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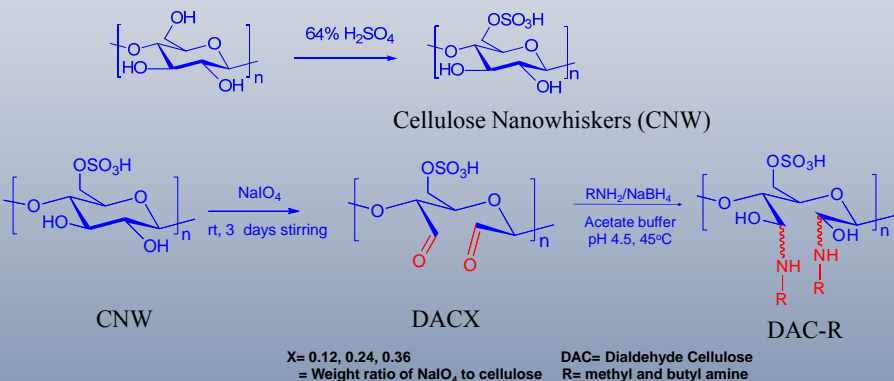
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Abstract

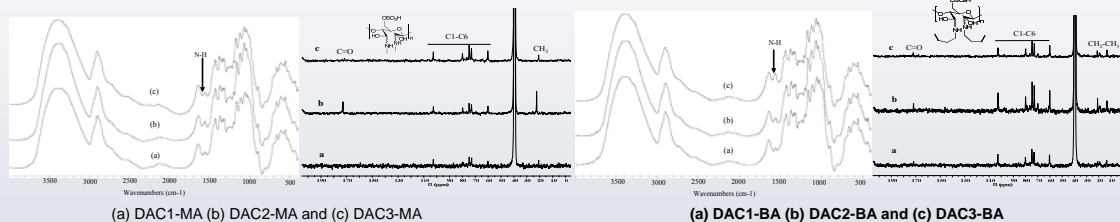
In the present work, cellulose nanowhiskers were chemically modified using primary amines via an oxidation-reduction scheme. Nanowhiskers resulting from 64% sulfuric acid hydrolysis of softwood pulp were regioselectively oxidized using 2.80-8.40 mmols of sodium periodate per 4g of whisker. Changes in the aldehyde content of the whiskers was monitored by copper number titration which indicated corresponding increase in carbonyl content (0.12-0.16 mmols/g) of the resulting dialdehyde products and this was further evidenced by FT-IR spectroscopy. The dialdehyde cellulose nanowhiskers were grafted with methyl and butyl amine through Schiff base reaction to obtain their amine derivatives in 92-95% yield. These derivatives were characterized by FT-IR, NMR, and AFM in order to study their physical and chemical properties. ¹³C NMR spectra confirmed the reduction reaction of amines to carbonyl group which was also supported by copper number titration and FT-IR spectroscopy. Morphological integrity, crystallinity and birefringence behavior of the nanowhiskers was maintained after chemical modification as studied by AFM, solid-state ¹³C NMR spectra, and observed through polarized films respectively.

Experimental

Periodate oxidation and reductive-amination scheme of cellulose nanowhiskers



FT-IR and NMR Spectra of Aminated Cellulose Nanowhiskers

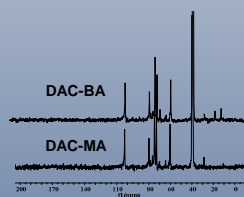
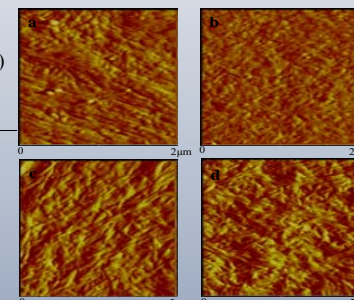


Carbonyl content of amine grafted nanowhiskers

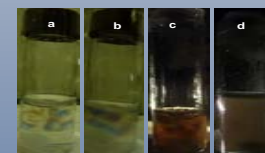
Samples	Initial carbonyl content (mmol g ⁻¹)	Carbonyl content (1:5 eq amines) (mmol g ⁻¹)	Carbonyl content (1:20eq amines) (mmol g ⁻¹)
DAC1	0.12	0.07	0.002
DAC2	0.14	0.06	0.001
DAC3	0.16	0.06	0.001

Crystallinity index of cellulose nanowhiskers before and after chemical modification

Samples	Crystallinity Index (CrI)
CNWs	71.70
DAC1	70.70
DAC2	70.40
DAC3	73.20
DAC3-MA	70.60
DAC3-BA	72.40



- ⇒ FT-IR and NMR spectra clearly shows the presence of grafted amines in nanowhisker
- ⇒ NMR spectra and Cu²⁺ confirms the residual aldehyde groups after adding 1:5 eq. amines to the whisker
- ⇒ Excess of amine compounds were required for complete reaction of aldehydes

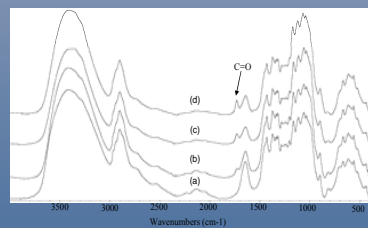


Flow birefringence behavior viewed through cross polarized films (a) whisker (b) DAC3 (c) DAC3-MA (d) DAC3-BA.

Results and Discussion

Carbonyl content of oxidized cellulose nanowhiskers

Samples	NaIO ₄ /CNW (w/w)	Carbonyl content (mmol g ⁻¹)
CNWs	0.0	0.006
DAC1	0.12	0.12
DAC2	0.24	0.14
DAC3	0.36	0.16



FT-IR spectra of (a) CNW (b) DAC1 (c) DAC2 (d) DAC3

- As the ratio of sodium periodate to cellulosic fiber increased the carbonyl group content of oxidized fiber also increased
- The characteristic band for the carbonyl group of DAC was observed at 1736 cm⁻¹ in FT-IR spectra and the intensity of this band is increasing with the level of oxidation

Conclusions

- Cellulose nanowhiskers obtained by sulfuric acid hydrolysis of bleached softwood pulp were successfully grafted with methyl and butyl amines through the combination of periodate oxidation and reductive-amination reaction.
- Interestingly, the modified whiskers were found to be soluble in DMSO even at a low content of amine groups, as a consequence effective grafting of amines to whiskers was demonstrated by ¹³C NMR with additional evidence from FTIR and Cu²⁺ titration experiments.
- The grafting procedure modifies cellulose nanowhiskers without any major change in morphology, crystallinity, and birefringence behavior.

Acknowledgement

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