# Cellulose Reinforced High Density Polyethylene

*Presented by*

Velu Palaniyandi

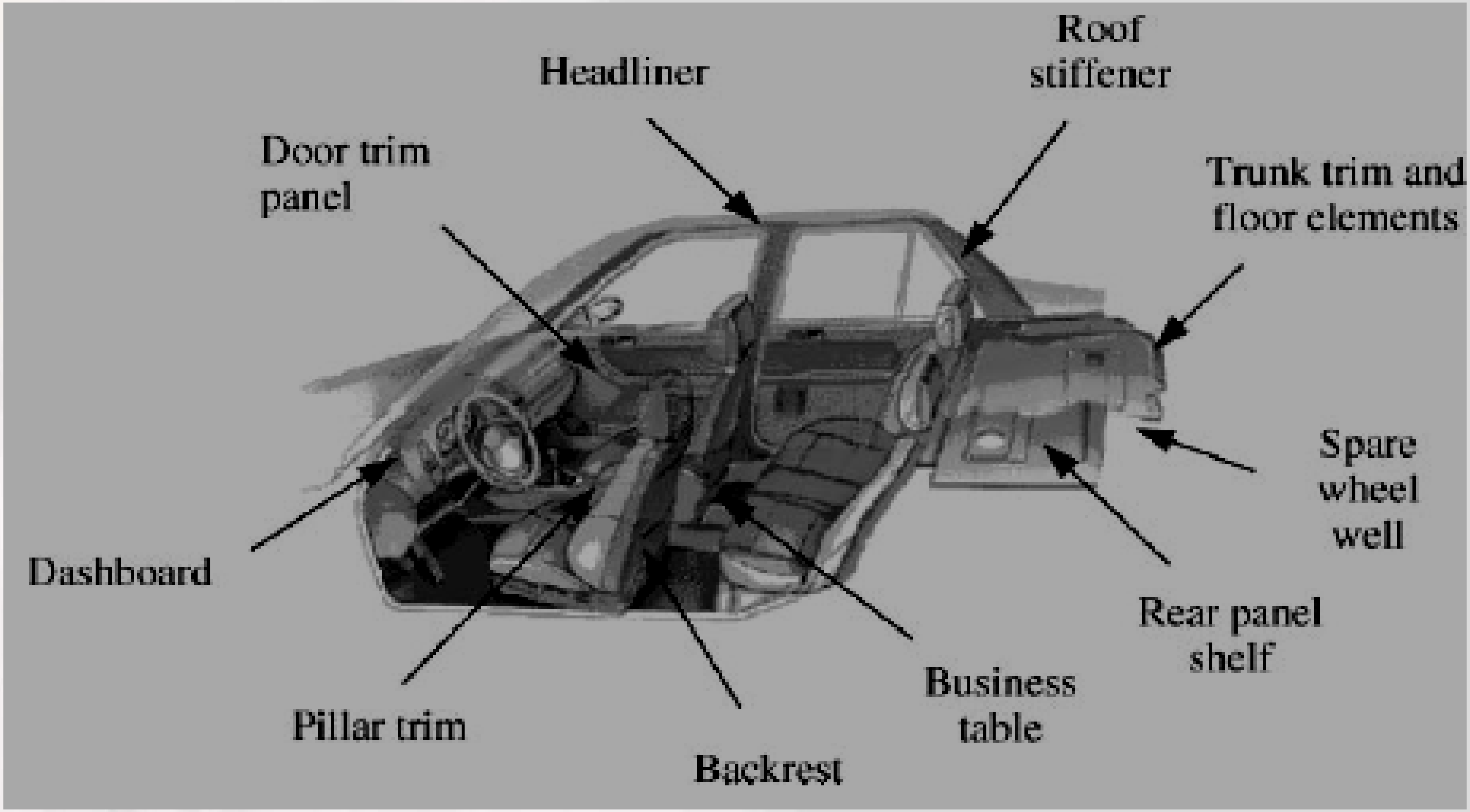
M.S. Thesis Defense

Advisors:
Dr.John Simonsen
Dr.Ralph Busch

# Contents

# Background

## *Natural Fiber Reinforced Composites (NFRP) applications in Car