CARBOXYMETHYL CELLULOSE NANOCOMPOSITES

YongJae Choi
Department of Chemical Engineering
and
John Simonsen
Department of Wood Science & Engineering
Oregon State University

Outline

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III. Result and discussion
    I. Comparison of cellulose nanocrystals (NCC) to microcrystalline cellulose (MCC)
    II. Thermal cross-linking
IV. Conclusions
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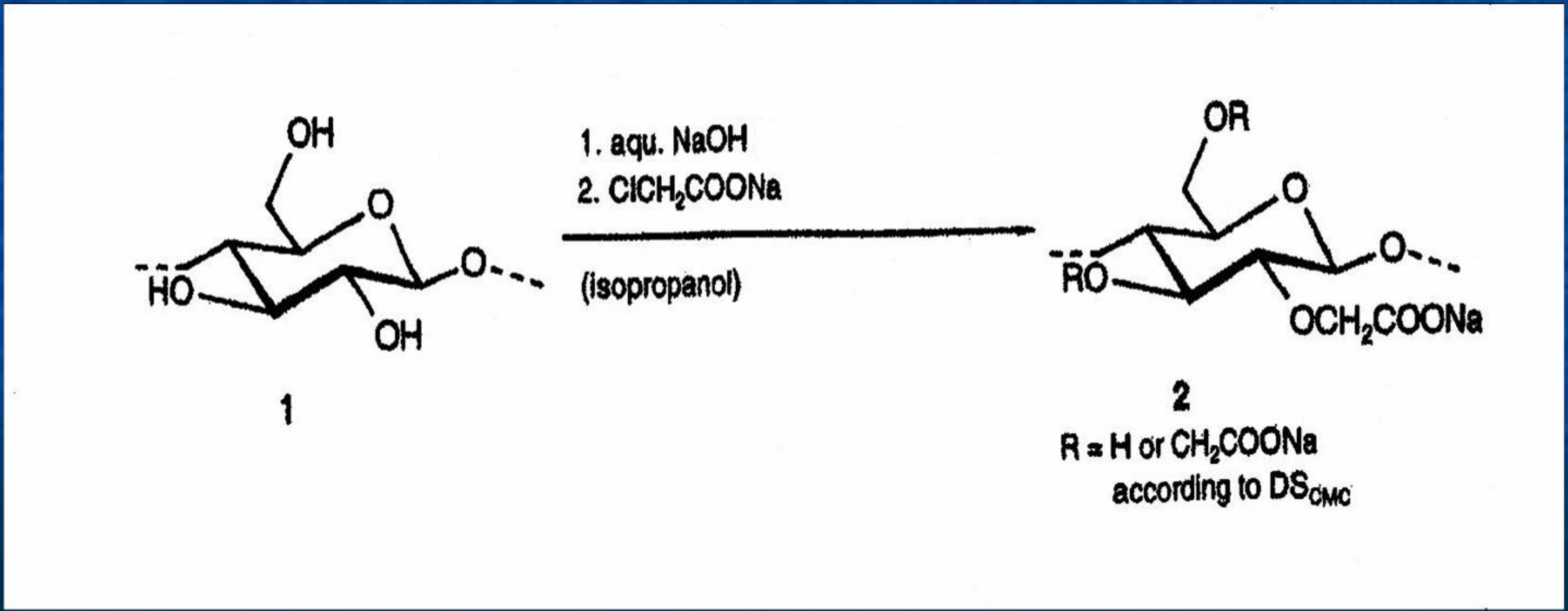
Introduction

- CMC-based hydrogels and films have many applications, from fruit leathers to medical implants, supports for electrocatalysis and pervaporation membranes
- Biodegradable, biocompatible, non-toxic, renewable natural resource, low cost
- Using MCC as a filler imparts improved mechanical properties to films and gels
- What is the effect of reduced particle size?

CMC Synthesis

- Carboxymethyl cellulose (CMC)
  - Derived from cellulose by carboxymethylation
  - Water soluble polymer
  - Efficient, inexpensive reaction
  - Usually sold as sodium salt



Commercial CMC

- CMC
  - First prepared in 1918
  - Commercially produced since 1920
- Three key parameters to control properties for various applications
  - Molecular weight
  - Degree of substitution (DS)
  - Distribution of the carboxymethyl group

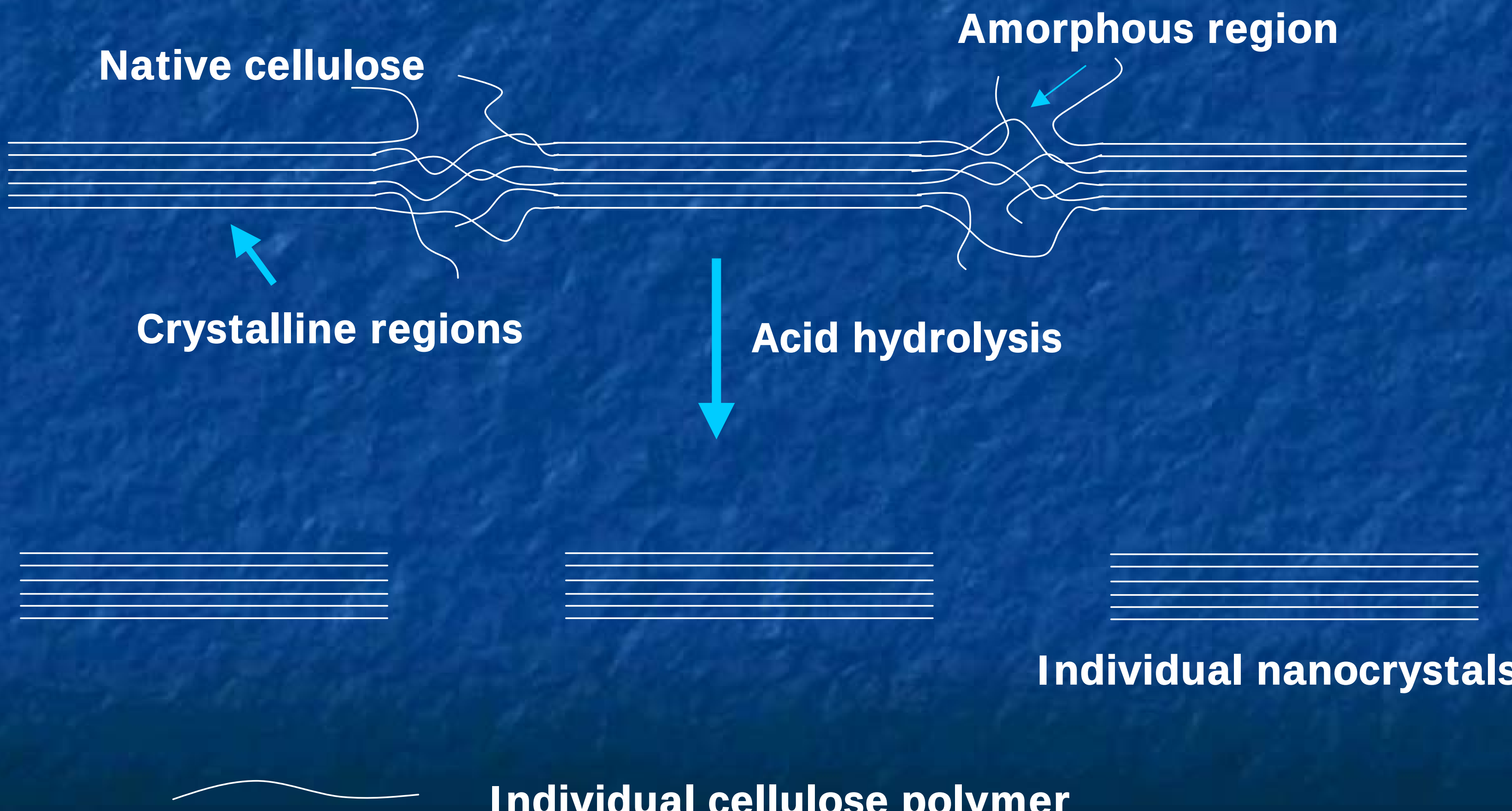
Commercial CMC

- Unique features of CMC
  - Soluble in water
  - Viscosity control
  - Excellent dispersion of MCC
  - Forms strong and transparent film
  - Immiscible in oil and organic solvent
  - High absorbent polymeric material

Nanocrystalline Cellulose

- Stronger than steel and stiffer than aluminum
- Produced by acid hydrolysis of natural cellulose
- Break microfibrils into elementary single crystallites

