# Poly(vinyl alcohol) / Cellulose Barrier Films

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# OUTLINE

- Introduction
- Materials
- Results and Discussion
- Conclusions
- Acknowledgements

# Introduction

**Barrier Films?**

- **Designed to reduce/retard gas migration**
- **Widely used in the food and biomedical industries**
- **Another application is as a barrier to toxic chemicals**

# Chemical Vapor Barrier

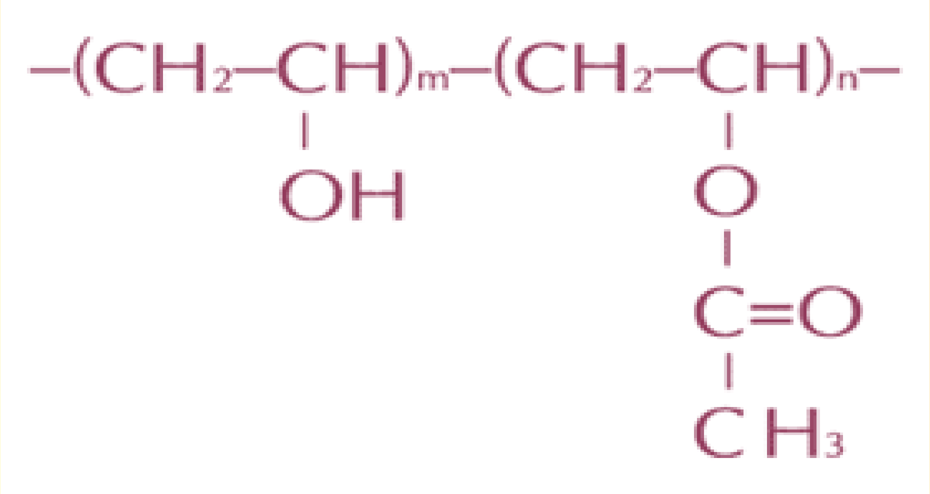
- To prevent the diffusion of toxic chemical vapors, while allowing water vapor to pass through
- Should be tough and flexible
- Useful in protective clothing

# Materials

- **Poly(vinyl alcohol) = PVOH**

- **Nontoxic, good barrier for oxygen, aroma, oil and solvents**
- **Prepared by partial or complete hydrolysis of poly(vinyl acetate)**

Structure:

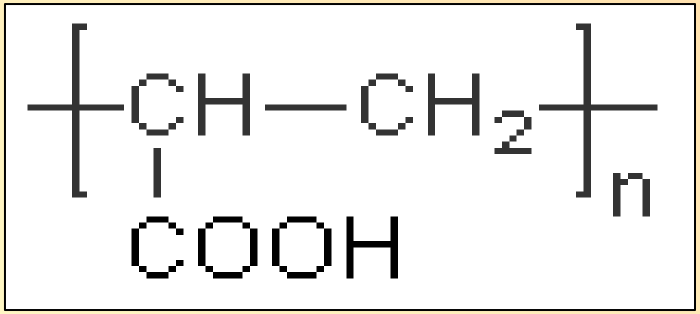


# PVOH Water Stability

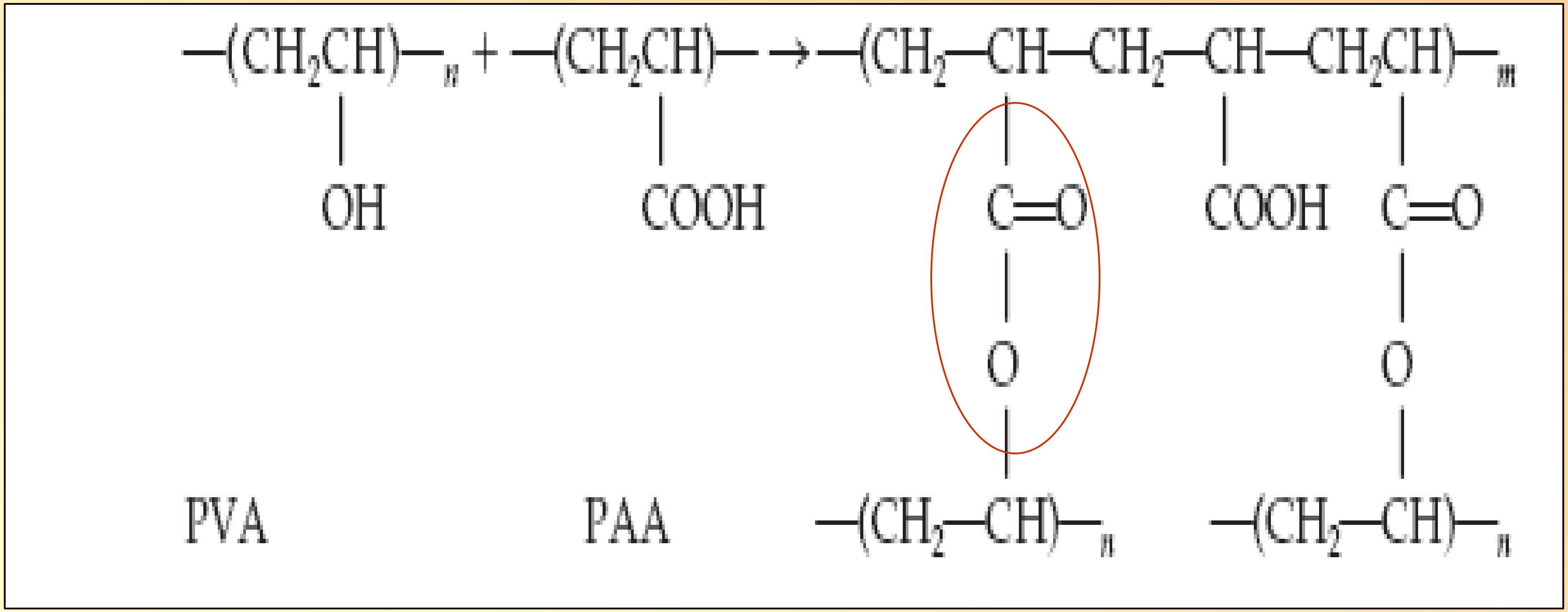
- PVOH films have poor resistance to water
- Crosslinking agent reduces water sorption and the crosslinks also act as a barrier to diffusion