Interiors*



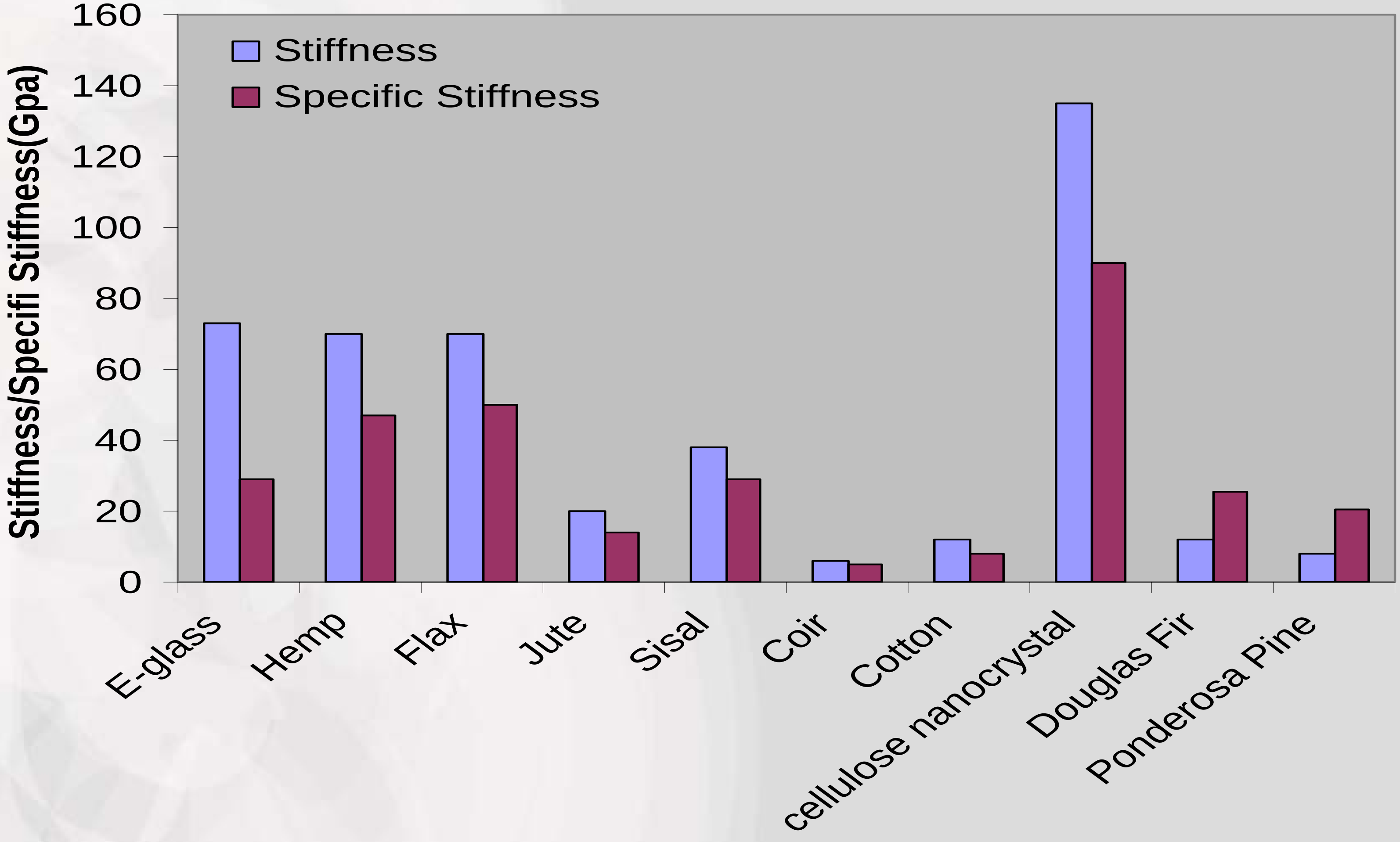

Source : Reinforced Plastics, Feb 2004

# Some More Applications

- Heat deflection temperature
- Gas barrier / permeability
  - Packaging materials
- Electrical conductivity
  - Electronics ,Housing appliances
- Flame retardancy