Cellulose Nanocrystal Production

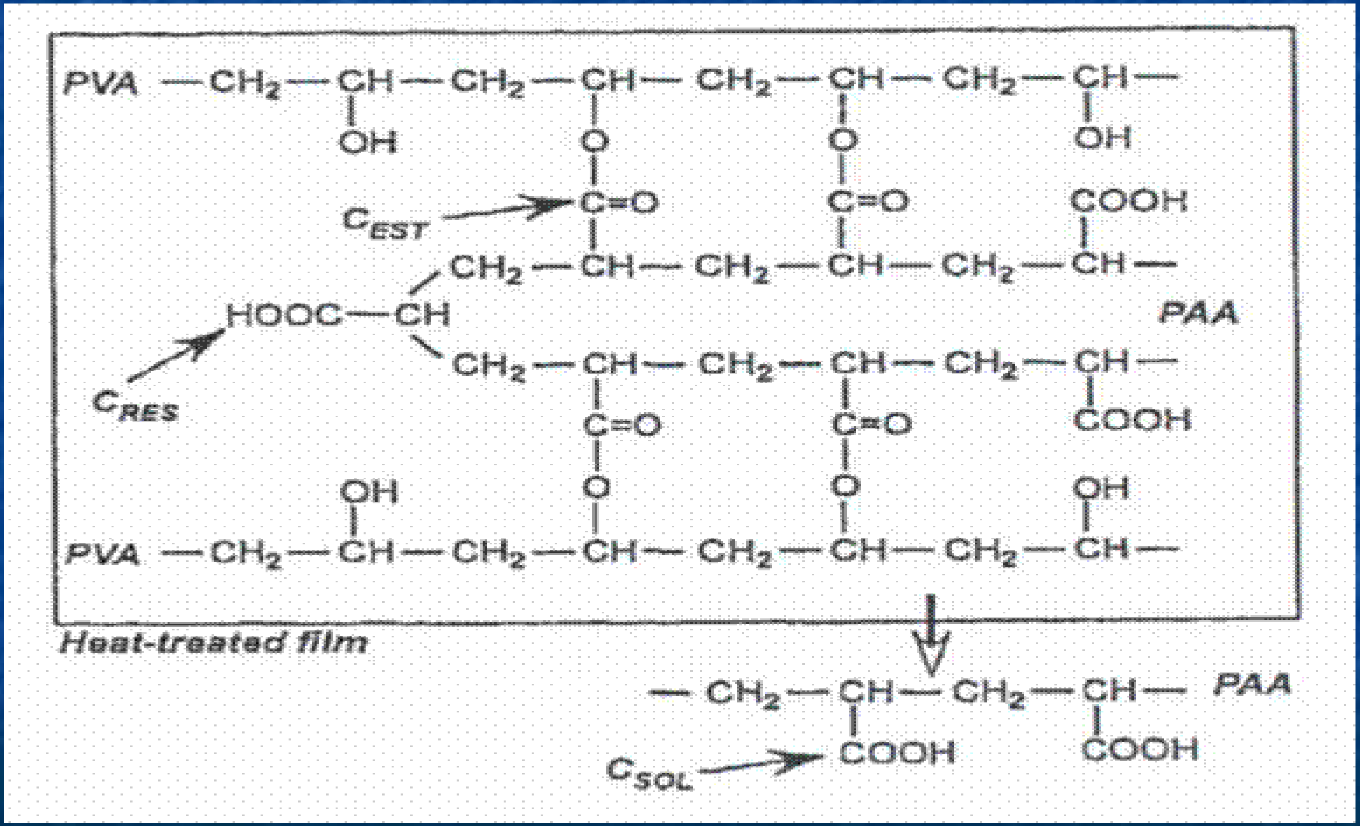


NCC

- Cellulose nanocrystal characterization with TEM
  - Average length = 85 nm
  - Average width = 3 nm
  - Agglomeration due to the attractive force

Thermal Dehydration for Cross-linking

- Alcohol group of poly(vinyl alcohol) (PVA) and acetic acid group of polyacrylic acid (PAA) are cross-linked under mild heat treatment



Objectives

1. Compare cellulose nanocrystal (NCC) to microcrystal cellulose (MCC) in carboxymethyl cellulose composite film

2. Preliminary investigation of thermal crosslinking between NCC and CMC

Materials and Methods

- Materials
  - Carboxymethyl cellulose (CMC)
    - M.W = 250,000
    - D.S = 1.2
    - Aldrich chemical company
  - Cellulose nanocrystal (NCC)
    - Derived from cotton cellulose
  - Glycerin
    - M.W = 92.10
    - Plasticizer
    - Fisher Scientific

Methods

- Cellulose nanocrystal preparation
  - Grind cellulose in Wiley mill with 40 mesh screen
  - Acid hydrolysis at 60°C with 65%(w/w) sulfuric acid for 50 min
  - Centrifugation, decant acid, rinse
  - Ultrasonic irradiation and/or Waring blender
  - Decant
  - Ultrafiltration

Film Formation

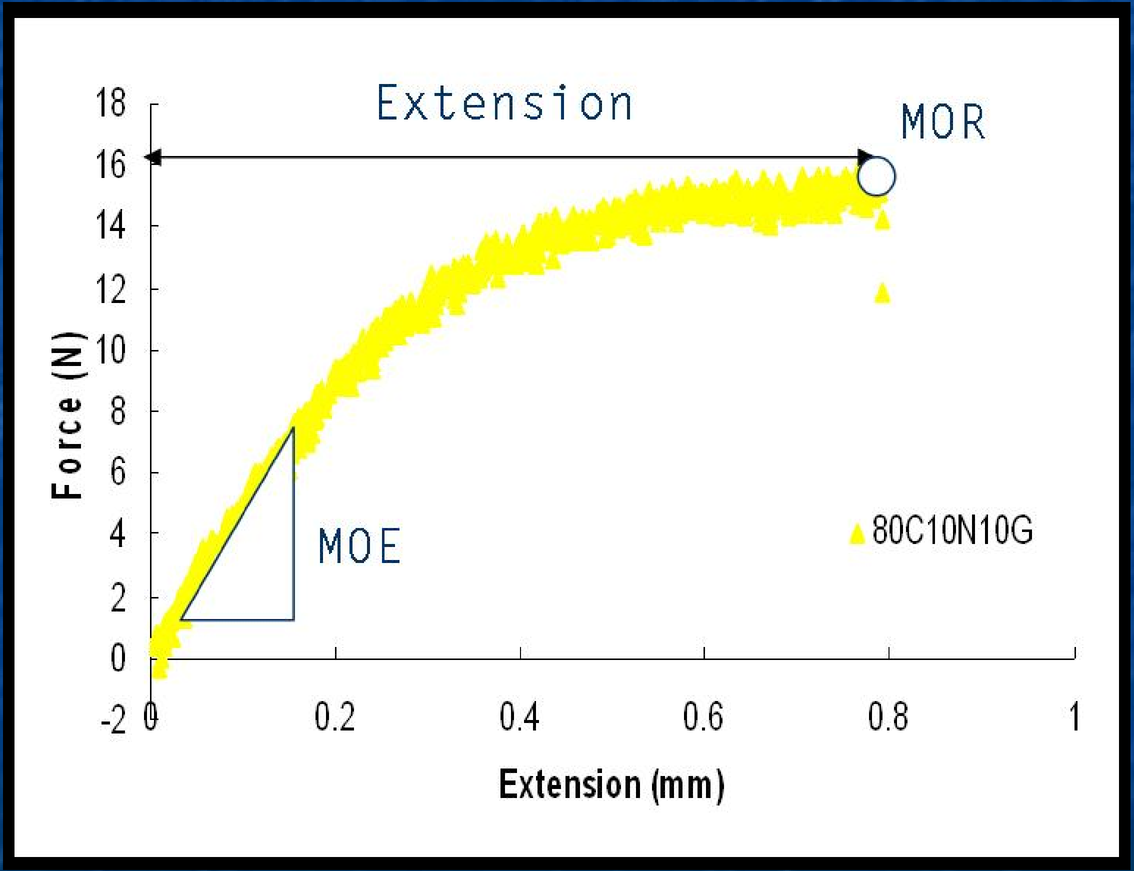
- Dissolve CMC in water
- Mix with NCC or MCC and glycerin
- NCC concentration 5% to 30%
  - Glycerin constant at 10%
- Pour into Petri dish and air dry

Thermal Cross-linking

- Acid form of CMC is achieved by ion exchange (cationic resin)
- Mix with NCC
- Glycerin omitted
- Ultrasonic irradiation
- Form in Petri dish
- Air dry
- Heat treatment at various temperatures for 3 h under nitrogen gas