# Poly(acrylic acid)-PAA

- **Poly(acrylic acid) PAA:**



# Crosslinking reaction

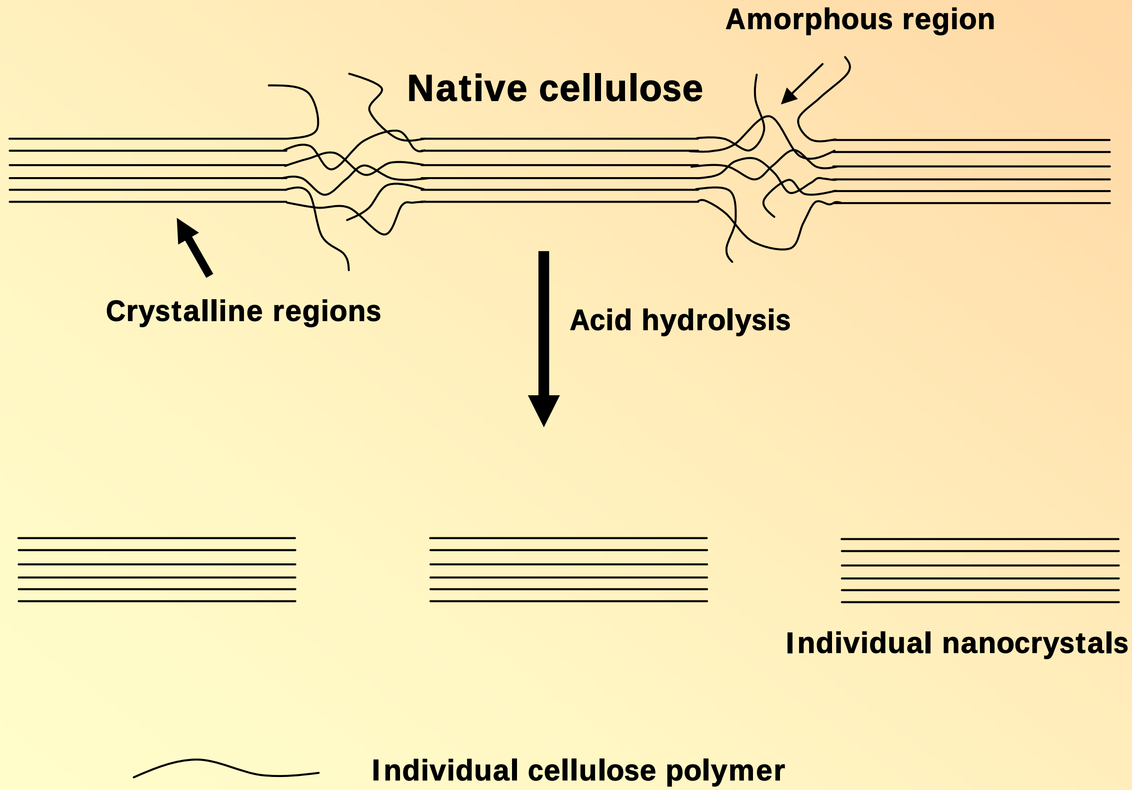



*Source: Sanli, O., et al. Journal of applied polymer science, 91( 2003)*

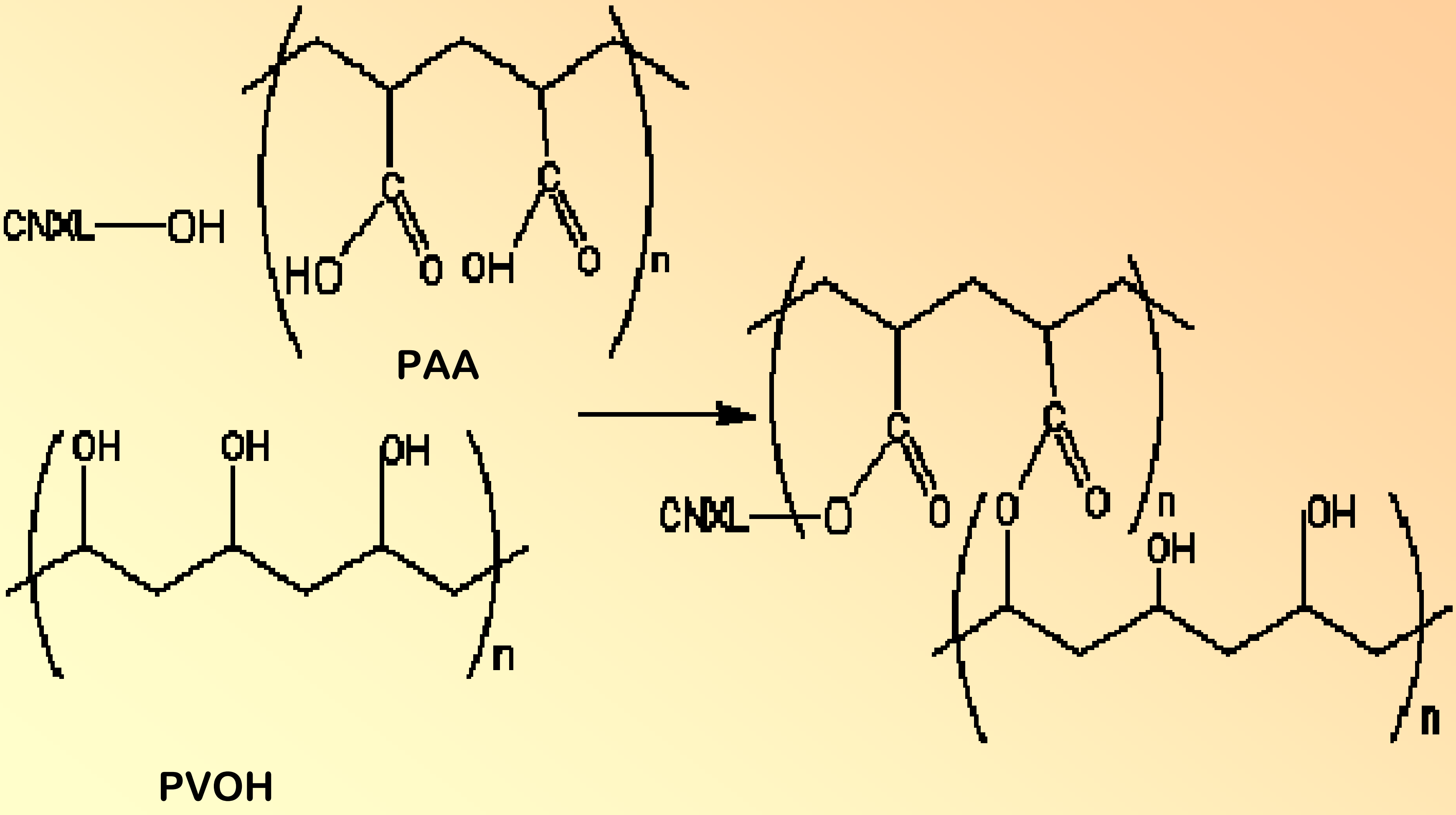
- **Heat treatment forms ester linkages**

# Cellulose Nanocrystals-(CNXLs)

- CNXLs were prepared by acid hydrolysis of cellulose obtained from cotton



# Proposed structure



# Objectives

- Prepare chemical barrier films with PVOH/ PAA/ CNXL system
- To understand the chemistry and physics of this system
- Select optimum time and temperature for heat treatment
- Find combination which allows moisture to pass through but restricts diffusion of toxic chemical vapors
- Select combination which is flexible and tough
- Surface modify CNXLs to improve interaction with matrix

# Methods

- Film Preparation

❖ **Testing methods**

- Water solubility - Optimize heat treatment
- Fourier Transform Infrared Spectroscopy - Bond analysis
- Polarized Optical Microscopy - Dispersion
- Water Vapor Transmission Rate (WVTR)
- Universal Testing Machine - Mechanical properties
- Differential Thermogravimetric Analysis - Thermal degradation
- Chemical Vapor Transmission Rate (CVTR)

# Preparation of the Blends

- 5 wt % solution of PVOH and PAA
- 1 wt % solution of dispersed CNXLs in DI water

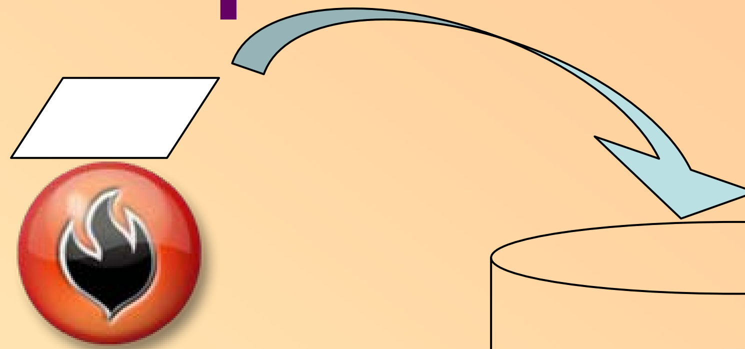
| Composition | 0% CNXL | 10% CNXL | 20% CNXL |
|---|---|---|---|
| 0% PAA | 0/0 | 0/10 | 0/20 |
| 10% PAA | 10/0 | 10/10 | 10/20 |
| 20% PAA | 20/0 | 20/10 | 20/20 |

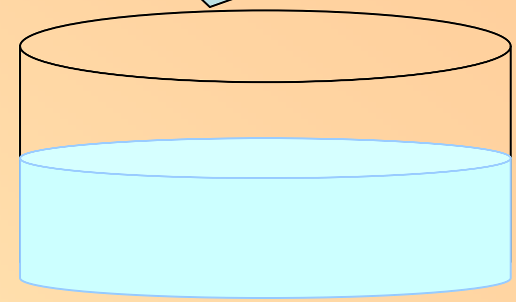
- **Remaining composition of the film consists of PVOH**

# Film Preparation

- Compositions were mixed, sonicated and then air dried for 40 hours
- The thickness of the film was controlled by the concentration (%solids) of the dispersion before drying

# Heat treatment optimization

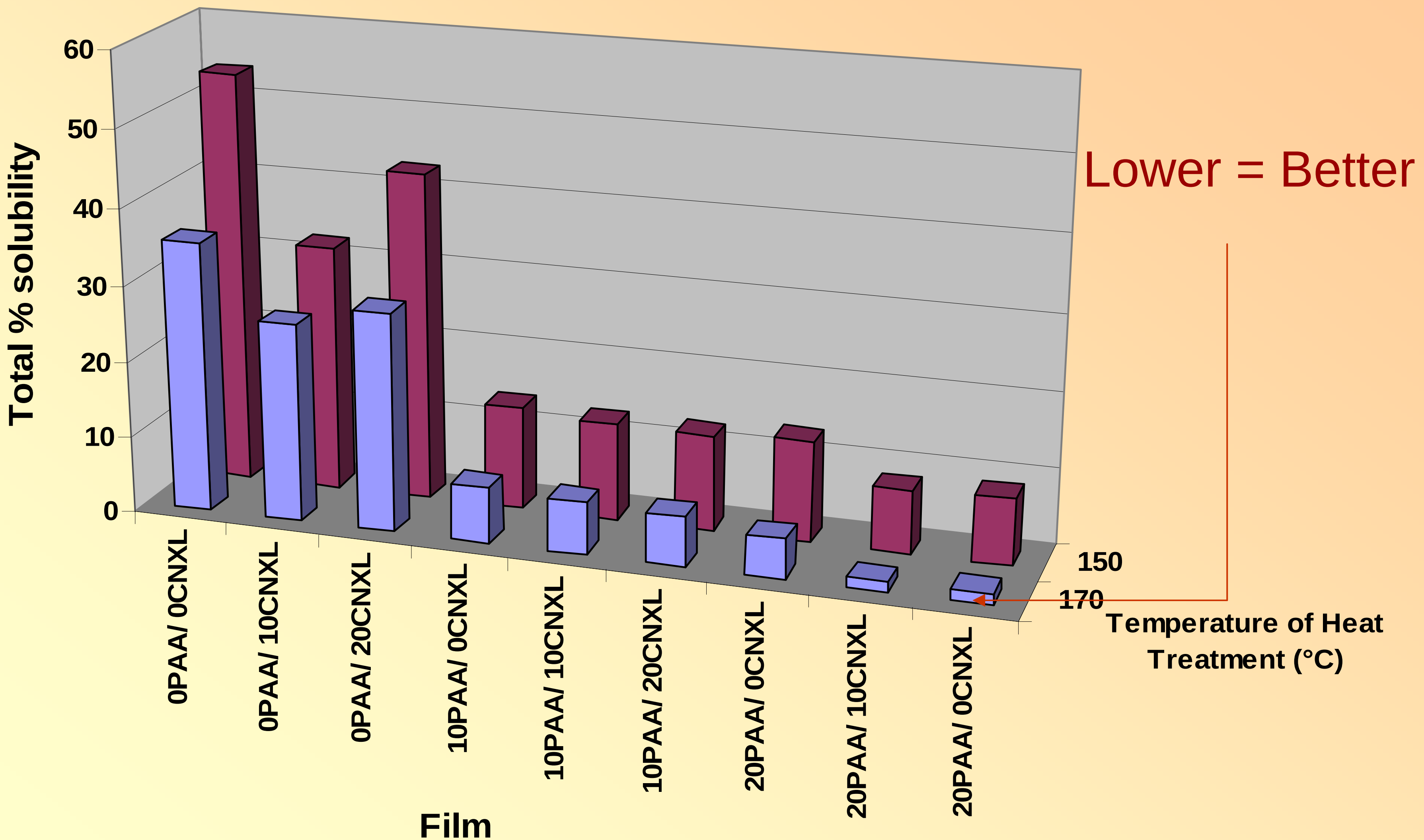




- Evaluate via water solubility test
  - At 125 °C/1 hr films were completely soluble in water after a day
  - At 185 °C/1hr color of the films changed to brown
  - At 150 °C and 170 °C/45 min films were clear and had good water resistance

# Total % Solubility after 72 hours of soaking time

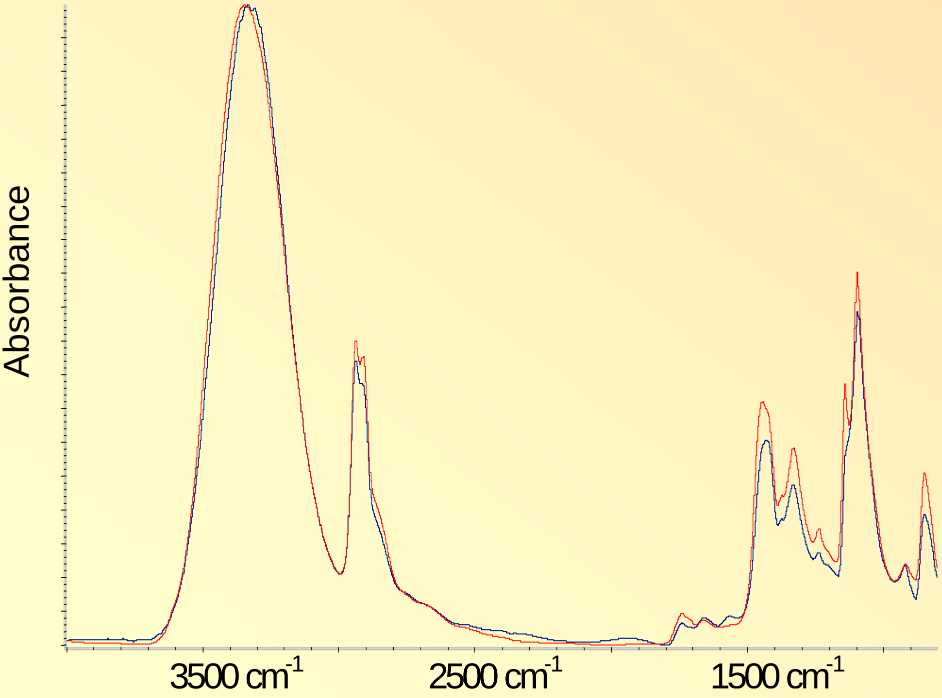
$$\% \text{ Solubility} = \frac{(Weight1 - Weight2)}{Weight1} * 100\%$$