Source :Plastic technology ,Feb 2004

# Property Comparison Among the Commonly Used Reinforced Fibers

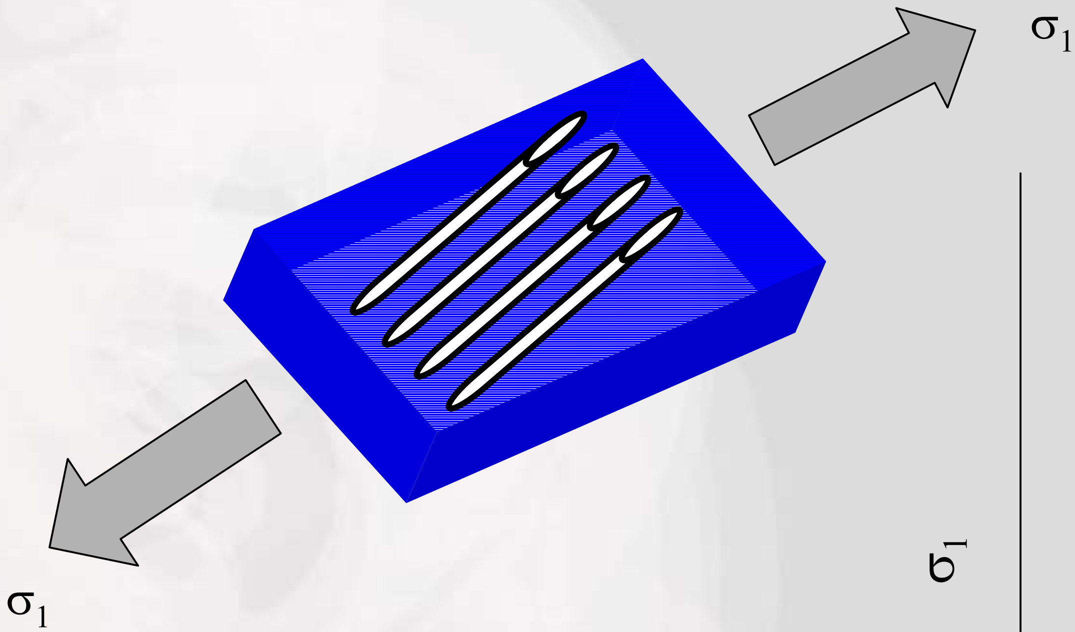


# Introduction

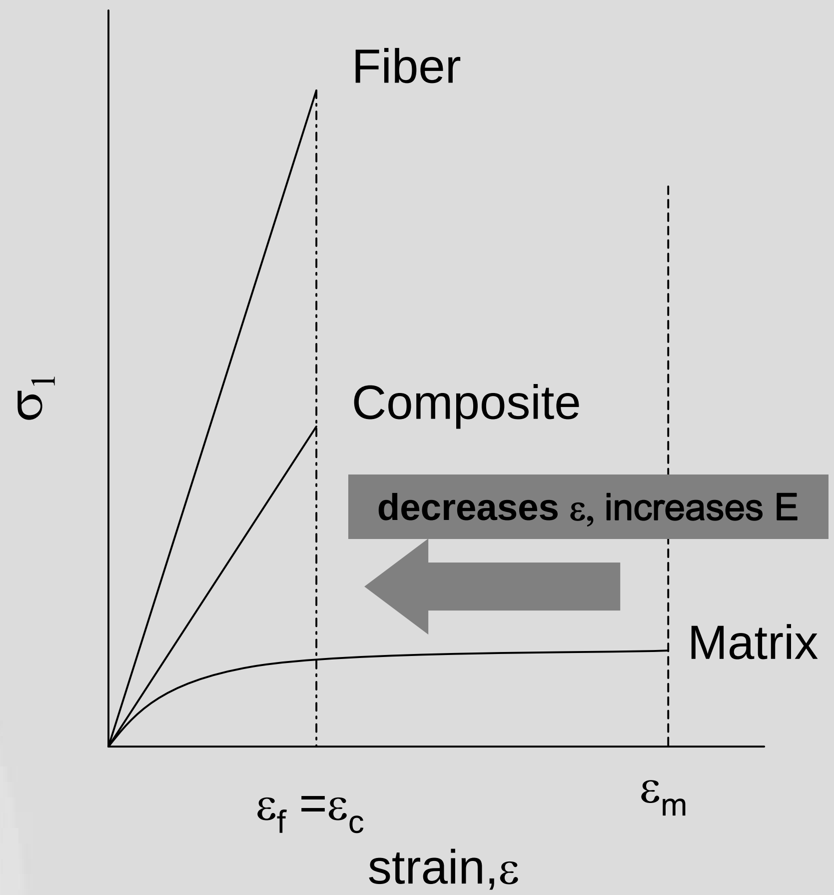
- **Why cellulose-reinforced thermoplastics?**
  - **Property enhancement at lower density and cost than synthetic fiber materials (glass, carbon)**
  - **Non-abrasive and easily recyclable compared to inorganic fillers**
  - **High strength to weight ratio**
  - **Sound abatement capability**
  - **Low energy for processing**