Methods

- Mechanical testing (Sintech)
  - Modulus of rupture (MOR)
  - Modulus of elasticity (MOE)
  - Extension at maximum yield strength



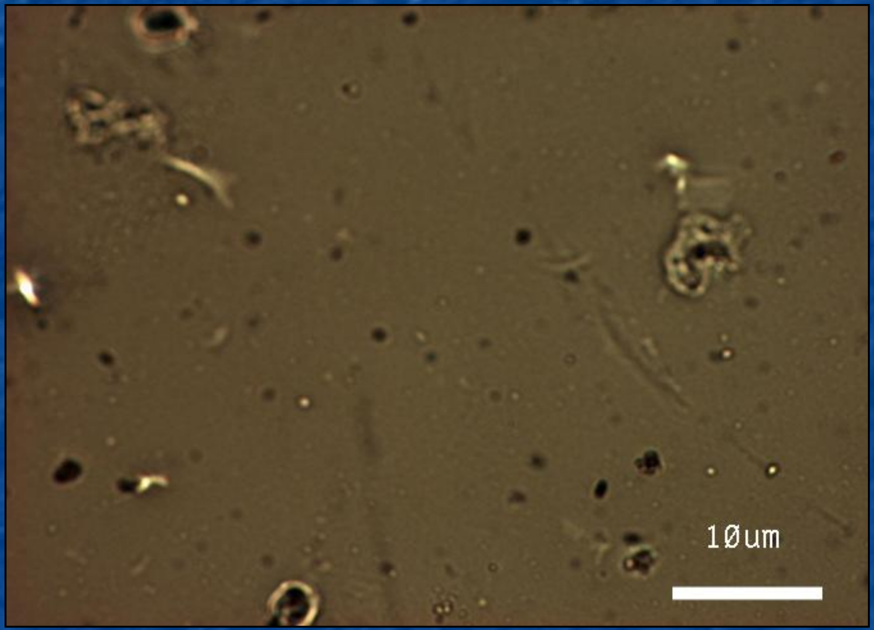
Methods

- Thermal testing (TGA)
  - Ramp 20°C/min

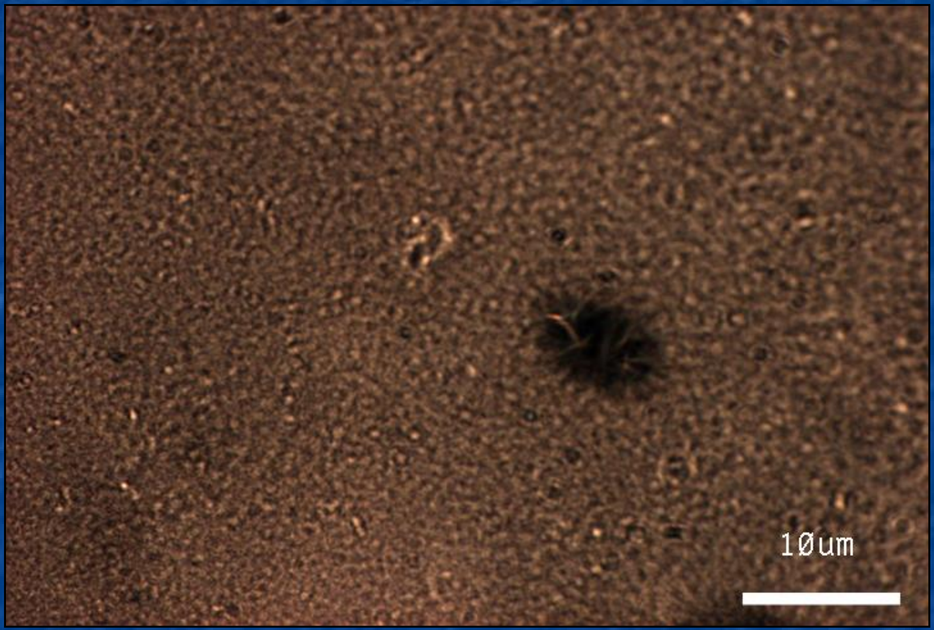
- Water dissolution test
  - Soak in water at room temperature
  - Measure weight loss

- Water vapor transmission rate
  - Film covered jar containing water
  - Measure weight loss with time
  - Hot-dry room (30°C, 25% humidity)
  - Mass flux (J) = $\frac{\text{Mass change (g)}}{\text{Area (m}^2\text{) * Time (hr)}}$