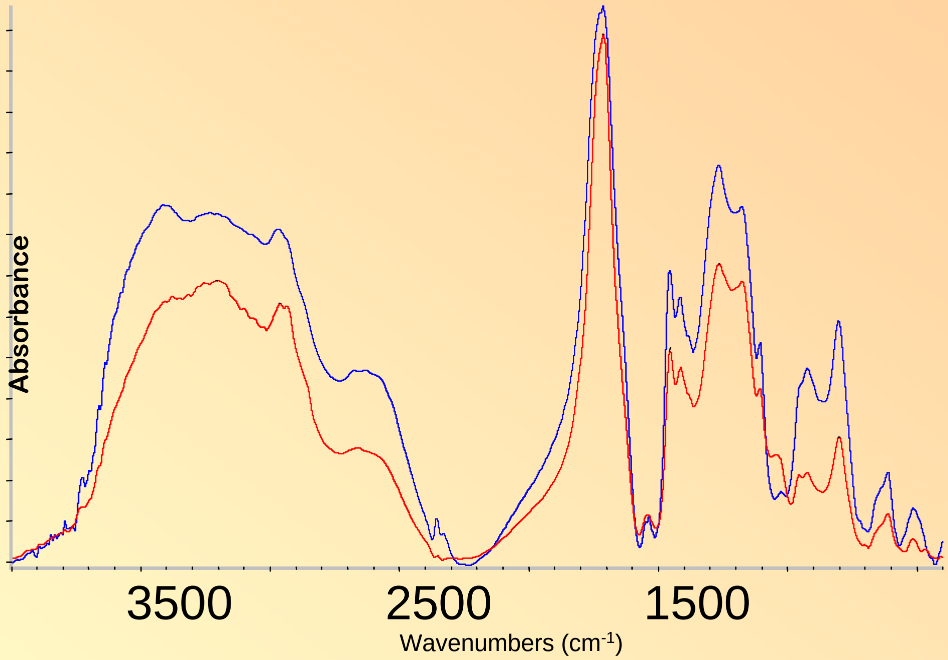


# Fourier Transform Infrared Spectroscopy

- PVOH
- PAA

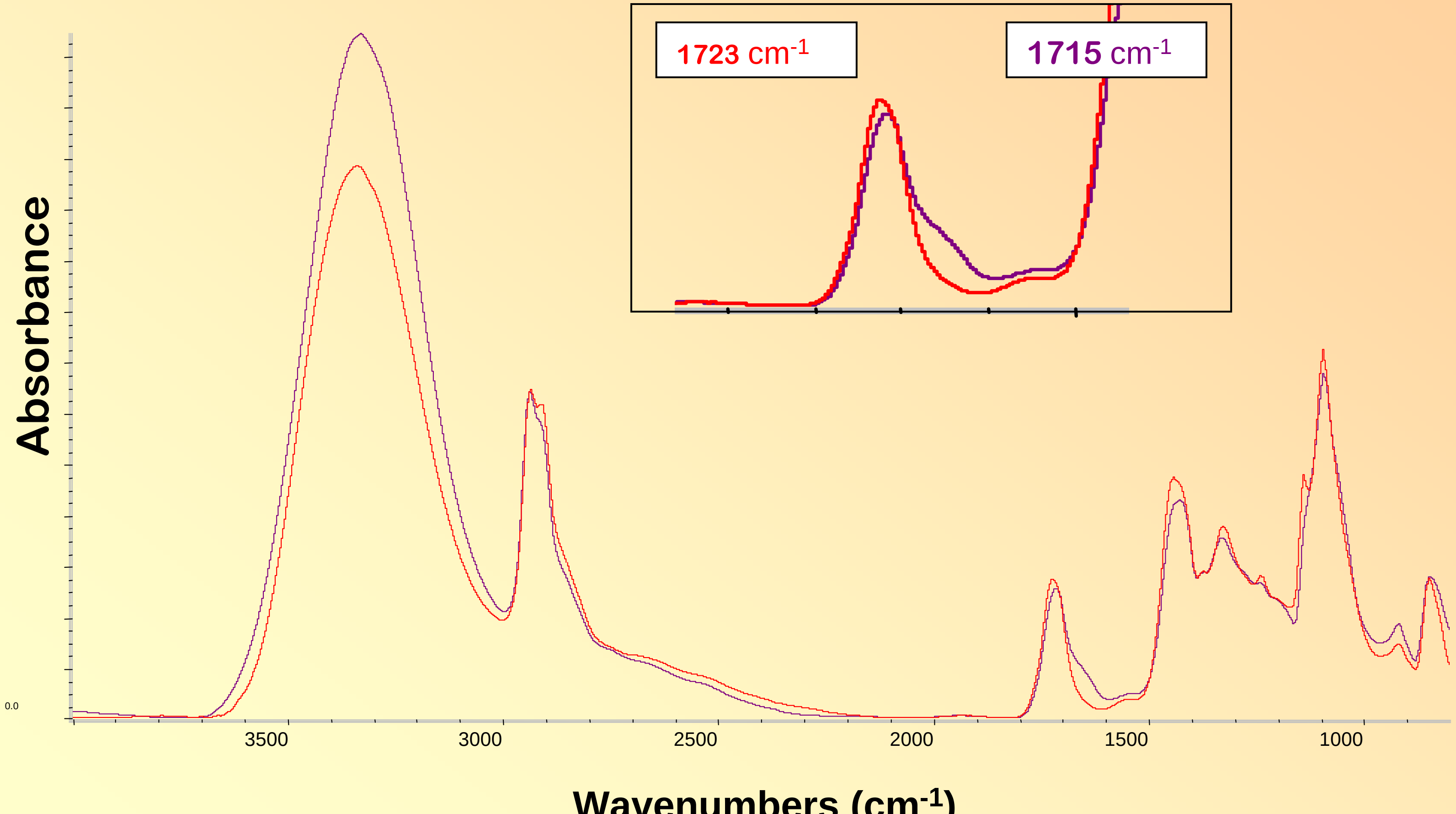
**Red: Heat treated film** **Blue: Non heat treated film**



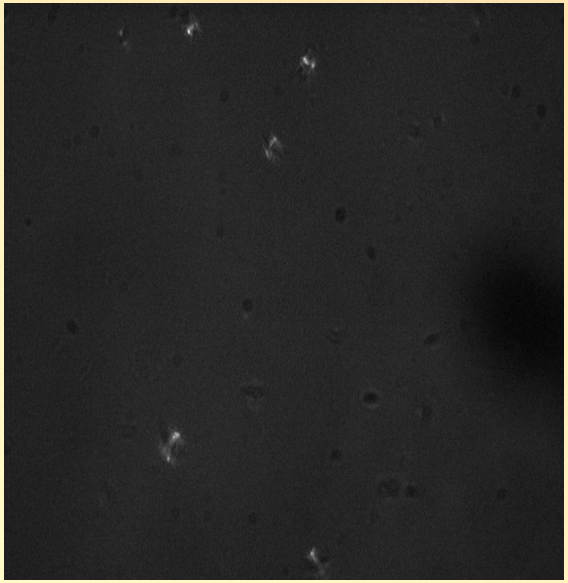



# FTIR of 10% CNXL/10% PAA/80% PVOH

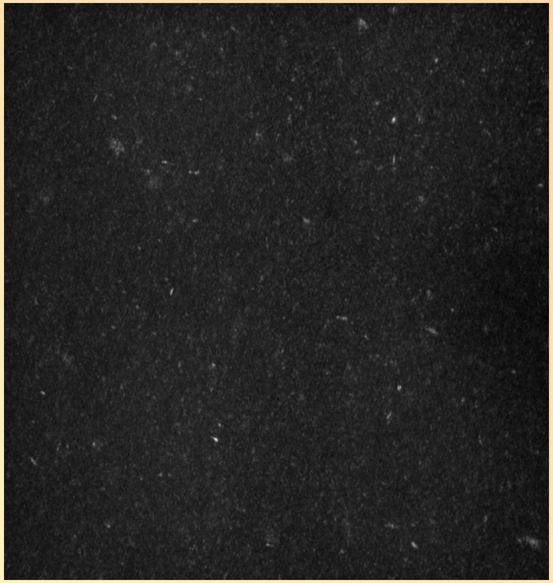
**Red: Heat treated film** **Blue: Non heat treated film**