    (6500 BTU/lb of kenaf ; 23,500BTU/lb of glass fiber)

# Role of fiber and Matrix in FRP




- **Fiber**
  - **High stiffness**
  - **Brittle**
- **Matrix**
  - **Medium for stress transfer**
  - **Binds the fiber together**

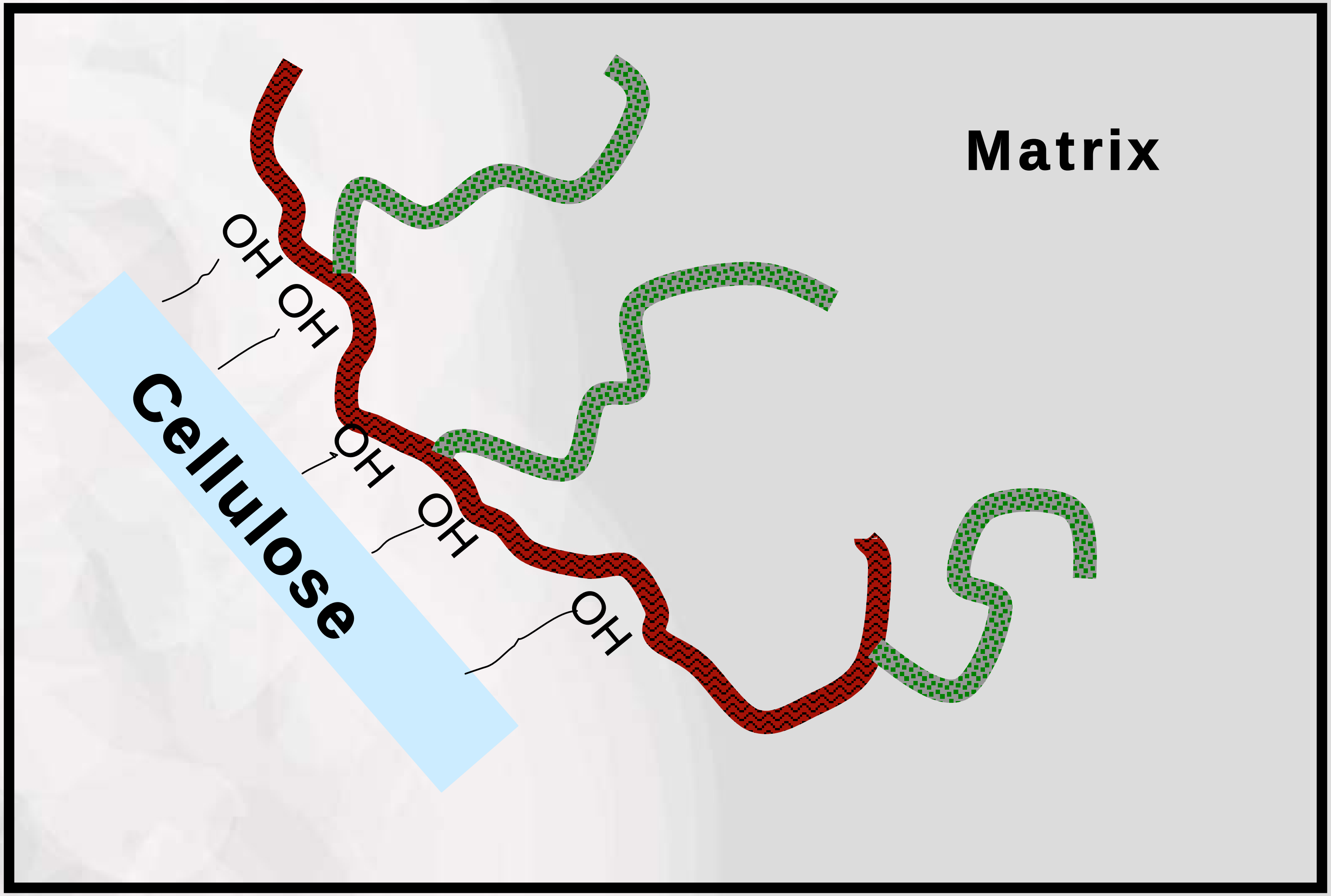



**Stress-Strain curve**

# Fiber Reinforced Composite - Issues

- Fiber dispersion
  - Dispersing agent
- Interfacial adhesion
  - **Compatabilizer or coupling agents**
  - Surface modification of fibers
- **Effect of filler on the crystallization behavior of polymer**