CMC/NCC/Glycerin Films

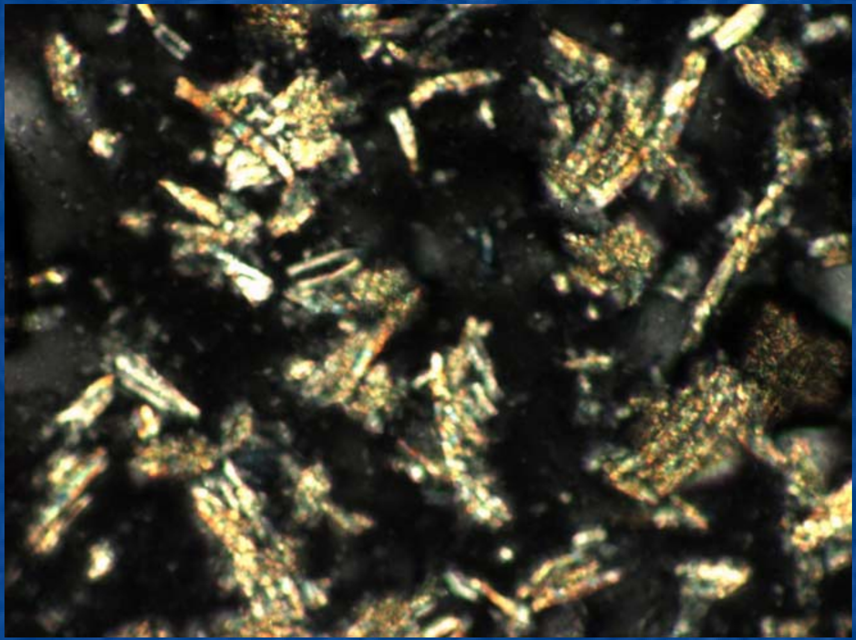


90%CMC/10%Gly

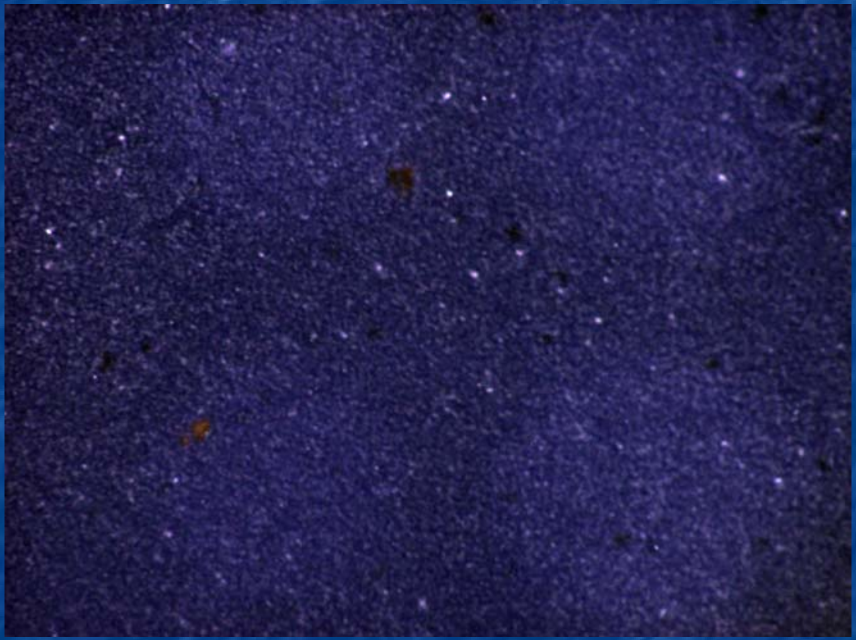


80%CMC/10%NCC/10%Gly

Comparison of Microcrystalline Cellulose (MCC) to CNXL in CMC



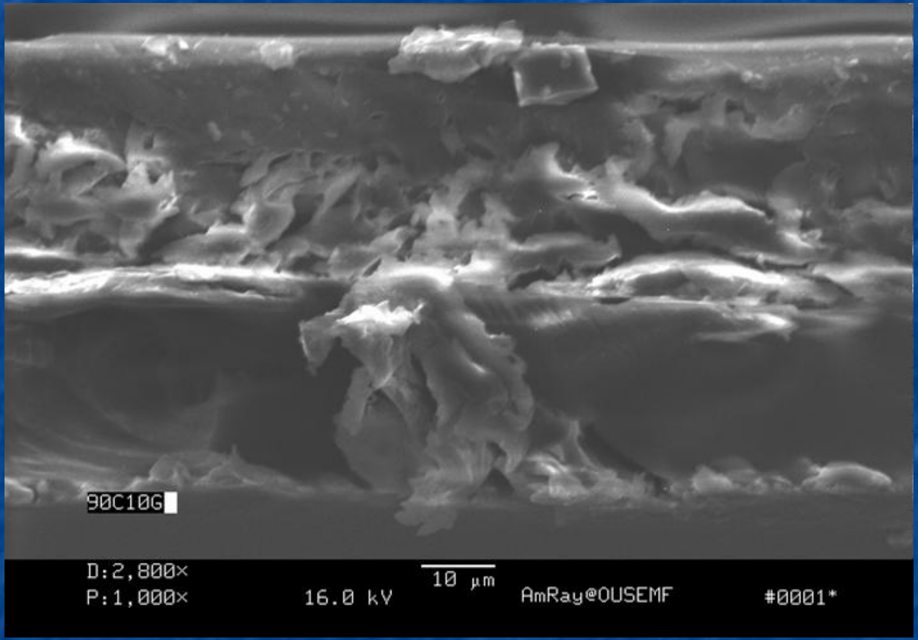
10% MCC



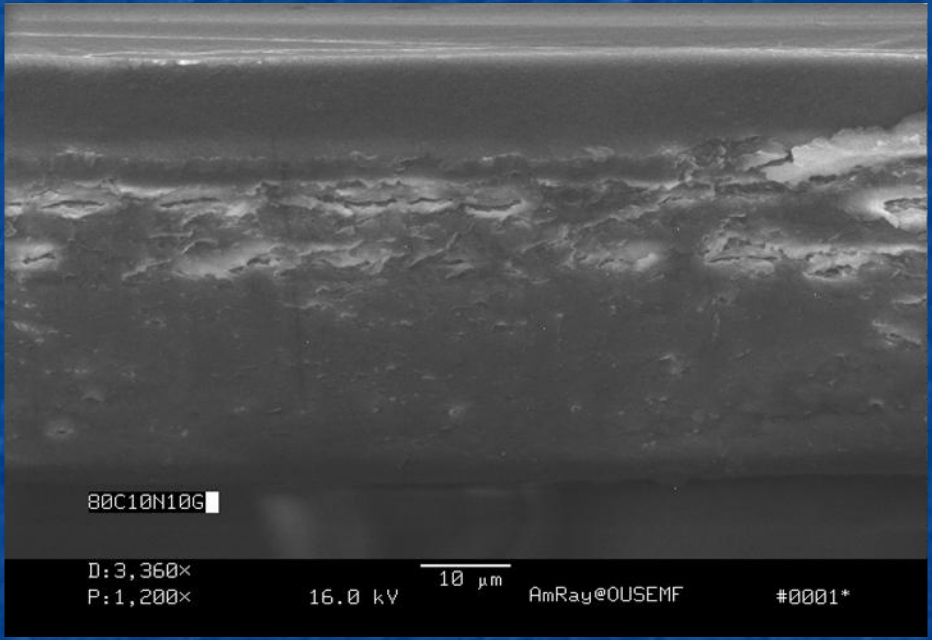
10% CNXL

200X optical (crossed polars)