# Polarized Optical Microscopy
# Dispersion of CNXLs



a) 5% CNXL/ 10%PAA

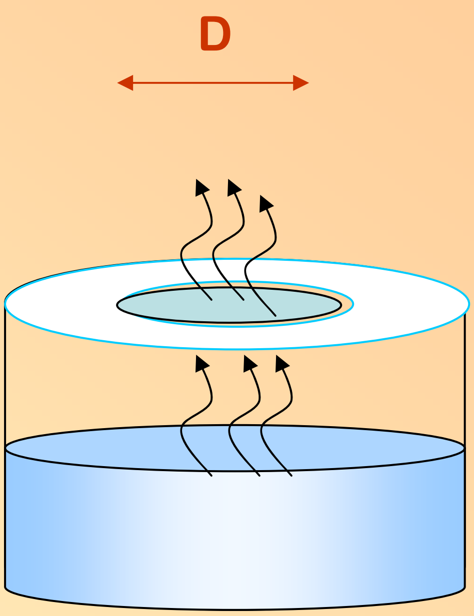


b) 10% CNXL/ 10% PAA

c) 15% CNXL/ 10% PAA

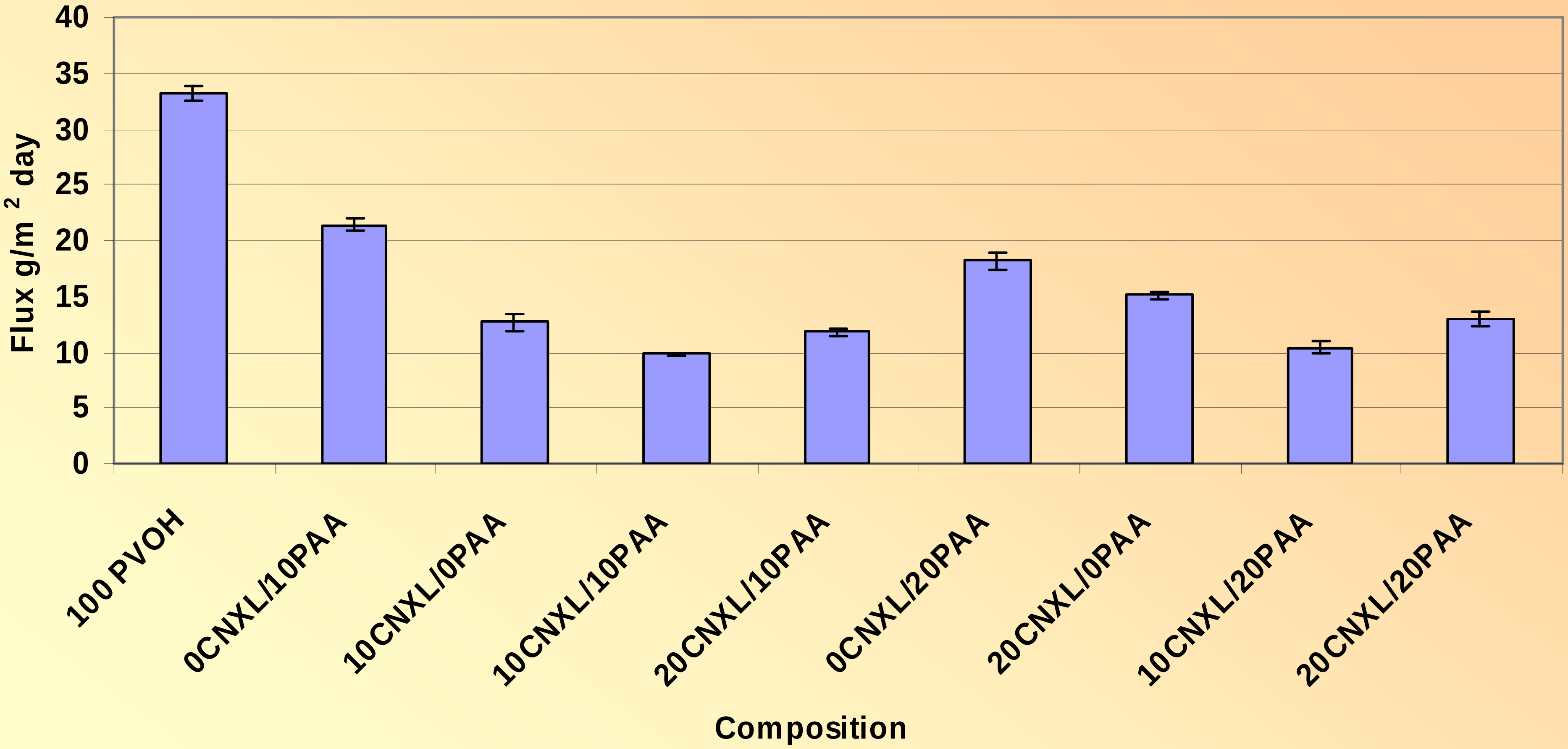
# Water Permeability
# Water Vapor Transmission Rate

- Test were conducted at 30°C and 30% relative humidity




$$J(Flux) = \frac{M}{A*t}\frac{Mass\ change\,(g)}{Area\,(m^2)*time\,(day)}$$

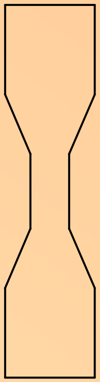
# WVTR



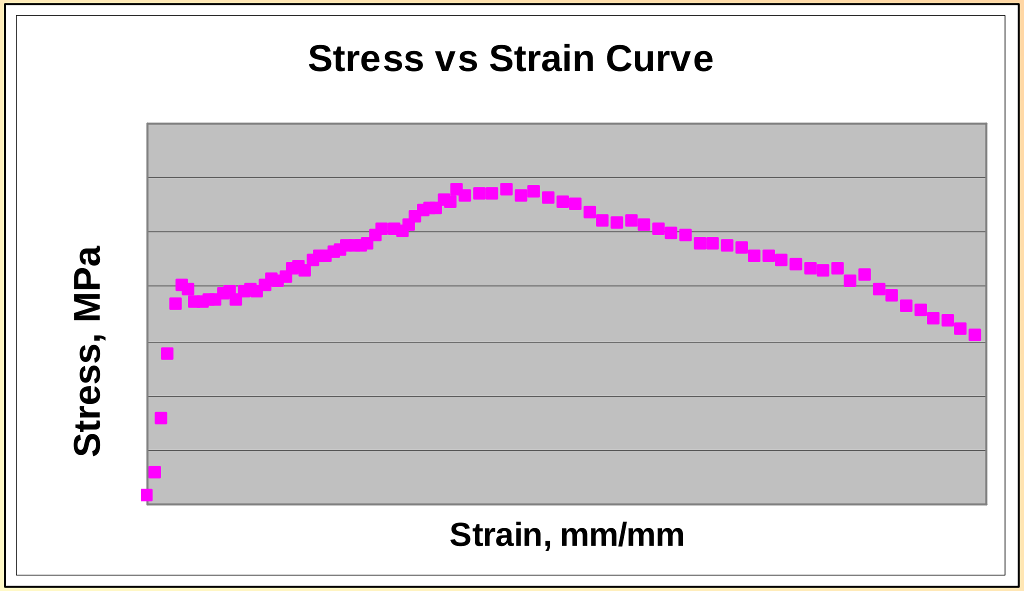
40
35
30
25
20
15
10
5
0
Flux g/m 2 day
100 PVOH
0CNXL/10PAA
10CNXL/0PAA
10CNXL/10PAA
20CNXL/10PAA
0CNXL/20PAA
20CNXL/0PAA
10CNXL/20PAA
20CNXL/20PAA
Composition

# Mechanical tensile testing

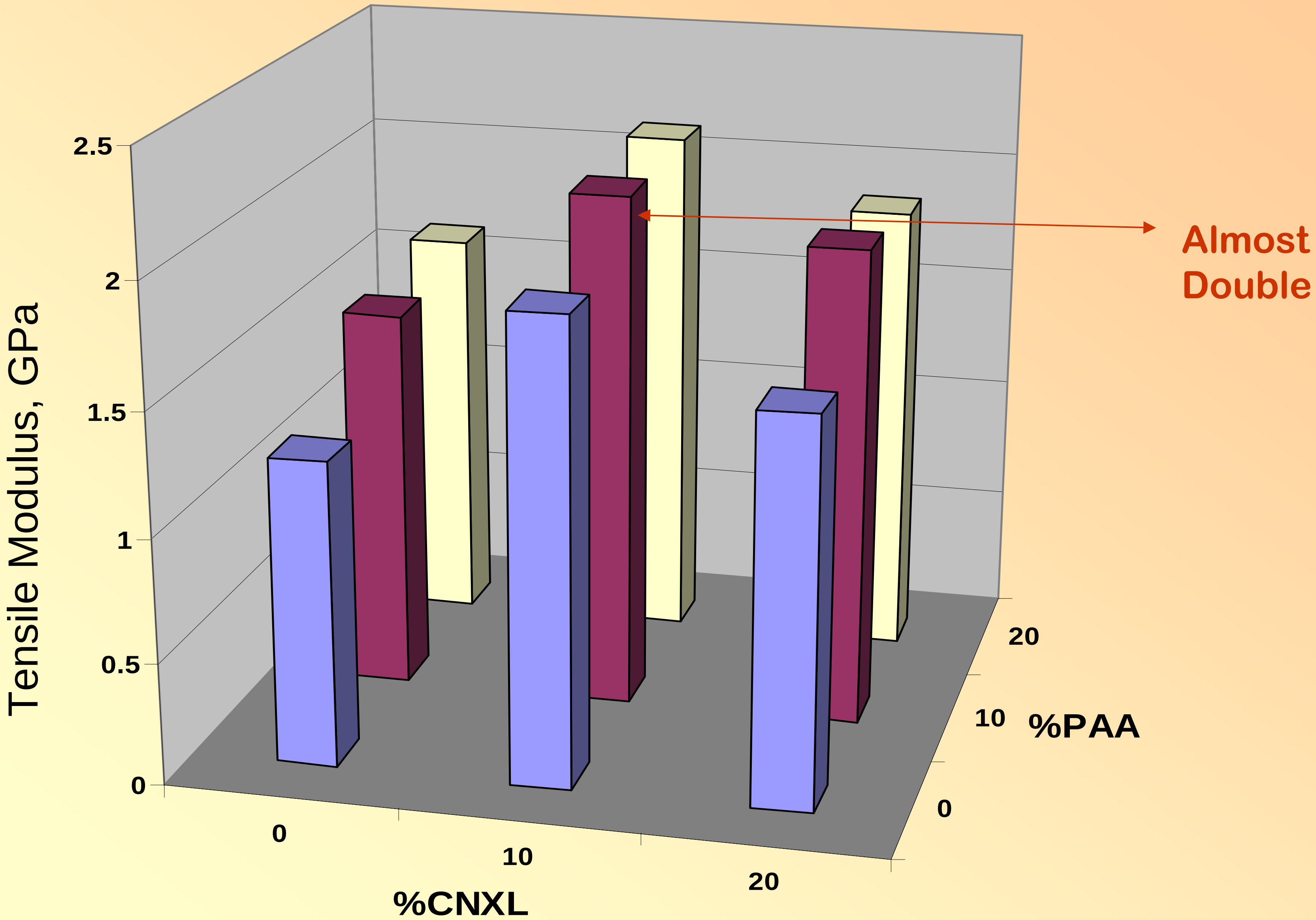
- 27 micron thick films were cut into a dogbone shape



