DEVELOPMENT OF NANOCRYSTALLINE CELLULOSE FOR PERSONAL HOME CARE APPLICATIONS

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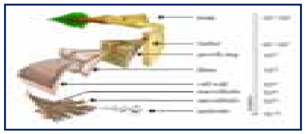
INTRODUCTION

NANOCRYSTALLINE CELLULOSE (NCC)

NCC is a rod-like crystalline polymer (Fig 1) extracted from woody biomass using sulphuric acid hydrolysis. During acid hydrolysis, the sulphate groups formed on the NCC render a negative charge to the NCC surface providing steric stabilization to the NCC rods such that NCC aqueous solutions (Fig 2) are extremely stable. It has unique strength and distinctive optical/conductive/magnetic properties. It has numerous potential applications in the form of aqueous suspension (Fig 2) or gels (Fig 3).

From Woods to Nanotechnologies



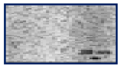


Fig 1. TEM image of NCC

Nanocrystalline Cellulose Production

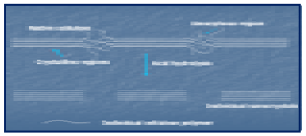


Fig 2. NCC Aqueous suspension

Fig 3. 7% NCC gel

APPLICATIONS

STRENGTH
- Paper & Packaging
- Textiles
- Composite Materials

Fig 4. Surface Nucleation on NCC substrate

OPTICAL PROPERTY
- Iridescent Pigments
- Cosmetics
- Additive in Paints

Fig 5. Iridescent Discs

HIGH SPECIFIC SURFACE AREA
- Catalyst Substrates
- Coating
- Formulation

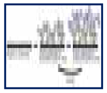


Fig 6. Multilayer Coating using NCC

SELF ASSEMBLY
- Reinforcement layers
- Biomimetic structures

Fig 7. Self assembled layers

RESEARCH OBJECTIVES

- Study the binding interaction of NCC with an oppositely charged surfactant for personal home care applications which requiring surfactant formulations for e.g. conditioners
- Steric stabilization (PEGylation) of aqueous NCC suspensions to prevent phase separation in the presence of an oppositely charged surfactant
- Cationic surface functionalization of NCC to make the NCC surface more polyamphoteric

INSTRUMENTATION

Isothermal Titration Calorimetry

Fig 8. ITC Technique measures thermodynamic heat changes as a ligand is titrated into a titrant

Surface Tensiometry

Fig 9. Computer controlled device for continuous measurement of surface tension

SURFACTANT BINDING STUDIES

Since NCC has a negatively charged surface, we studied its interaction with an oppositely charged surfactant (TTAB). A study of this kind would be highly beneficial for cosmetic applications like hair-conditioning. Fig. 10 shows a negatively charged hair surface being covered with a positively charged polyelectrolyte used in hair-conditioners. We have studied the NCC-TTAB interactions using two techniques:

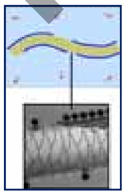


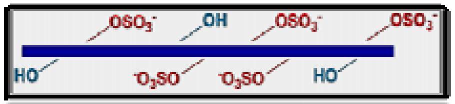
Fig 10. Polyelectrolytes for Hair-conditioning

Isothermal Titration Calorimetry
- Binding interaction in bulk

Surface Tensiometry
- Interaction at liquid-air interface

Tetradecyl Trimethyl Ammonium Bromide (TTAB)

Nanocrystalline Cellulose (NCC)



SURFACTANT BINDING - RESULTS

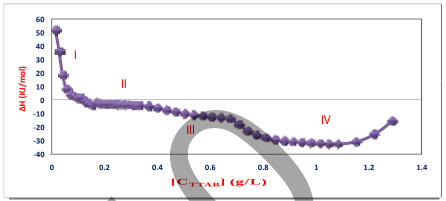


Fig 11. ITC Binding Curve for Titration of TTAB into NCC

Fig. 11 shows 4 distinct regions of interaction
1. Electrostatic interaction between TTAB and NCC
2. Reorganization of the adsorbed TTAB molecules on NCC
3. Formation of TTAB micelles on NCC substrate (Polymer Induced Micellization)
4. Bulk micellization of TTAB