# Compatabilizer – Function and Mechanism



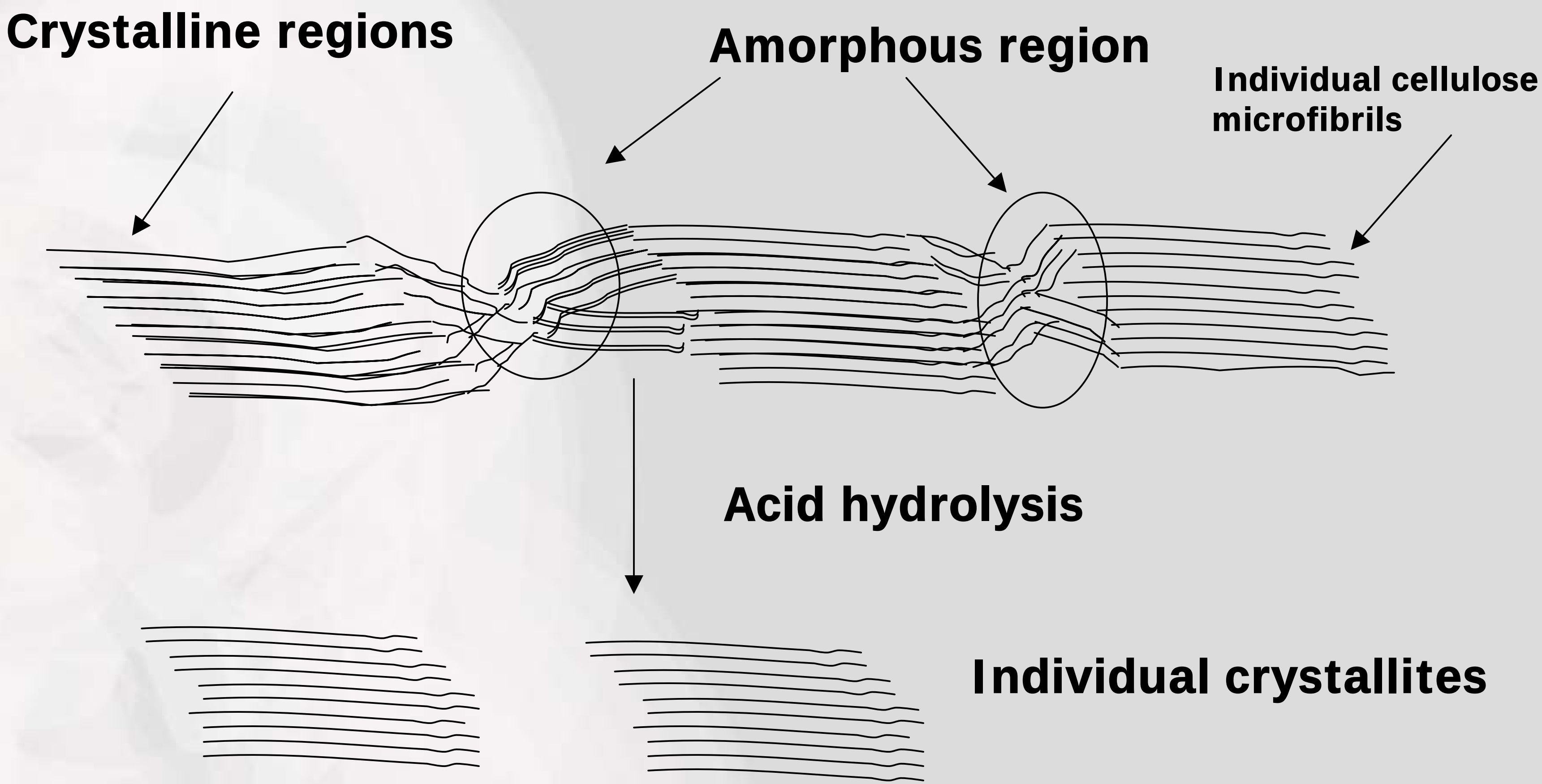
# Objectives

- To prepare nanocrystalline cellulose with high aspect ratio
- To investigate the material properties of nanocrystalline cellulose (NCC) filled high density polyethylene (HDPE)
- To use microcrystalline cellulose (MCC) as a model filler for NCC
- To disperse MCC using a coupling agent system
- To study the non-isothermal crystallization kinetics of the filled composites