Cross Section of Film

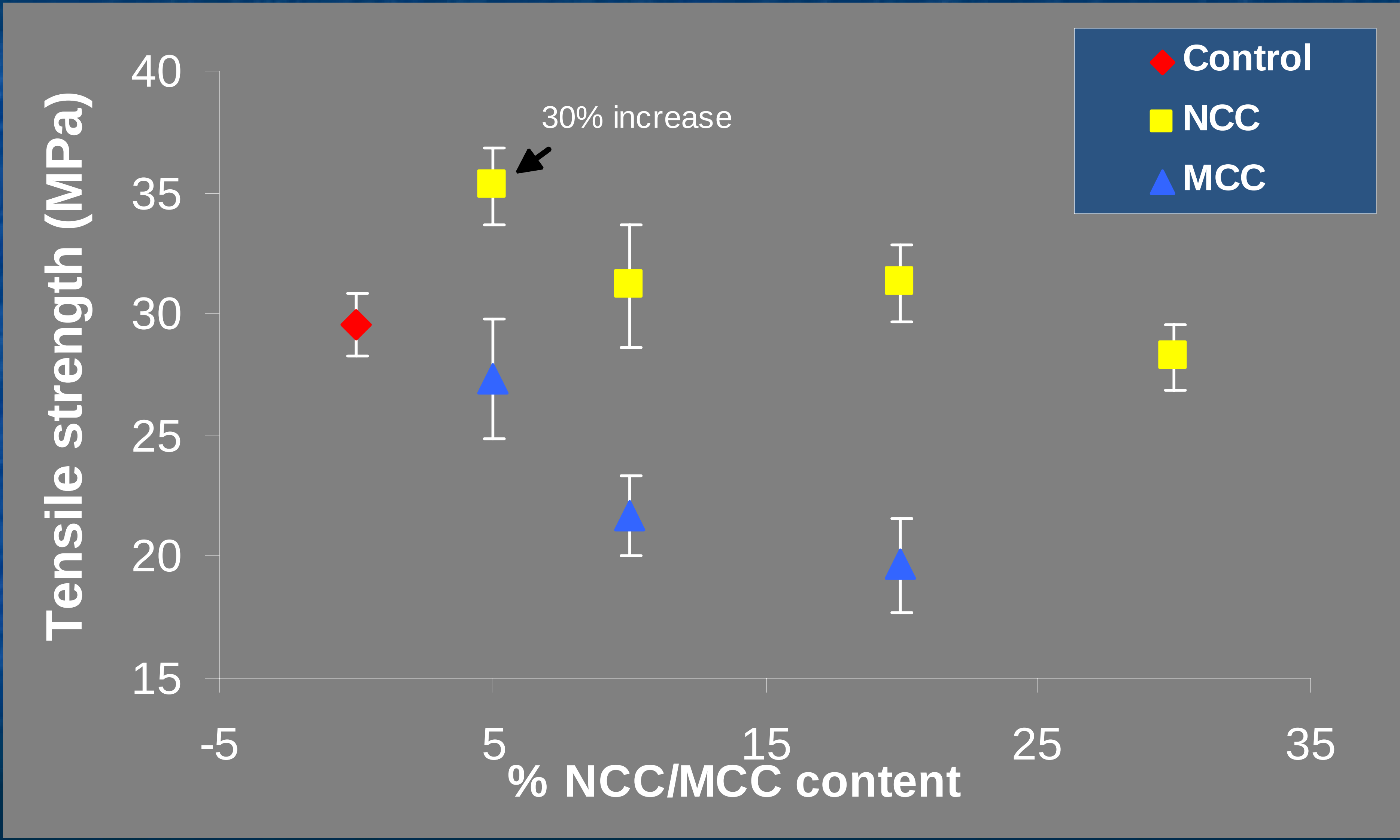


90%CMC/10%Gly

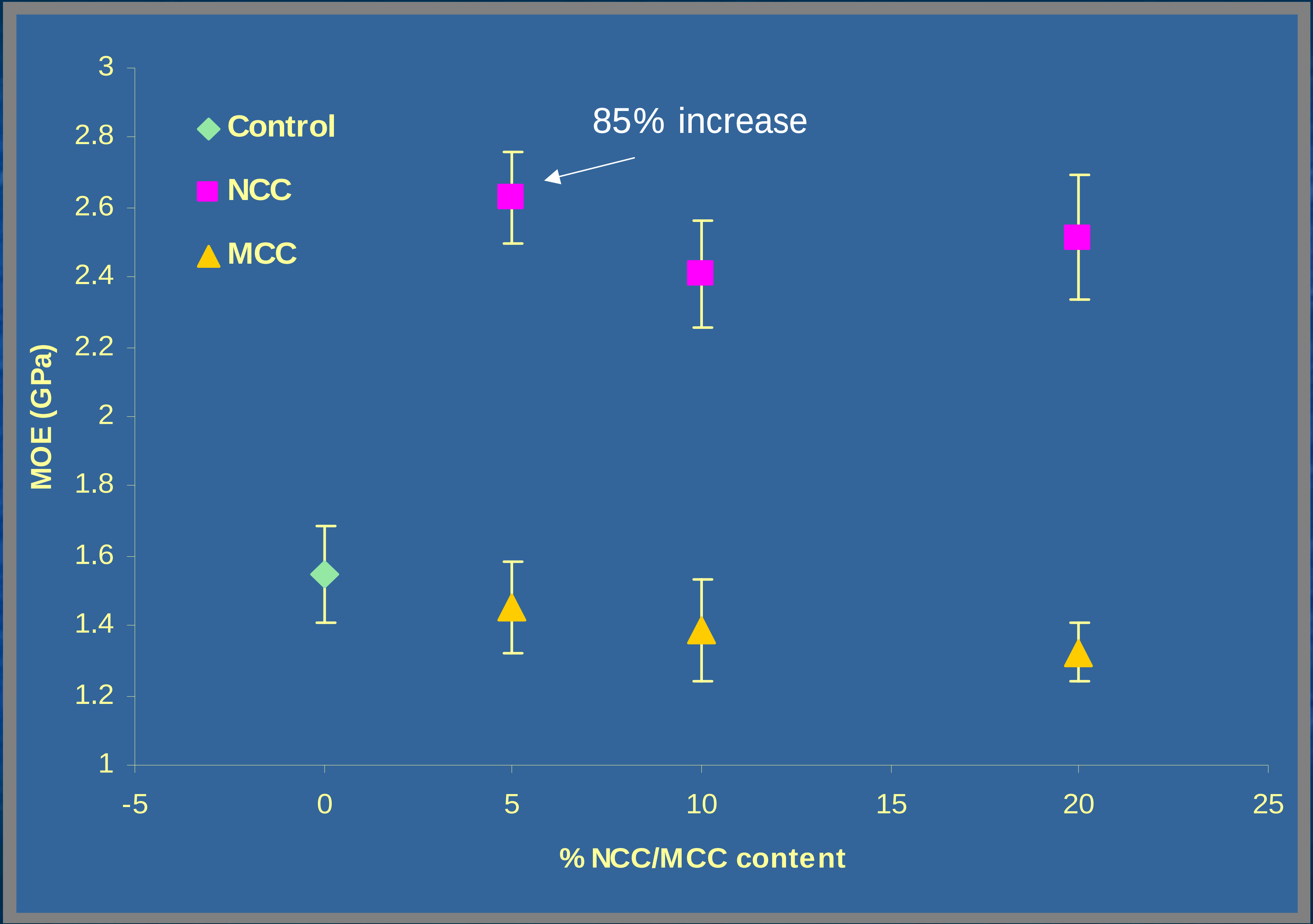


80%CMC/10%NCC/10%Gly

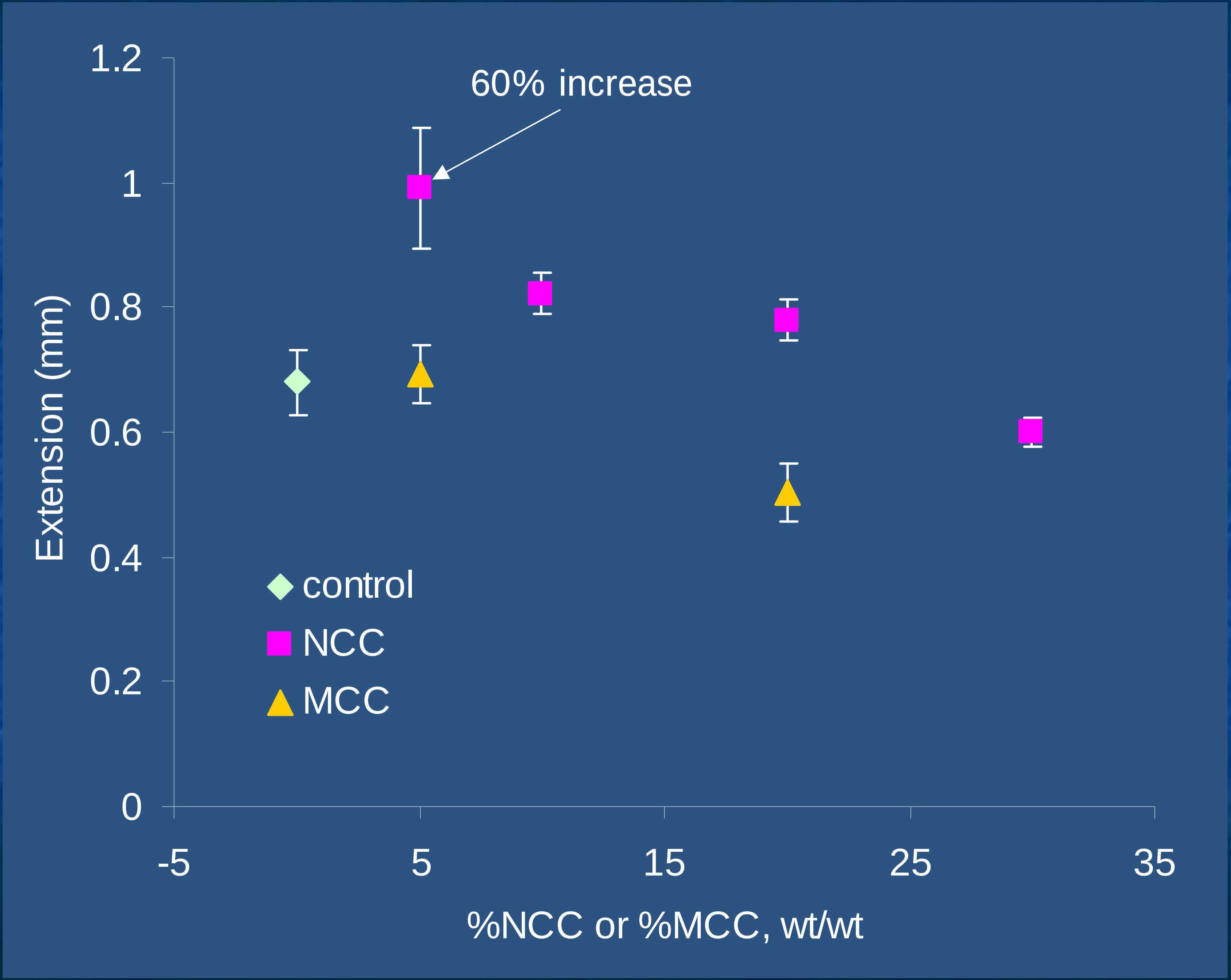
Mechanical properties (MOR)



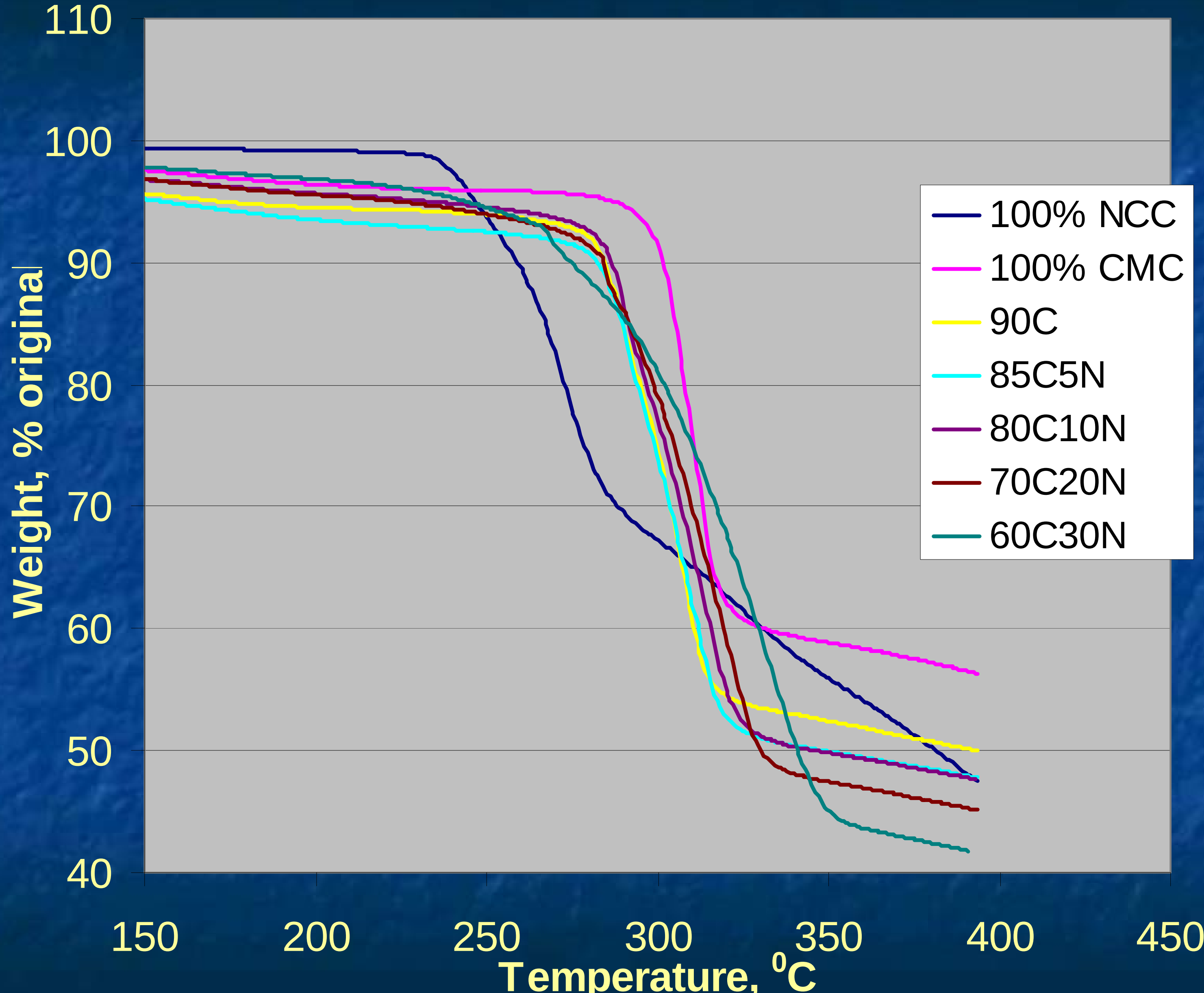
Mechanical properties (MOE)