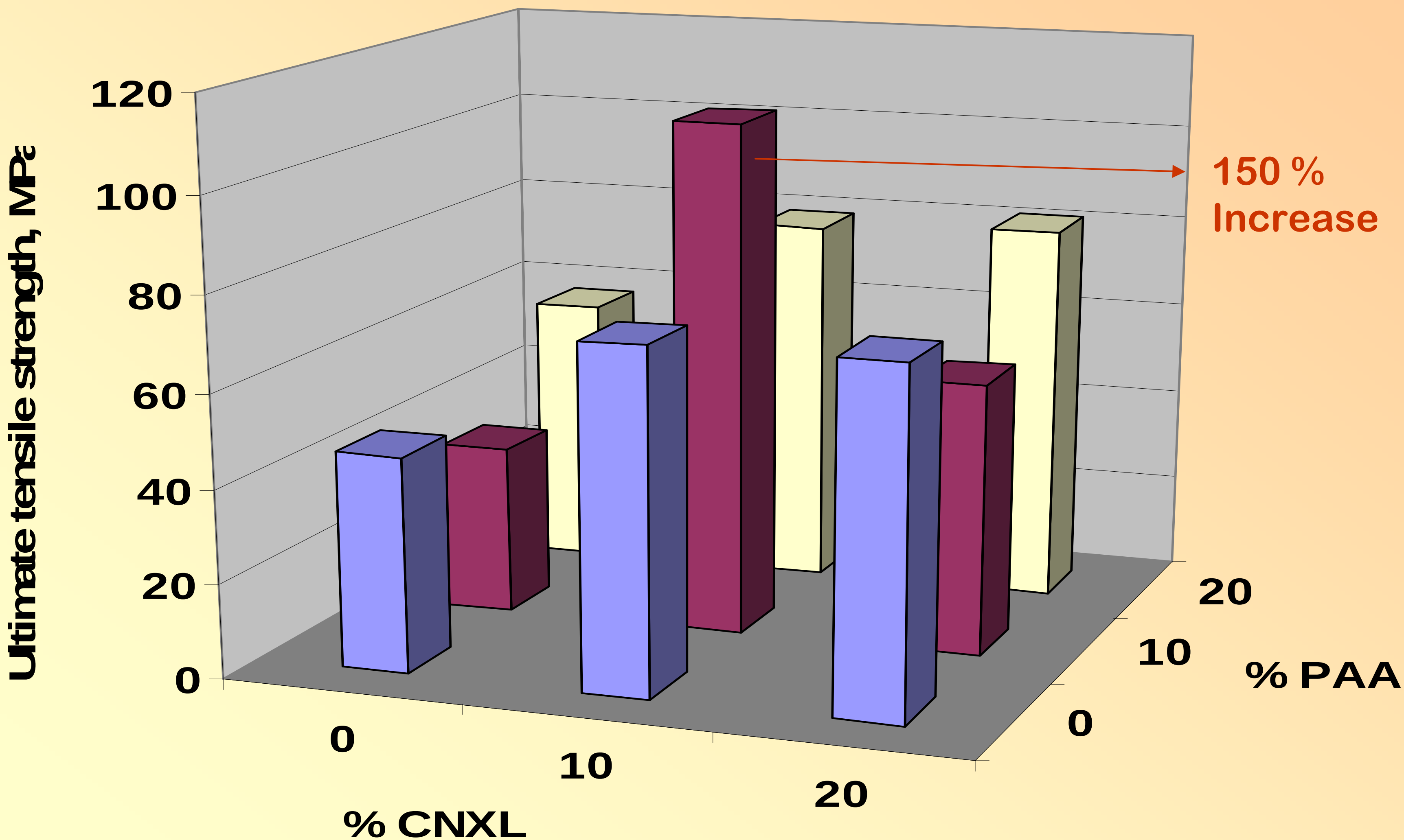
- Strain rate: 1 mm/min
- Span: 20 mm



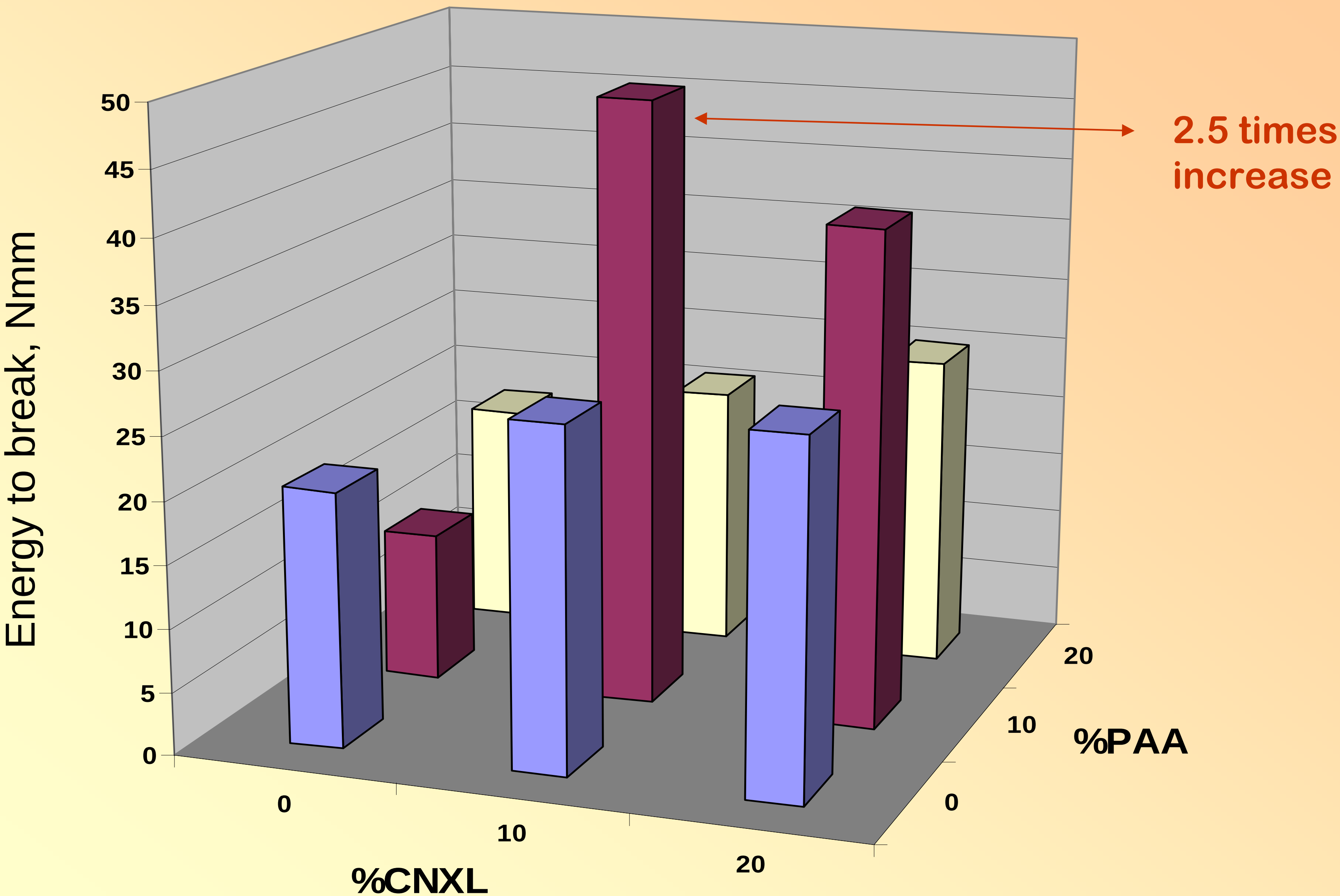
# Tensile Modulus



# Ultimate Tensile Strength

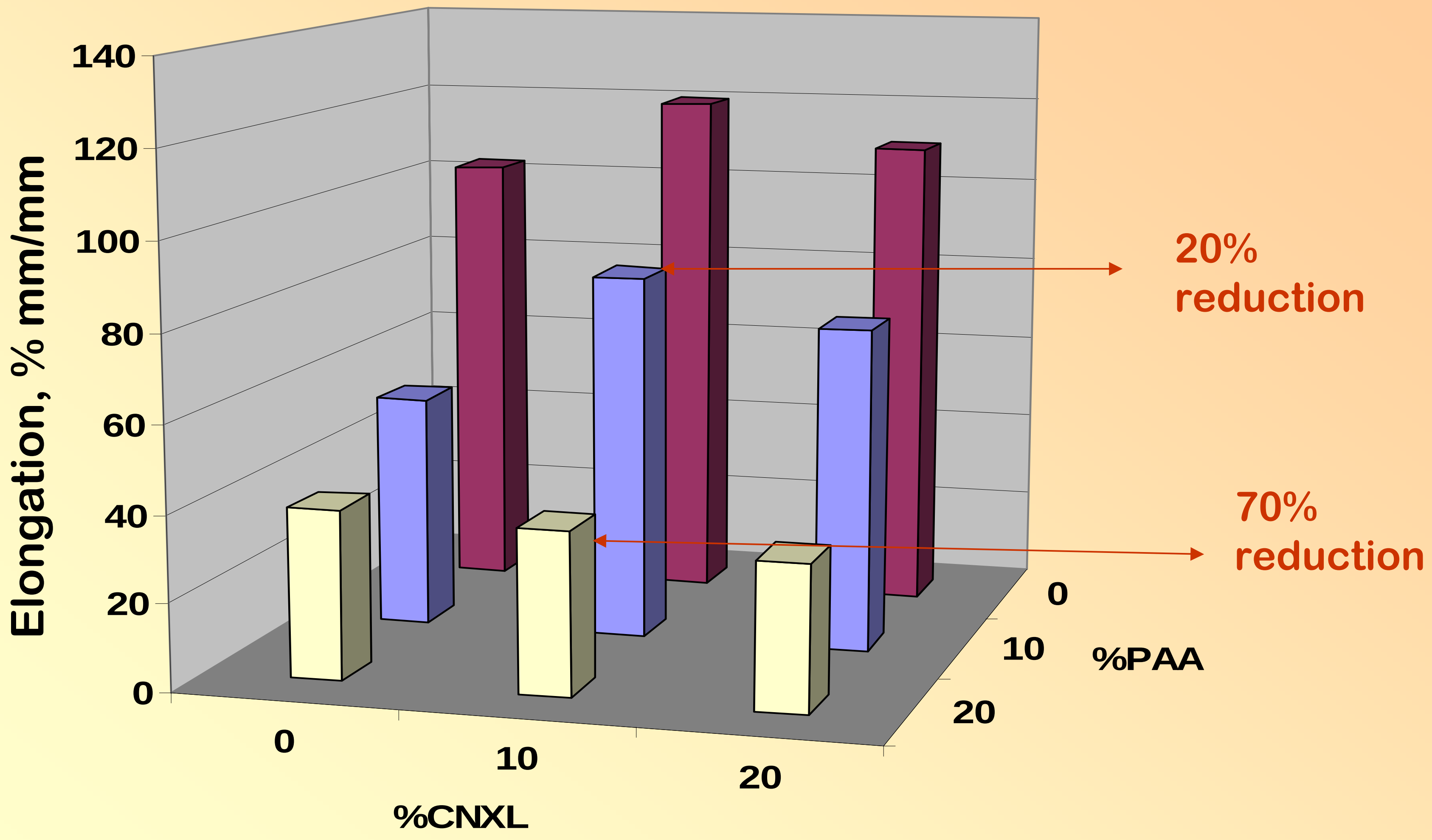


# Toughness



Energy to break, Nmm
50
45
40
35
30
25
20
15
10
5
0
0
10
20
%CNXL
0
10
20
%PAA
2.5 times
increase

# % Elongation



140
120
100
80
60
40
20
0
Elongation, % mm/mm
0
10
20
%CNXL
0
10
20
%PAA
20% reduction
70% reduction