# Materials

- Matrix: High Density Polyethylene
- Filler
  - Cellulose nanocrystal from Cotton
  - Microcrystalline cellulose (FMC Corp, NJ)
- Coupling agent:
    - MAPE (Optipak 210)
  - Developed by Kaichang Li's lab
    - AKD (Aquapel 364)
    - PMDI (Rubinate 1840)

# Experimental Methods




## Schematic of acid hydrolysis of cellulose

# Composite Preparation Method

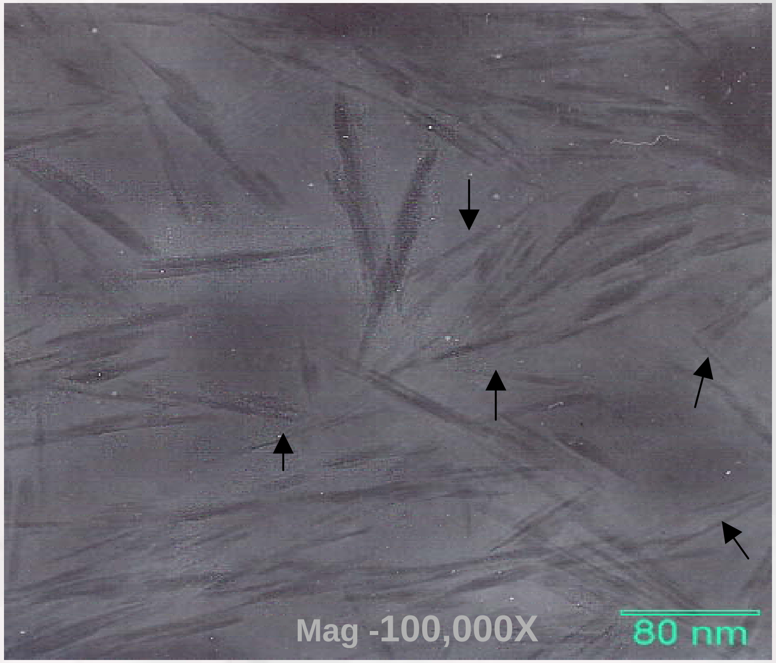
- Brabender Plasticorder
  - Melt mixing HDPE and NCC/MCC at 180 $^{o}$C for 10 min
  - MAPE (0.4 wt%) and AKD-PMDI (1.0 wt%) was added during mixing
- Carver Hot press
  - Compression molding at 185 $^{o}$C at 348.5 kPa for 10 min