Extension at failure

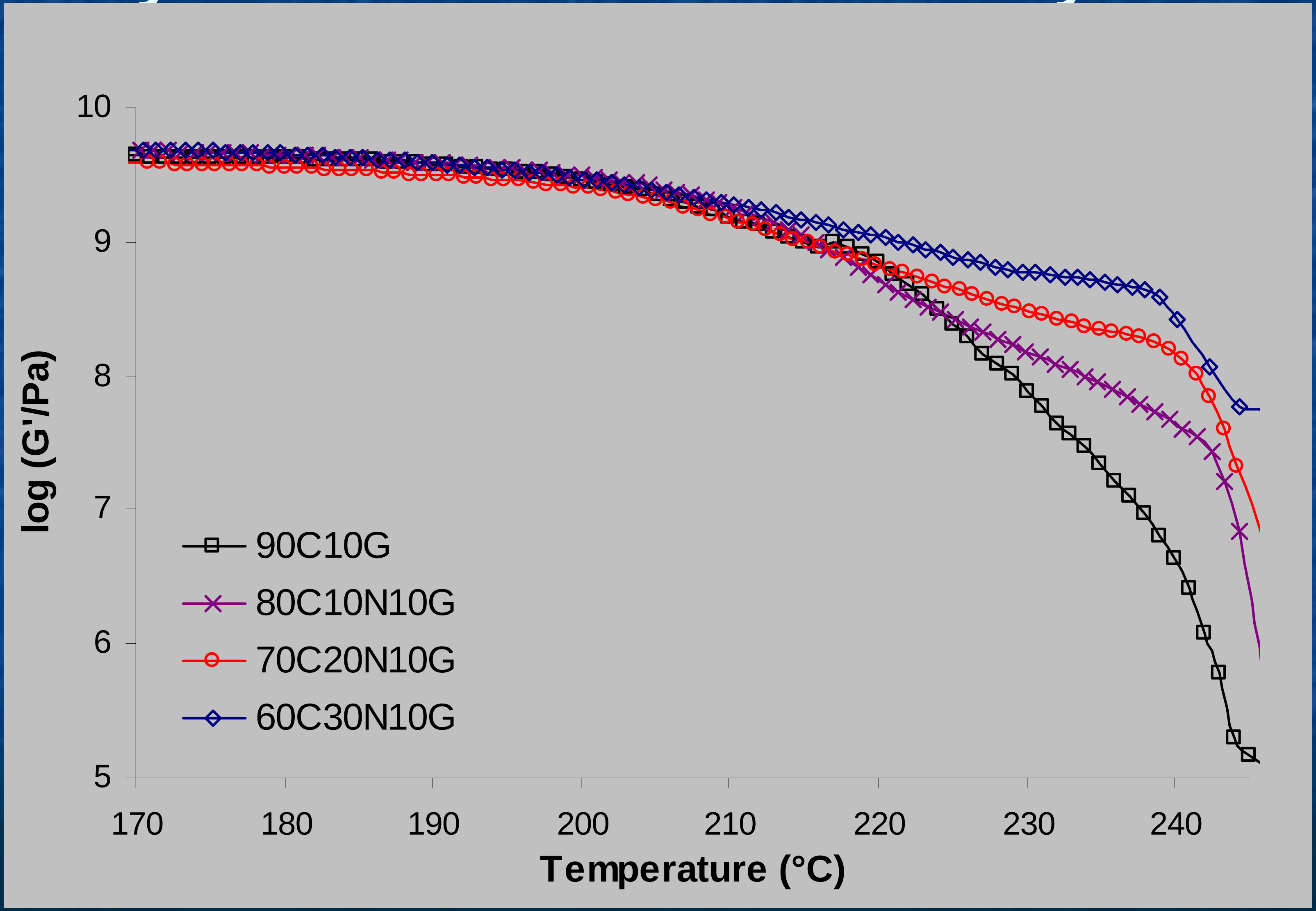


TGA



110
100
90
80
70
60
50
40
Weight, % original
150
200
250
300
350
400
450
Temperature, 0C
100% NCC
100% CMC
90C
85C5N
80C10N
70C20N
60C30N