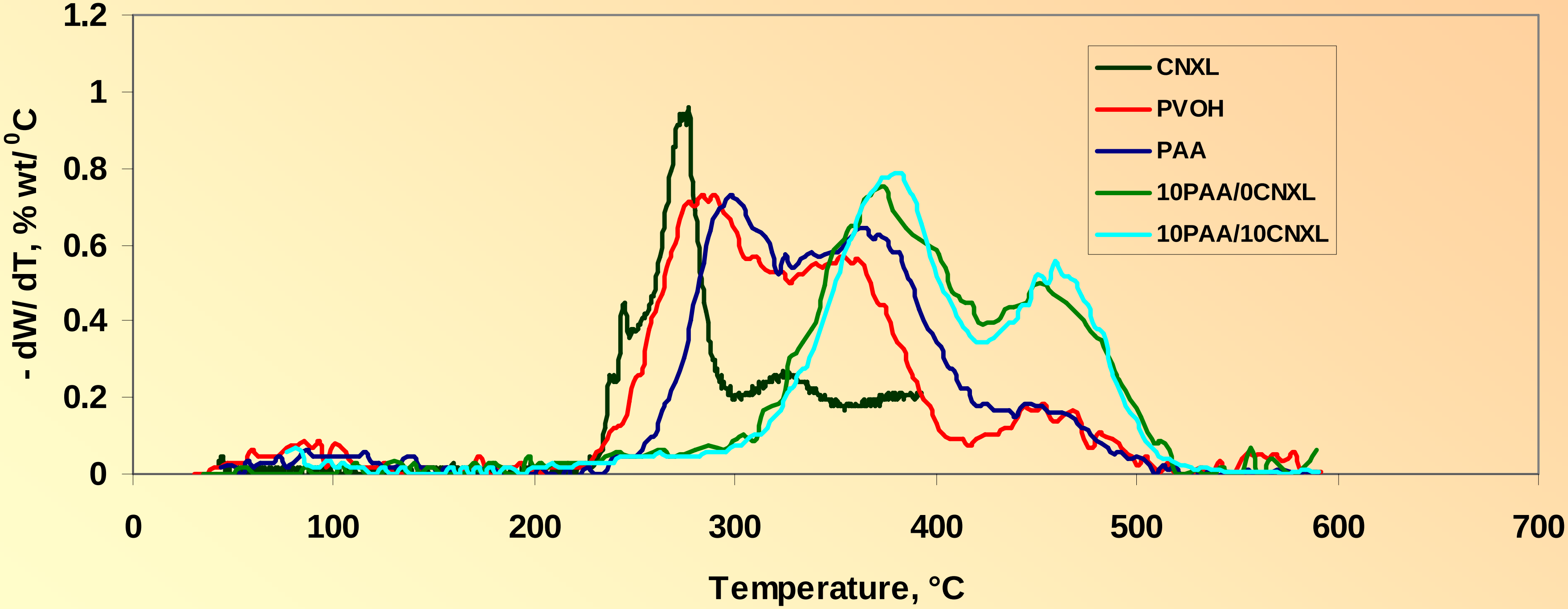
# Thermal degradation
# Thermo gravimetric Analysis

- Change in weight with increasing temperature

- Test is run from room temperature to 600°C

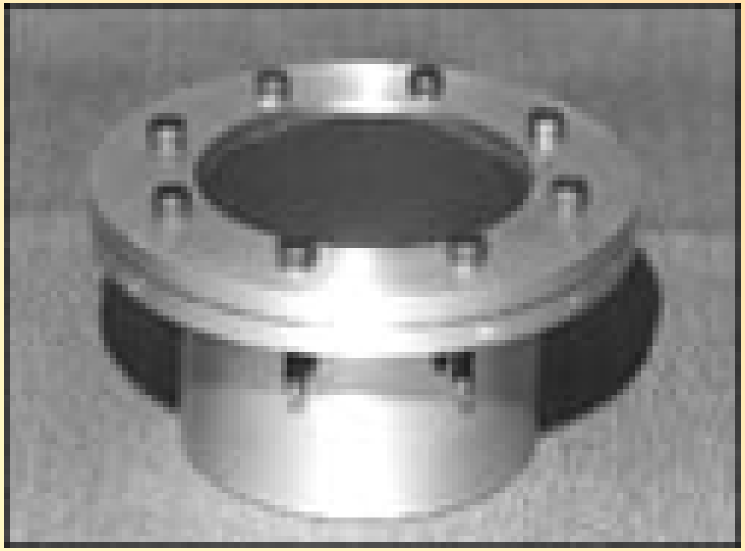
- Ramping 20°C/min

# PAA boosts initial $T_{degradation}$ CNXL no effect



# Chemical Vapor Transmission Rate-CVTR

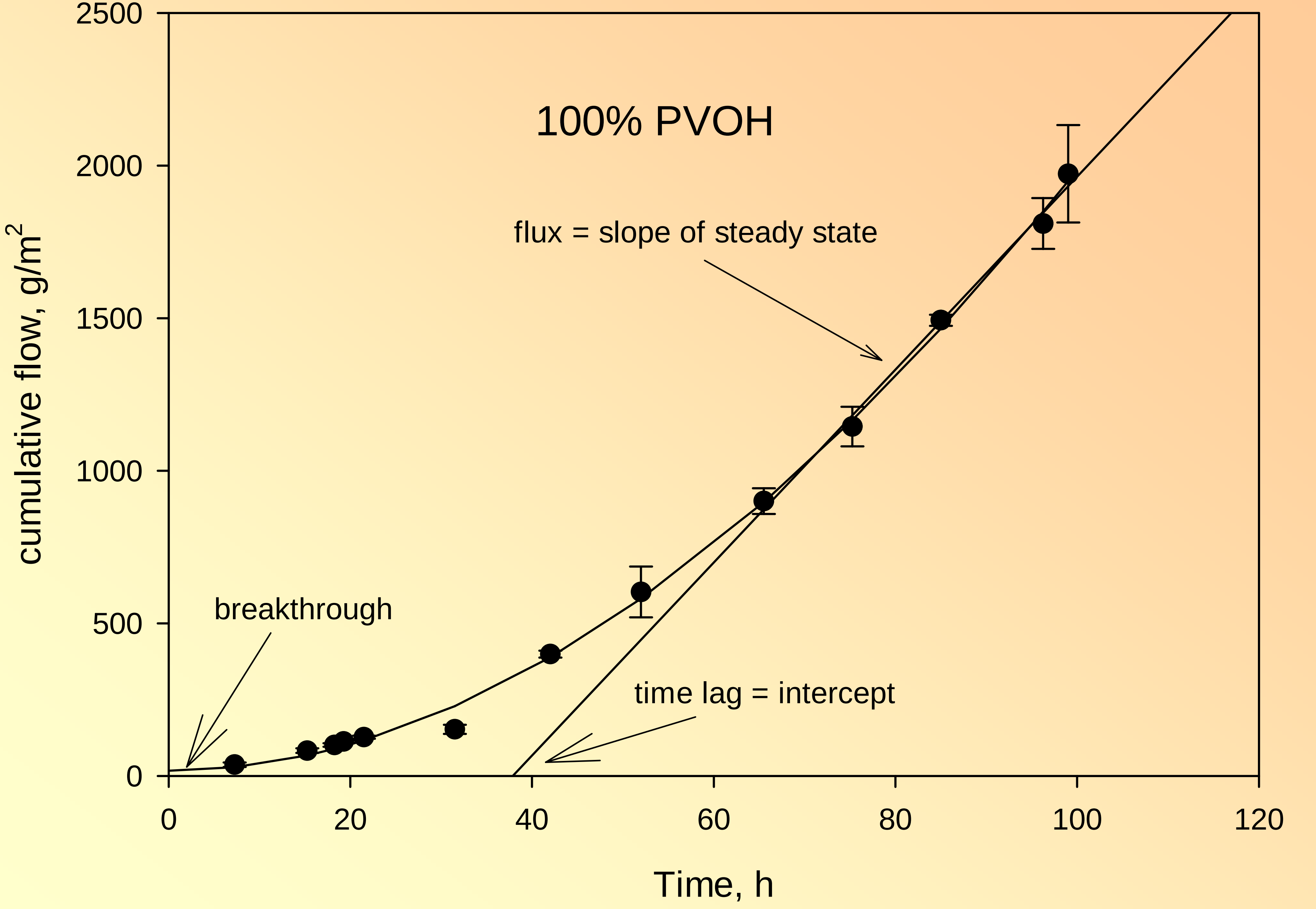
- ASTM standard F 1407-99a (Standard method of resistance of chemical protective clothing materials to liquid permeation).



- Permeant = 1,1,2 Trichloroethylene (TCE), listed in CERCLA and EPCRA as hazardous

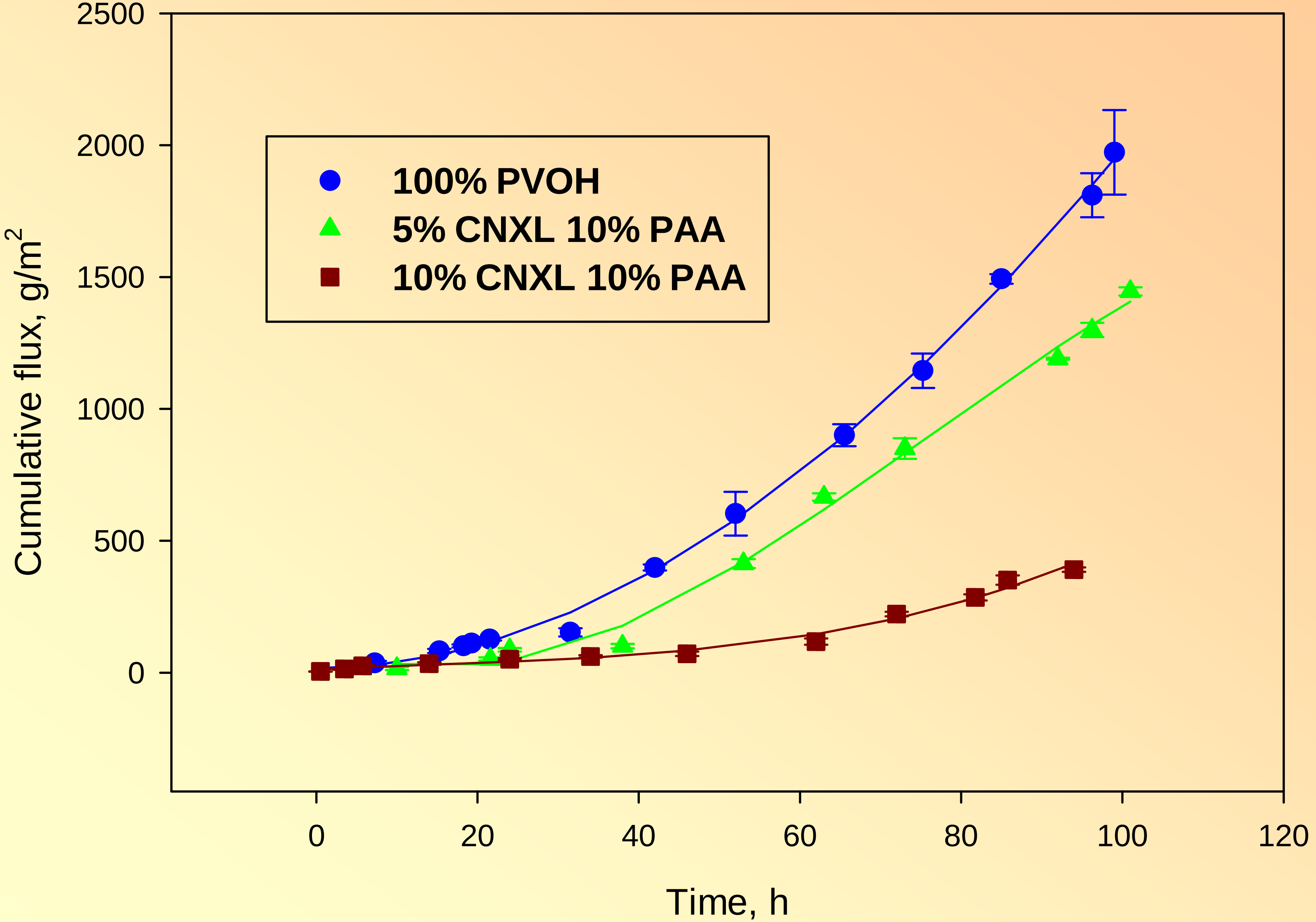
# CVTR Assumptions

- The assumptions made for the experimental setup are as follows.
  - 1) Mass transfer occurs in the z-direction only, as the lateral directions are sealed
  - 2) The temperature and relative humidity of the system remains constant throughout the experiment
  - 3) A semi-steady state mass transfer occurs, where the flux becomes constant after a certain time interval
  - 4) The concentration of the simulant outside the film is zero as it is swept away by the air in hood