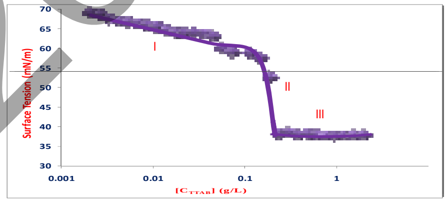


Fig 12. Surface Tension Curve for Titration of TTAB into NCC

Fig. 12 shows 3 distinct regions of interaction
1. TTAB-NCC complexes formed at the interface (due to electrostatic attraction) reducing the surface tension
2. Saturation of the entire interface with TTAB-NCC complexes leading to sudden drop in surface tension
3. TTAB bulk micellization

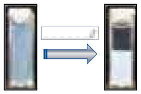


Fig 13. Phase Separation of NCC in the presence of TTAB

During production, negative charges formed on NCC provide electrostatic stabilization to an NCC suspension in water. But, when we add TTAB surfactant to an NCC suspension, destabilization occurs due to which we see a clear phase separation (Fig 13). This occurs due to formation of large aggregates driven by hydrophobic interactions between the adsorbed TTAB chains.

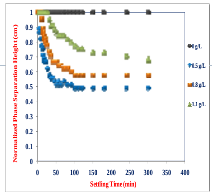


Fig 14. Phase Separation Height vs. time

Fig. 14 shows the measurement of phase separation heights with time. We observed that more phase separation was observed at lower surfactant concentrations. But as the surfactant concentration nears that of the CMC, then we observe lower phase separation due to two competing interactions:
1. Bulk micellization of TTAB
2. Hydrophobic flock formation

STERIC STABILIZATION (PEGYLATION)

PEGMA (M.W 2080) was grafted on the NCC surface using free-radical method (Fig 15 a). ITC result (Fig 15 b) shows that the presence of PEG delays all transition points for NCC-PEG(X1) sample and thereafter the transition point for polymer induced micellization vanishes for NCC-PEG(X3) & NCC-PEG(X5). This result confirms that PEG grafted on NCC prevents the flocculation of NCC suspensions in the presence of TTAB surfactant.

Fig 15. (a) Grafting PEG on NCC

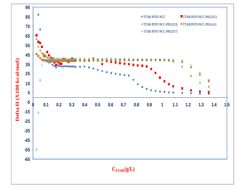


Fig 15. (b) ITC Curves for NCC-PEG samples with different amounts of PEG

CATIONIC SURFACE FUNCTIONALIZATION

This synthesis technique involves the functionalization of NCC with amino groups such that the NCC surfaces are capable of possessing positive charges. This is due to the protonation of amino groups at low pH thus imparting a positive charge on the NCC surface. Hence, NCC which naturally possesses negative charges on its surface is now capable of exhibiting positive charges at low pH, showing a typical polyamphoteric behavior.

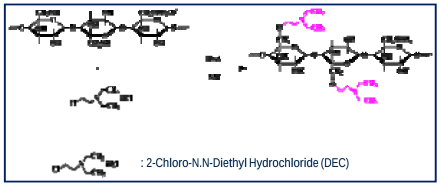


Fig 16. Reaction Scheme for Surface Cationization of NCC

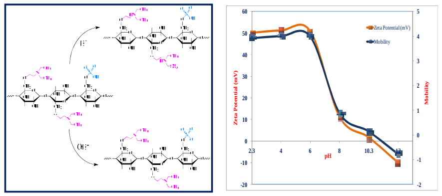


Fig 17. (a) pH Controlled Surface Functionalization of NCC (b) Zeta Potential measurements showing positive charges at low pH indicating successful cationic functionalization

CONCLUSION

- The NCC-TTAB interactions were studied and three main interactions were identified: electrostatic, hydrophobic and polymer induced micellization
- NCC was modified using PEGMA to prevent destabilization in presence of TTAB
- NCC was functionalized to possess a cationic surface for conditioning applications