Dynamic Mechanical Analysis

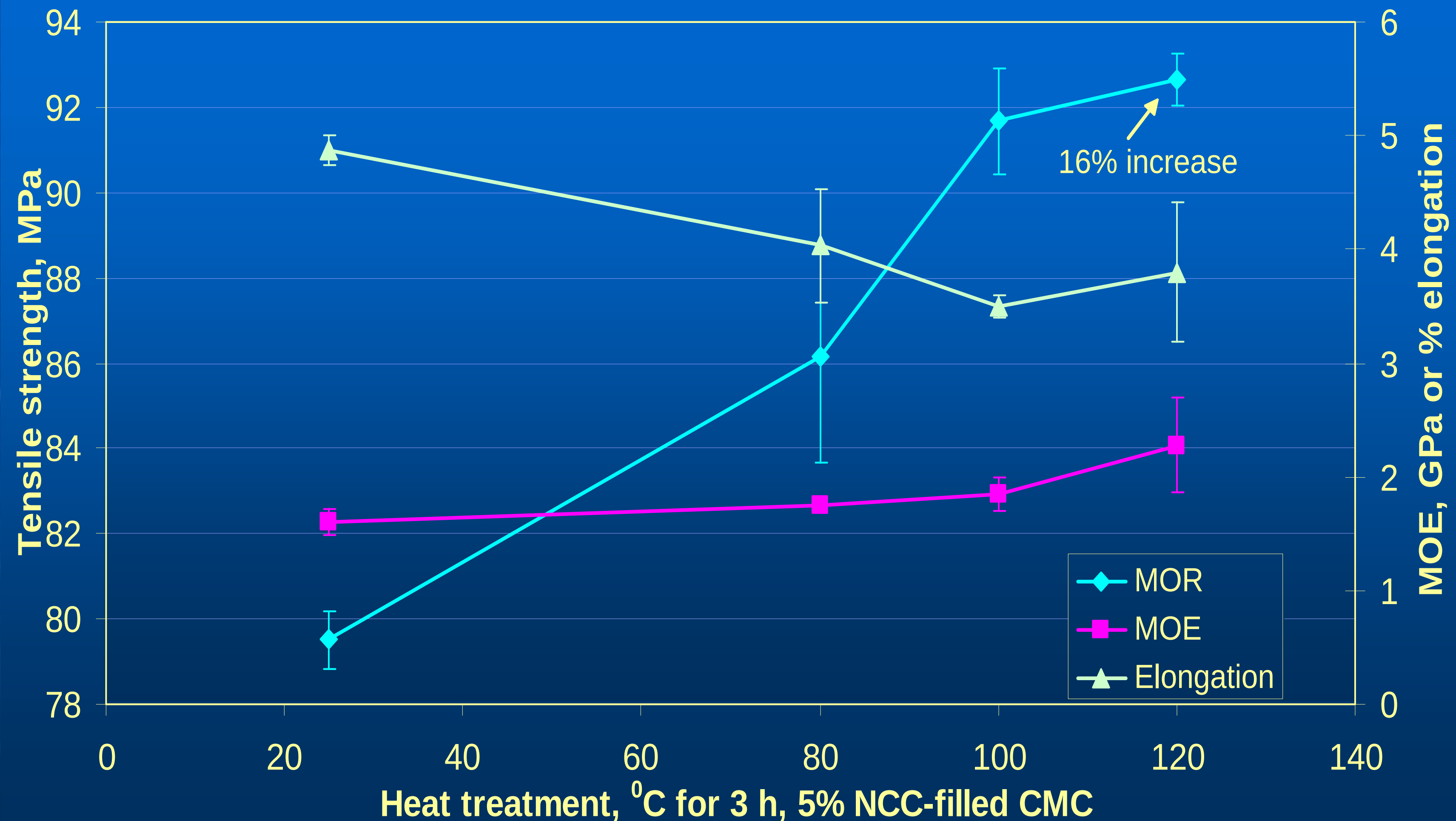


HEAT TREATMENT

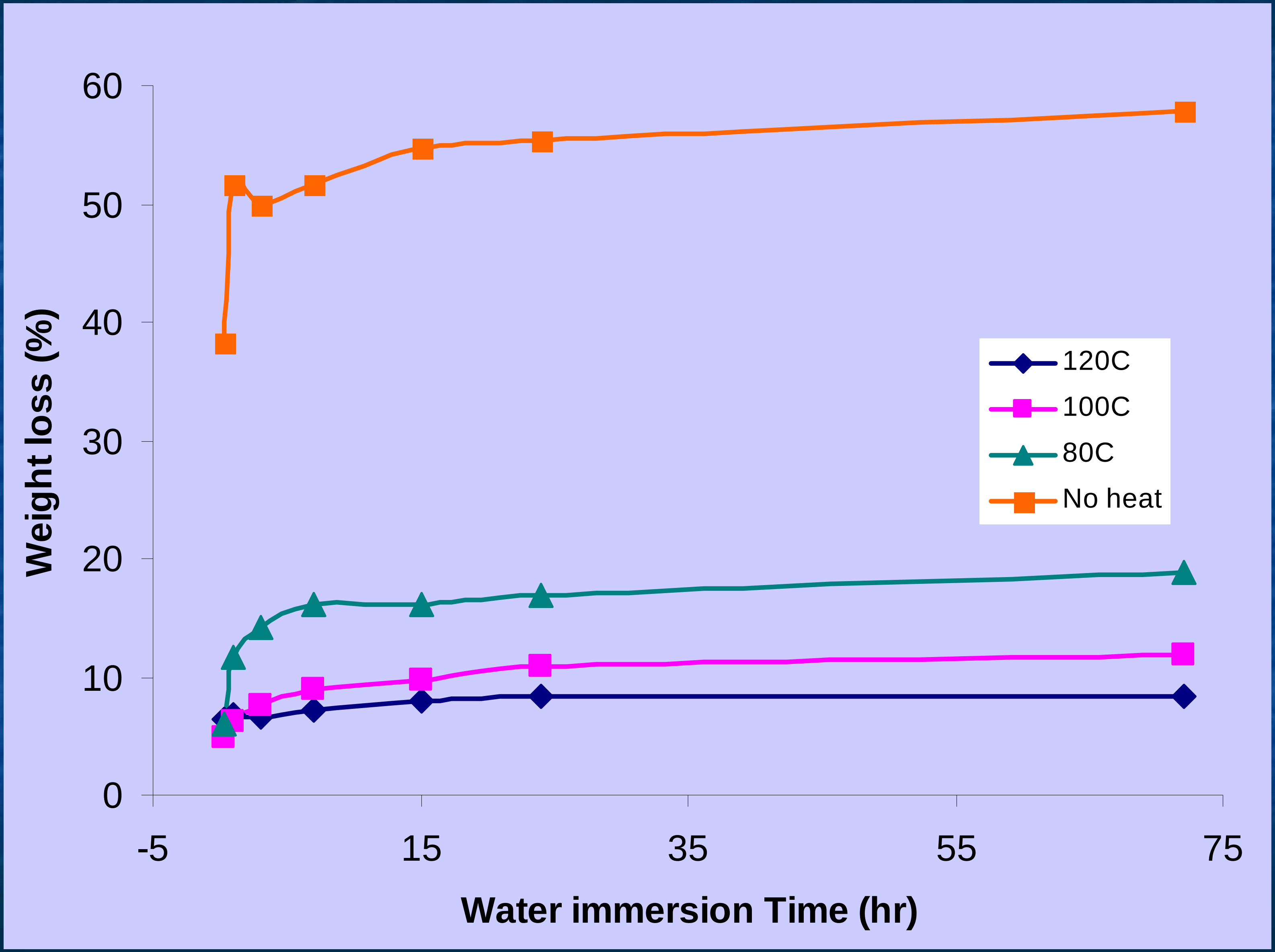
5% NCC in CMC

No plasticizer

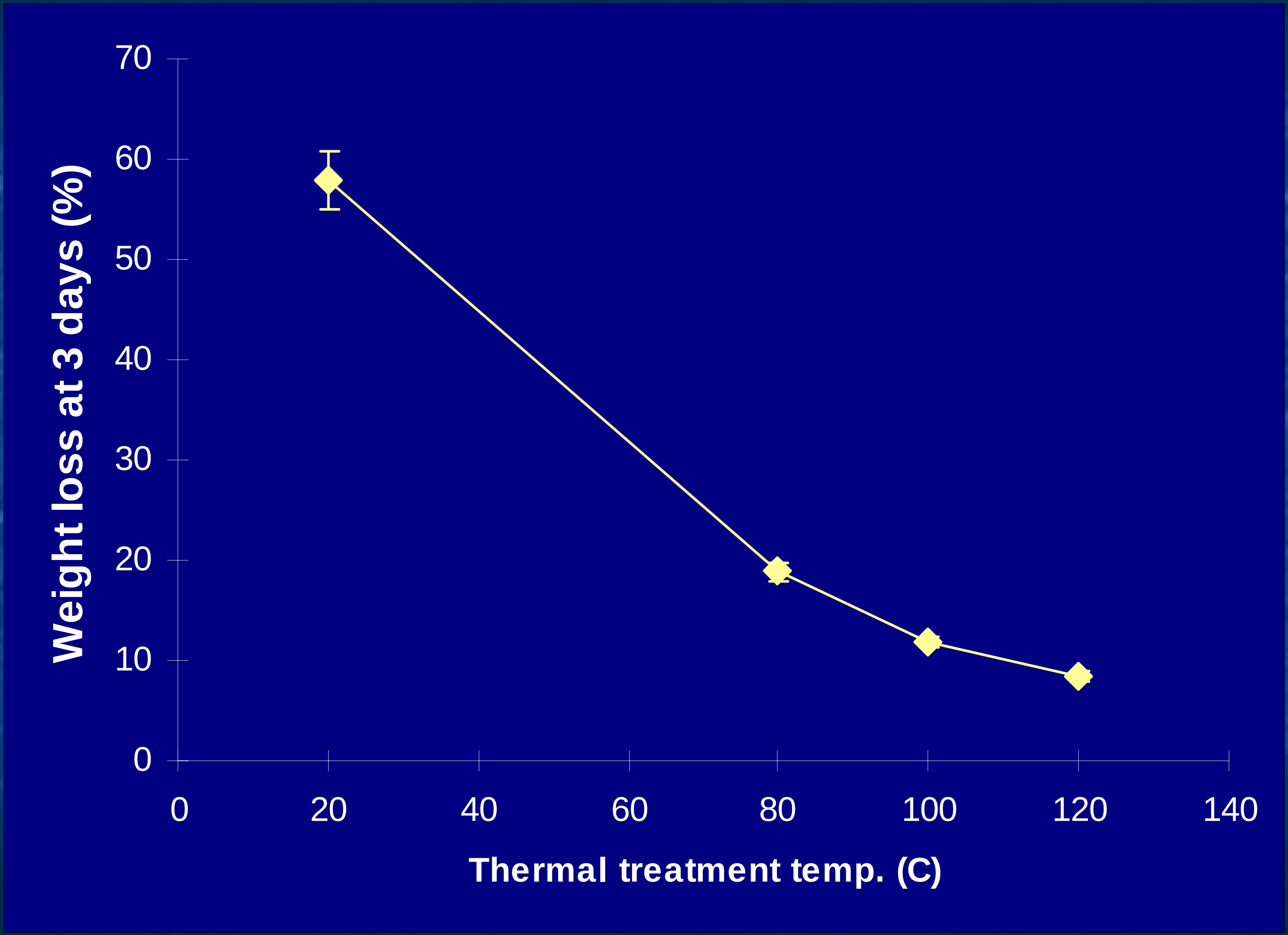
HEAT TREATMENT



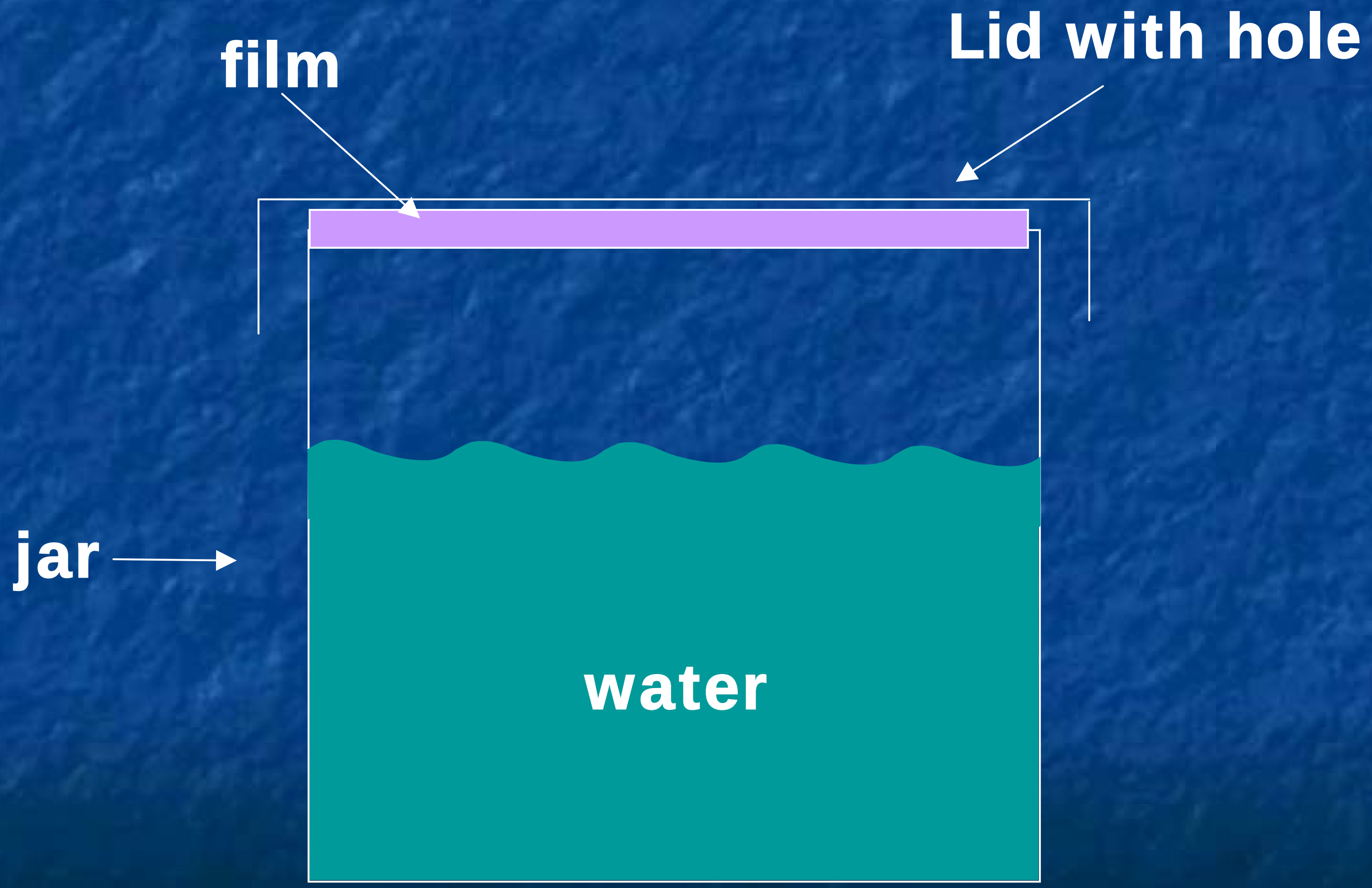
Water Dissolution



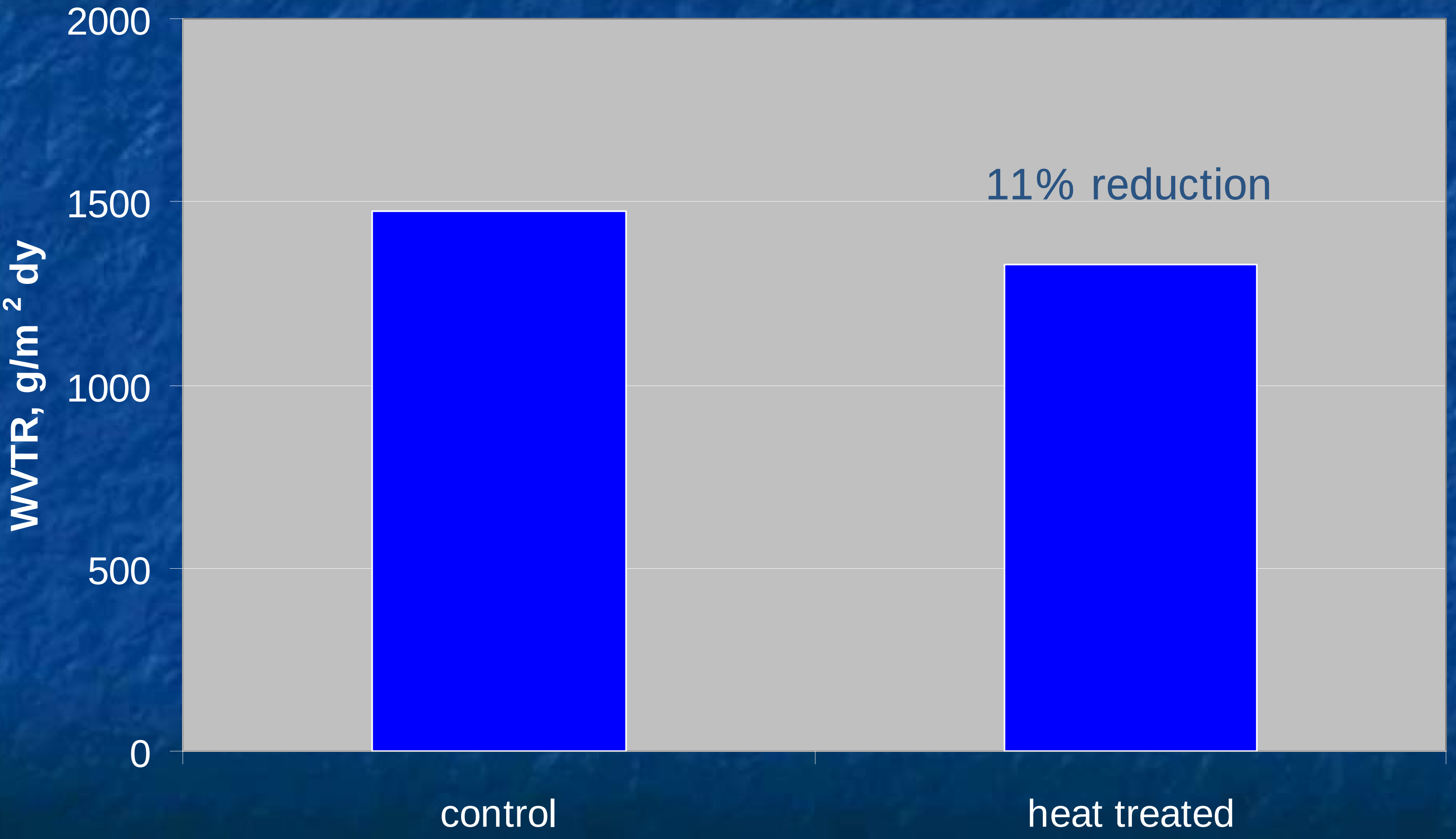
Water Dissolution



Water Vapor Tranmission Rate



Water Vapor Transmission Rate



Conclusions

- At low concentration NCC is well dispersed in the composites without observed agglomeration of cellulose
- NCC improved the mechanical properties (strength, stiffness and elongation) as a reinforcing filler compared to MCC
- TGA suggests close association between NCC and CMC

Conclusions

- Cross-linking between CMC and NCC can be obtained by heat treatments
- Higher degree of cross-linking is achieved at higher temperature
- Cross-linking composites have improved water resistance
- Cross-linking appears to reduce water vapor permeability slightly

Acknowledgement

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