100% PVOH
flux = slope of steady state
breakthrough
time lag = intercept
cumulative flow, g/m2
Time, h
2500
2000
1500
1000
500
0
0
20
40
60
80
100
120

# Chemical Vapor Transmission Rate



# Surface Modification of CNXLs

## OBJECTIVES

- To improve the interaction between CNXLs and PVOH

- To understand if the CVTR observations are more influenced by CNXLs or PAA

# Surface modification of CNXLs


CNXLs

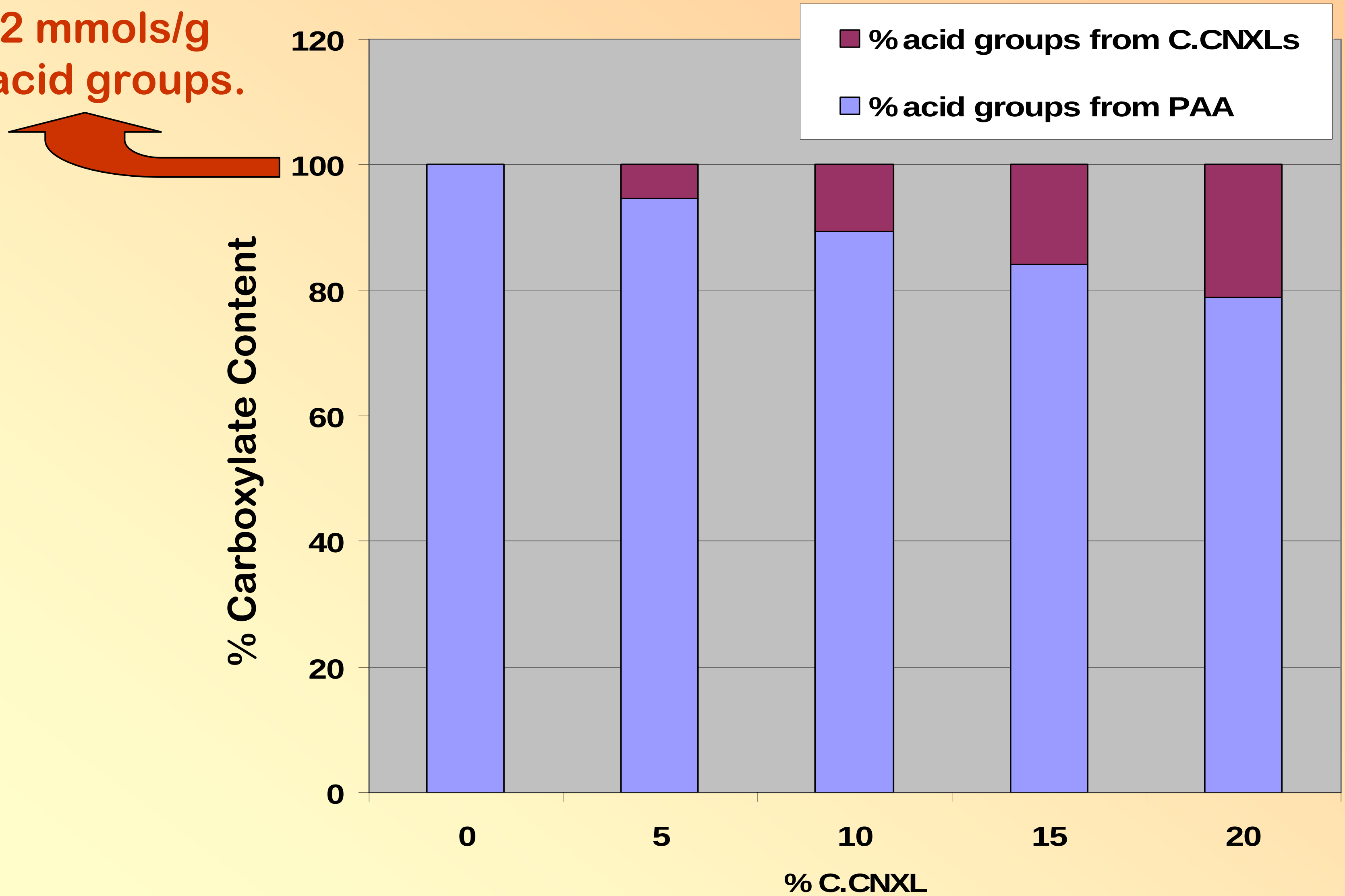
C.CNXLs

***Source: Araki et.al, Langmuir, 17: 21-27, 2001.***

- Titration of C.CNXLs indicated the presence of 1.4 mmols of acid/ g CNXLs

- Titration of PAA indicated the presence of 13.2 mmols of acid/ g PAA

1.32 mmols/g
of acid groups.




Acid content (mmols) of C.CNXLs+PAA = Acid content (mmols) of 10 wt% PAA

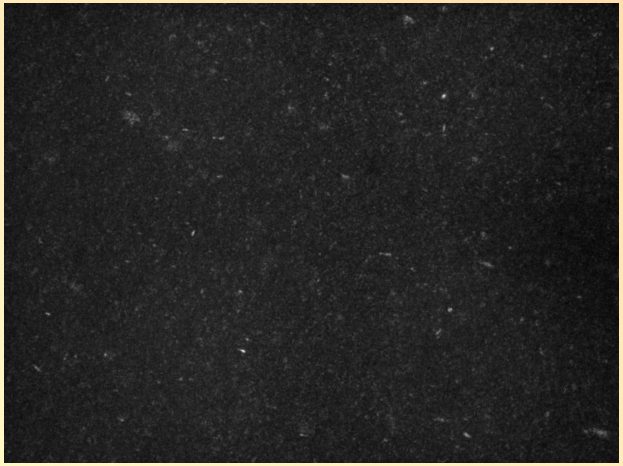
# Methods

- Polarized optical microscopy
- Water vapor transmission
- Thermal degradation
- Chemical vapor transmission