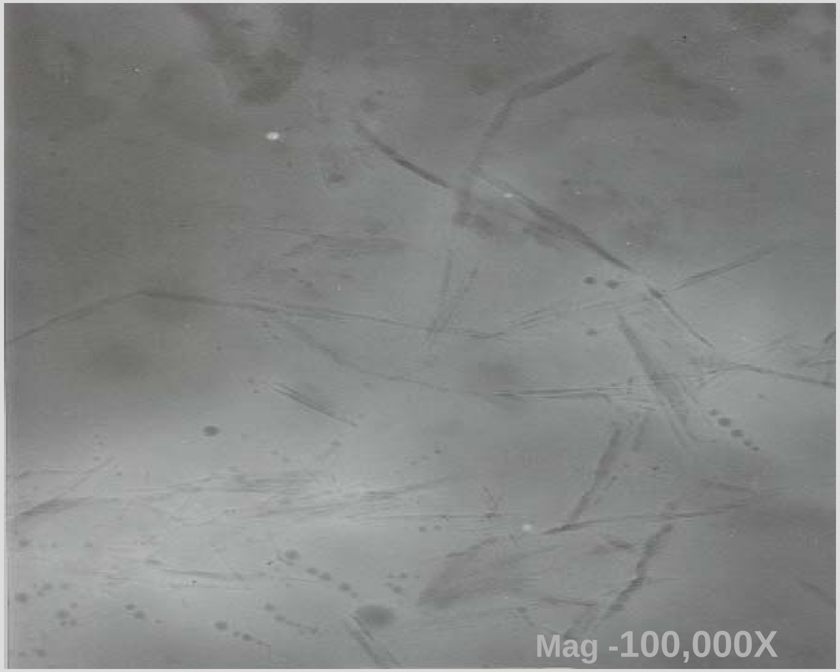
# Composite Characterization Techniques

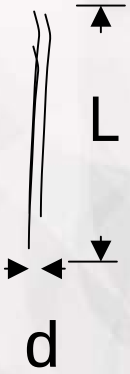
- **Mechanical testing –Sintech 1G, Universal testing machine**
  - Flexural strength (MOR) and Flexural modulus (MOE) were measured according to ASTM D 790-02
- **Thermal Analysis**
  - Differential Scanning Calorimetry, TA Instruments DSC 2920
    - -Temperature range – 20-200$^{o}$C
    - - Heating/cooling rate – 5, 10, 12.5, 15$^{o}$C/min
  - Thermo gravimetric analysis , TA Instruments, Q500
    - - Temperature range – 40-600$^{o}$C
    - - Heating rate –10$^{o}$C/min

