional properties, and applications. Nanotechnology Science and Applications, 8, 45-54. https://doi.org/10.2147/NSA.S64386

[2] Newman, R. H., & Hemmingson, J. A. (1995). Carbon-13 NMR distinction between categories of molecular order and disorder in cellulose. Cellulose, 2, 95-110

[3] Domingues, R. M., Gomes, M. E., & Reis, R. L. (2014). The potential of cellulose nanocrystals in tissue engineering strategies. Biomacromolecules, 15, 2327-2346.

[4] Habibi, Y., Lucia, L. A., & Rojas, O. J. (2010). Cellulose Nanocrystals: Chemistry, Self-Assembly, and Applications. Chemical Reviews, 110, 3479-3500

[5] Eichhorn, S. J. (2011). Cellulose nanowhiskers: promising materials for advanced applications. Soft Matter, 7, 303

[6] Hu, Z., Berry, R. M., Pelton, R., & Cranston, E. D. (2017). One-Pot Water-Based Hydrophobic Surface Modification of Cellulose Nanocrystals Using Plant Polyphenols. ACS Sustainable Chemistry & Engineering, 5(5), 5018-5026

[7] Eyley, S., & Thielemans, W. (2014). Surface modification of cellulose nanocrystals. Nanoscale, 6, 7764-7779

[8] Mahmoud, E., Yu, J., Gorte, R. J., & Lobo, R. F. (2015). Diels–Alder and Dehydration Reactions of Biomass-Derived Furan and Acrylic Acid for the Synthesis of Benzoic Acid. ACS Catalysis, 5(11), 6946-6955. https://doi.org/10.1021/acscatal.5b01892

[9] Mather, B. D., Viswanathan, K., Miller, K. M., & Long, T. E. (2006). Michael addition reactions in macromolecular design for emerging technologies. Progress in Polymer Science, 31(5), 487-531. https://doi.org/10.1016/j.progpolymsci.2006.03.001

[10] Khalil, H. P. S. A., Ismail, H., Rozman, H. D., & Ahmad, M. N. (2001). Effect of acetylation on interfacial shear strength between plant fibers and various matrices. European Polymer Journal, 37(5), 1037-1045. https://doi.org/10.1016/S0014-3057(00)00199-3

[11] Reddy, C. E., Albanito, L., De Marco, P., Aiello, D., Maggiolini, M., Napoli, A., & Musti, A. M. (2013). Cell Death and Disease, 4, e852. https://doi.org/10.1038/cddis.2013.381

[12] Xiao, B., Sun, X., & Sun, R. (2001). Chemical, structural, and thermal characterizations of alkali-soluble lignins and hemicelluloses, and cellulose from maize stems, rye straw, and rice straw. Polymer Degradation and Stability, 74, 307–319

[13] Bassett, K. H., Liang, C. Y., & Marchessault, R. H. (1963). The infrared spectrum of crystalline polysaccharides. IX. The near-infrared spectrum of cellulose. Journal of Polymer Science Part A, 1, 1687–1692

[14] Zaltariov, M.-F., Filip, D., Varganici, C.-D., & Macocinschi, D. (n.d.). ATR-FTIR and Thermal Behavior Studies of New Hydrogel Formulations Based on Hydroxypropyl Methylcellulose/Poly (Acrylic acid) Polymeric blends "Petru Poni" Institute of Macromolecular Chemistry, 41A, Gr. Ghica-Voda Alley, 700487, Iasi, Romania

[15] Ul-Islam, M., Ha, J. H., Khan, T., & Park, J. K. (2013). Carbohydrate Polymers, 92, 360–366

[16] Correia, M., Lopes, J., Silva, R., MartinsRosa, I., Henriques, A. G., et al. (2016). FTIR Spectroscopy - A Potential Tool to Identify Metabolic Changes in Dementia Patients. Journal of Alzheimers & Neurodegenerative Diseases, 2, 007

[17] Kavitha, A. A., Choudhury, A., & Singha, N. K. (2006). Controlled Radical Polymerization of Furfuryl Methacrylate. Macromolecular Symposia, 240, 232-237. https://doi.org/10.1002/masy.200650828

[18] Tarducci, C., Badyal, J. P. S., Brewer, S. A., & Willis, C. (2005). Diels–Alder chemistry at furan ring functionalized solid surfaces. Chemical Communications, 406-408. https://doi.org/10.1039/B412906G

[19] Colthup, N. B., Daly, L. H., & Wiberley, S. E. (1975). Introduction to Infrared and Raman Spectroscopy. New York: Academic Press

[20] Nandiyanto, A. B. D., Oktiani, R., & Ragadhita, R. (n.d.). How to Read and Interpret FTIR Spectroscopy of Organic Material. Departemen Kimia, Universitas Pendidikan Indonesia, Jl. Dr. Setiabudi no 229 Bandung 40154, Indonesia

[21] Romano, E., Castillo, M., Pergomet, J., Zinczuk, J., & Brandán, S. (2013). Synthesis, Structural Study and Spectroscopic Characterization of a Quinolin-8-Yloxy Derivative with Potential Biological Properties. Open Journal of Synthesis Theory and Applications, 2(1), 8-32. https://doi.org/10.4236/ojsta.2013.21002

[22] Chao, C., Liu, J. D., Wang, J. T., Zhang, Y. W., Zhang, B., et al. (n.d.). Surface modification of halloysite nanotubes with dopamine for enzyme immobilization. ACS Applied Materials & Interfaces, 5, 10559-10564. https://doi.org/10.1021/am4022973

[23] Chen, C. M., Huang, J. Q., Zhang, Q., Gong, W. Z., Yang, Q. H., Wang, M. Z., & Yang, Y. G. (2012). Carbon, 50, 659-667

[24] Yu, Y., Shapter, J. G., Popelka-Filcoff, R., Bennett, J. W., & Ellis, A. V. (n.d.). Copper removal using bio-inspired polydopamine coated natural zeolites. Journal of Hazardous Materials, 273, 174-182. https://doi.org/10.1016/j.jhazmat.2014.03.048

[25] Taflick, T., Schwendler, L. A., Rosa, S. M. L., Bica, C. I. D., & Nachtigall, S. M. B. (2017). Cellulose nanocrystals from acacia bark – influence of solvent extraction. International Journal of Biological Macromolecules, 101, 553–561

[26] Antarat, C., Sirathanarun, P., Songserm, W., SRINORNATE, W., & DAENGPROM, S. (2013). A Simple and Rapid HPLC Technique for Determination of Arecoline in Areca Nut (Areca catechu L.) Extract. Walailak Journal of Science and Technology. https://doi.org/10.2004/wjst.v10i1.439

[27] Faraj, H., Sollogoub, C., Guinault, A., Gervais, M., Bras, J., Salmi-Mani, H., Roger, P., Le Gars, M., & Domenek, S. (2021). A comparative study of the thermo-mechanical properties of polylactide/cellulose nanocrystal nanocomposites obtained by two surface compatibilization strategies. Materials Today Communications, 29, 102907. ISSN 2352-4928