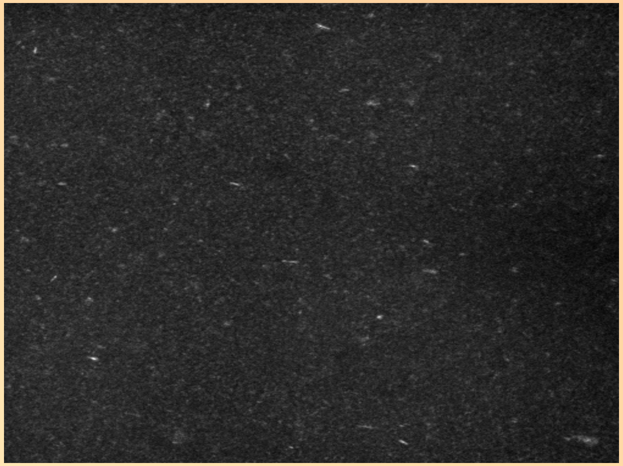
# Dispersion of C.CNXLs

CNXLs

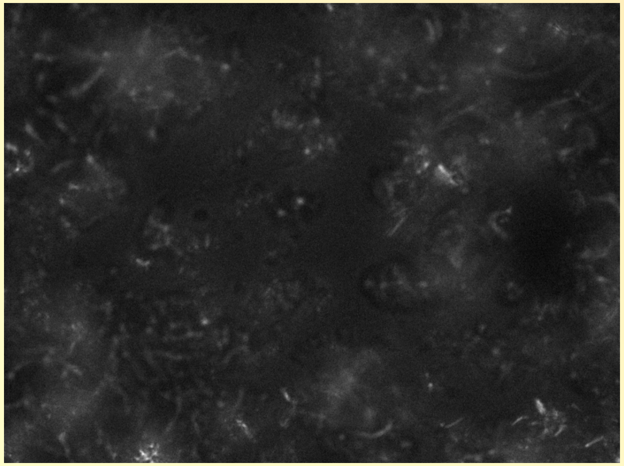
C.CNXLs



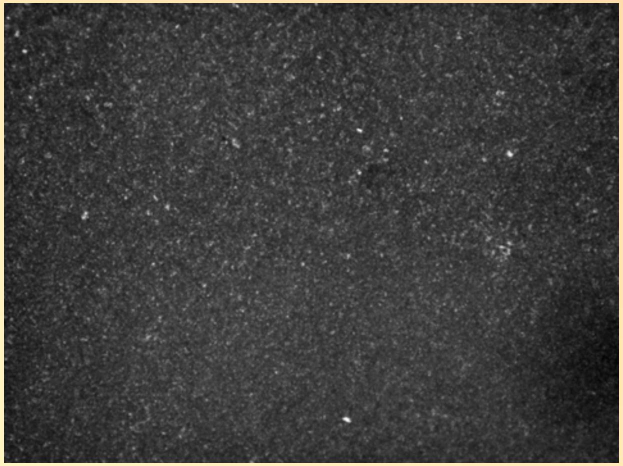
10%



10%

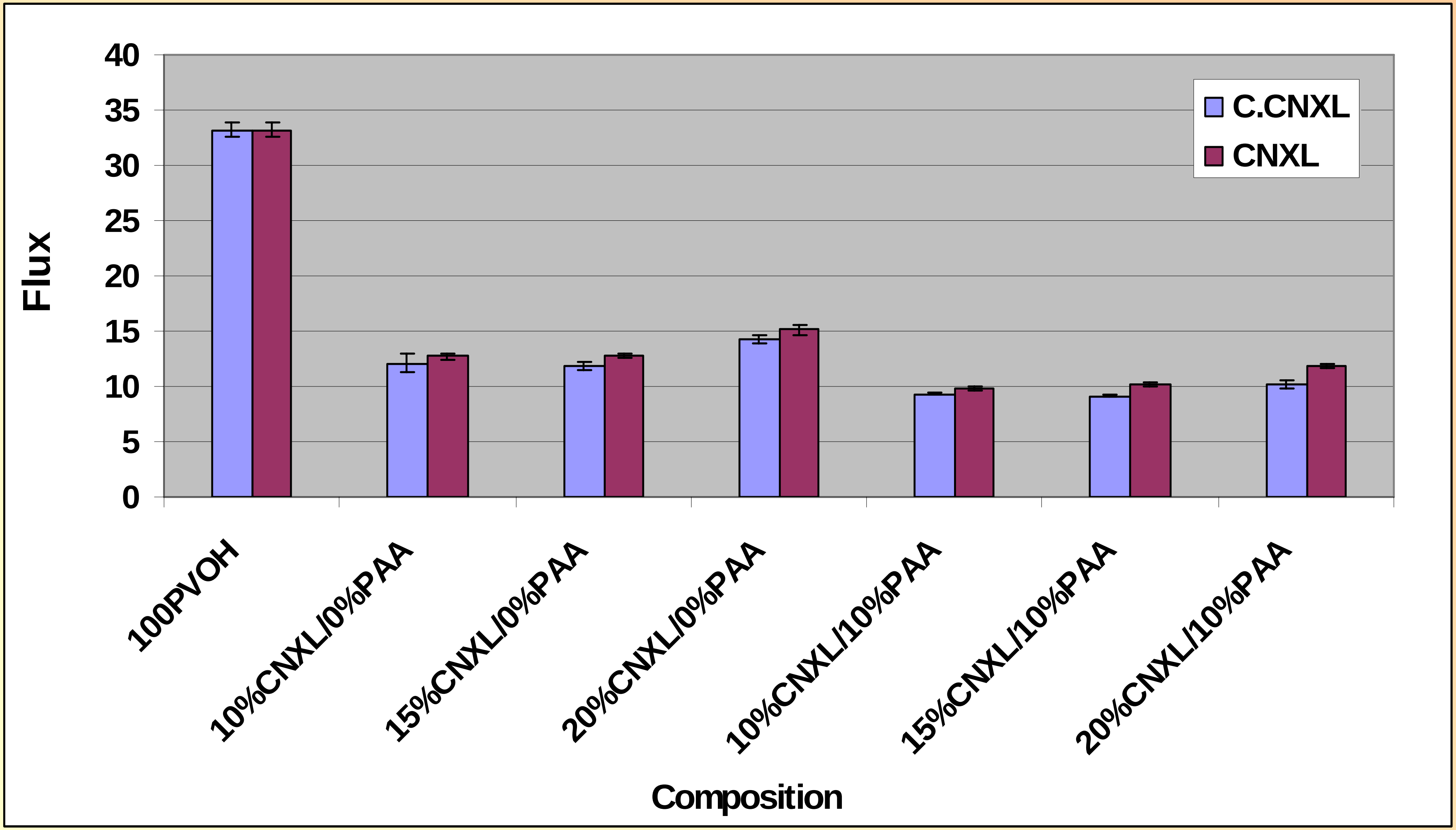


15%



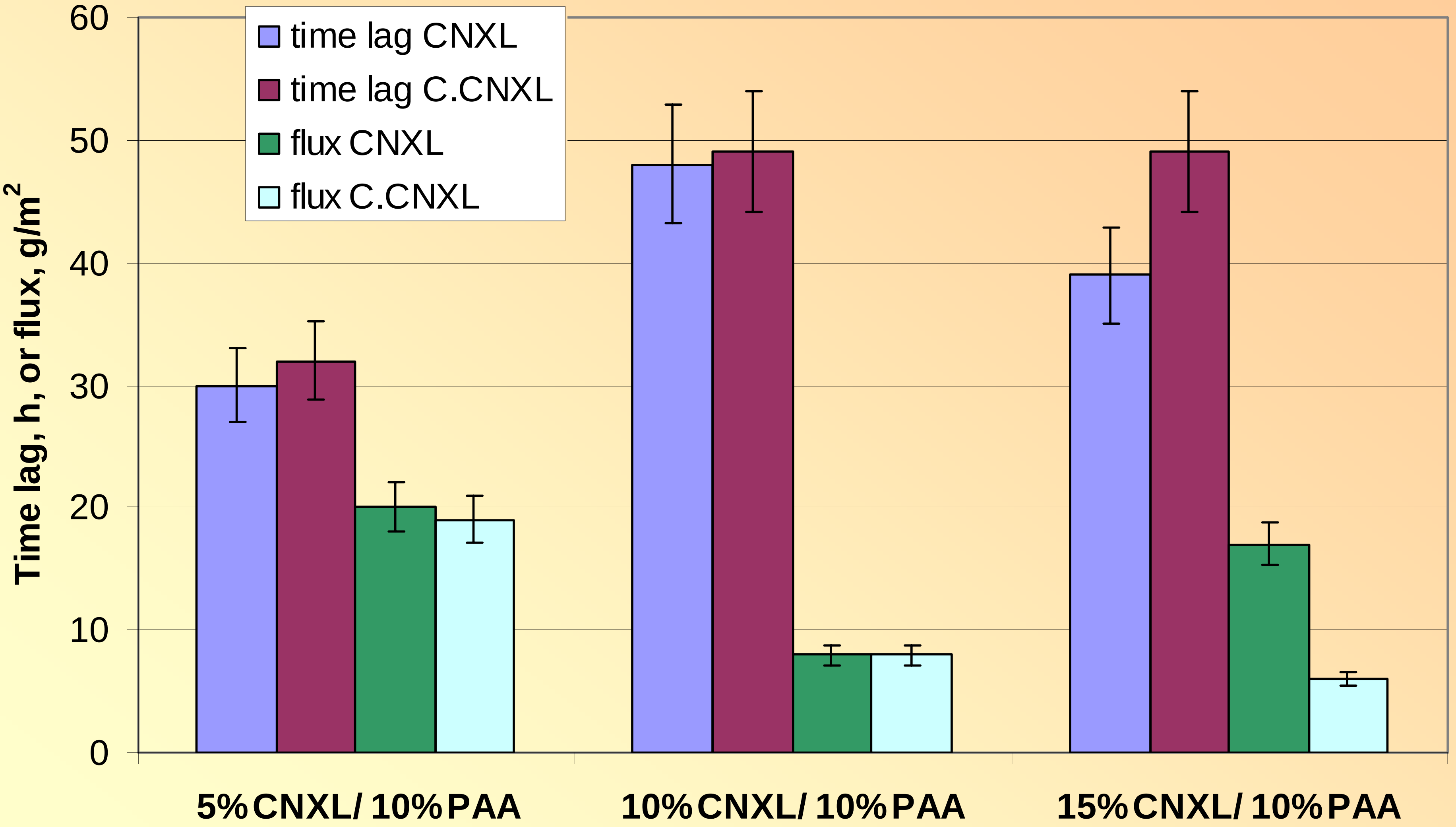
15%

# Water Vapor Transmission Rate



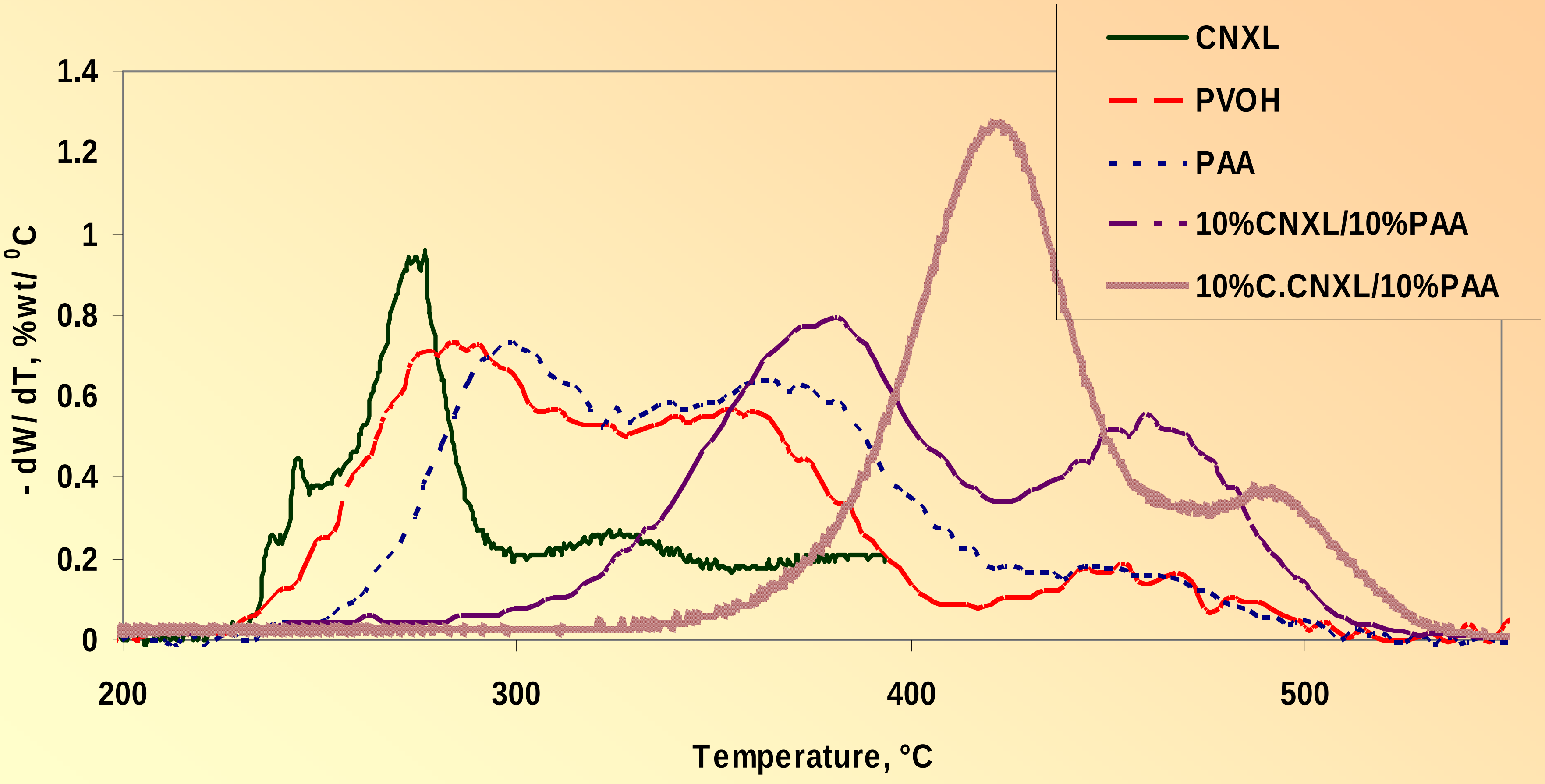

**Flux : g / $m^2$ * day**

# CVTR



Time lag, h, or flux, g/m2
60
50
40
30
20
10
0
time lag CNXL
time lag C.CNXL
flux CNXL
flux C.CNXL
5% CNXL/ 10% PAA
10% CNXL/ 10% PAA
15% CNXL/ 10% PAA

# Thermal degradation DTGA



# Conclusions

- 170 °C temperature and 45 minutes of heat treatment were found to be optimum temperature and time to reduce dissolution of films
- CNXLs were well dispersed in blend films of PVOH and PAA up to 10% by weight content
- The presence of CNXLs with PAA crosslinking almost doubles the strength, stiffness and toughness, while the elongation is reduced by 20% compared to the control (PVOH)
- The CVTR experiments show a significant increase in the time lag and reduced flux compared to pure PVOH

# Conclusions

- C.CNXLs show better dispersion at 15% filler loading than CNXLs
- C.CNXLs showed slightly reduced flux and increased time lag
- DTGA showed significant increase in thermal stability
- Toughness does not alter to a great extent

# Acknowledgements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