# Results – TEM Characterization/ Mechanical Testing

# Transmission Electron Micrograph From Cellulose Nanocrystal Suspension Negatively Stained With Ammonium Molybdate



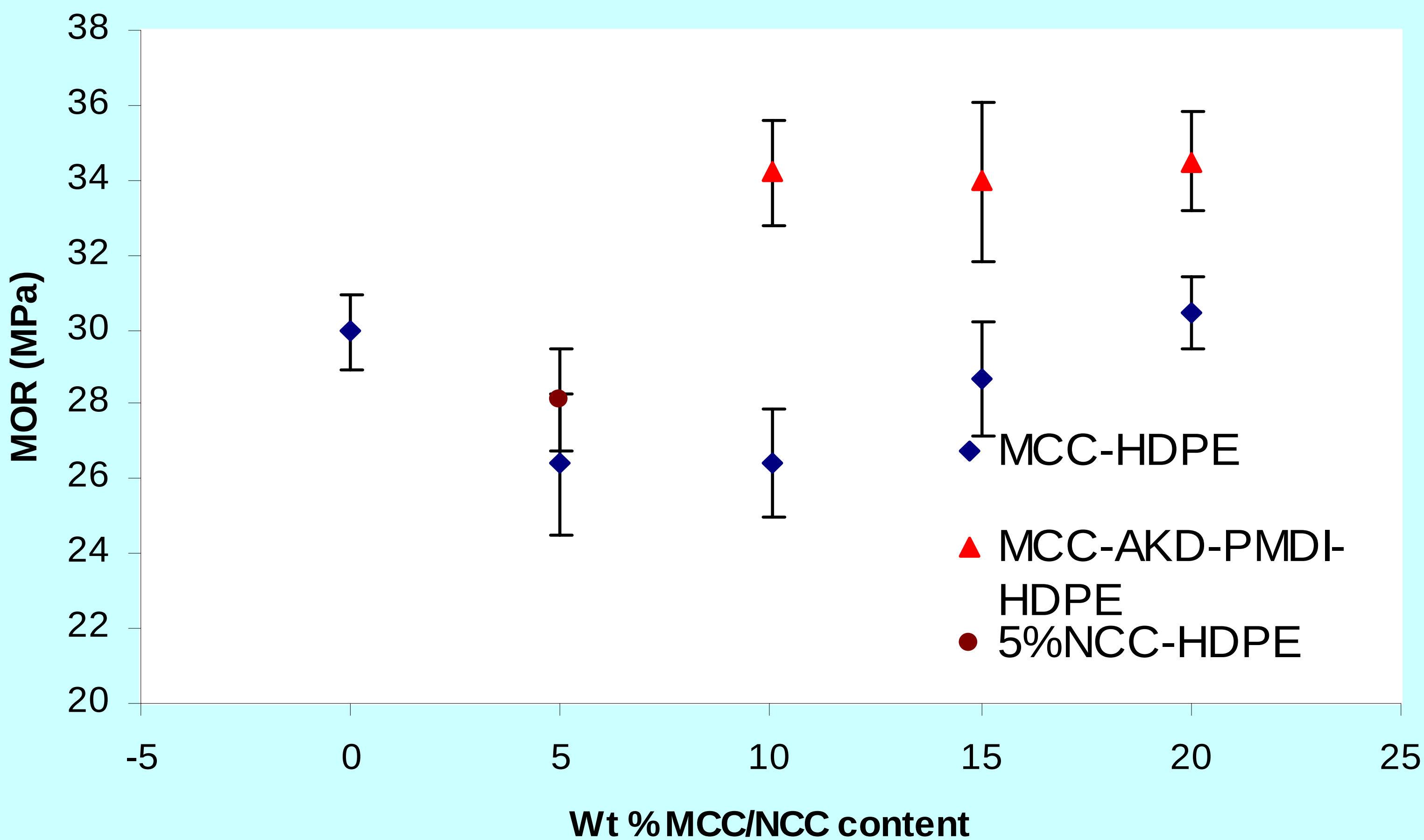



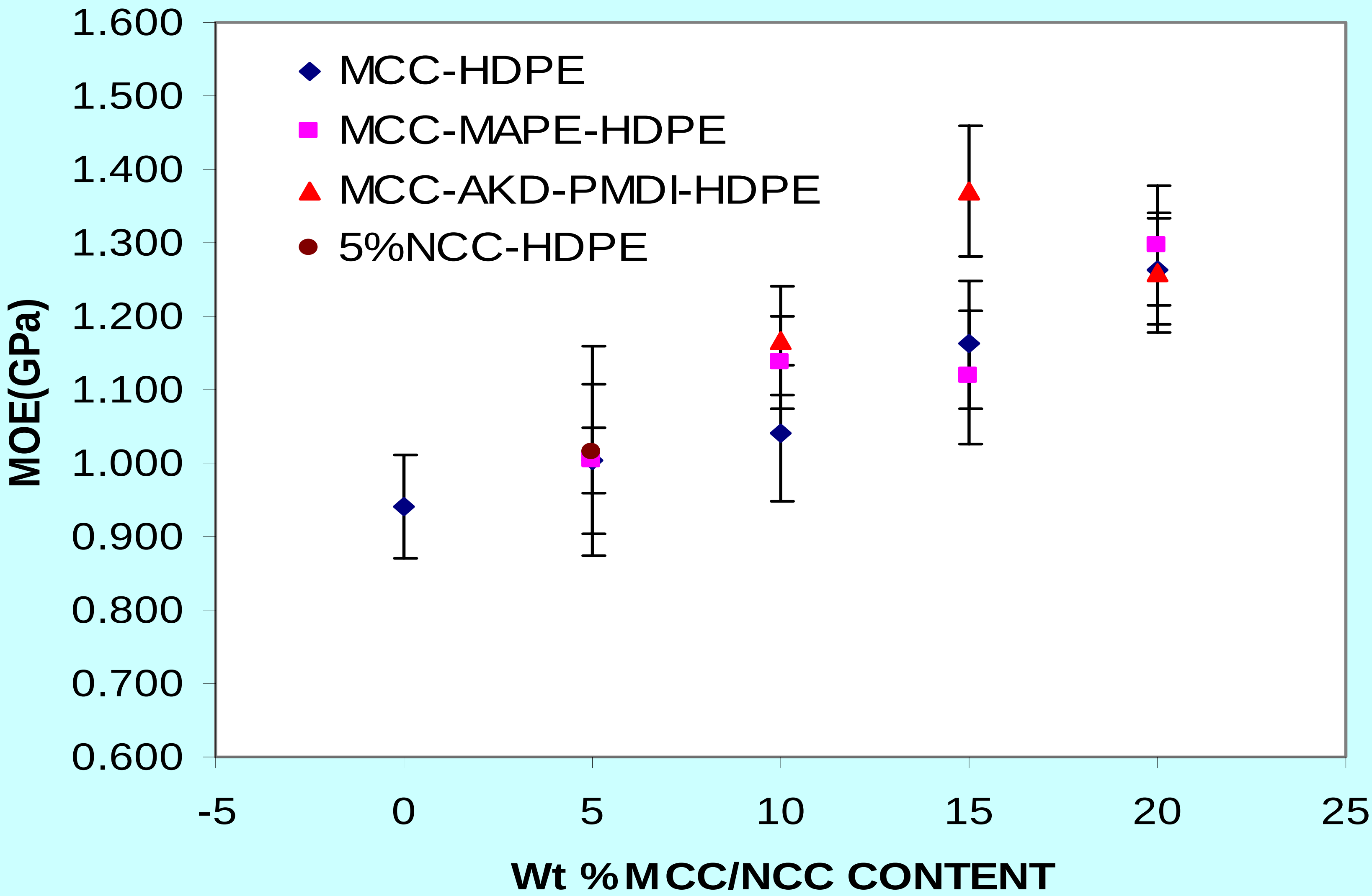

Aspect ratio =L/d

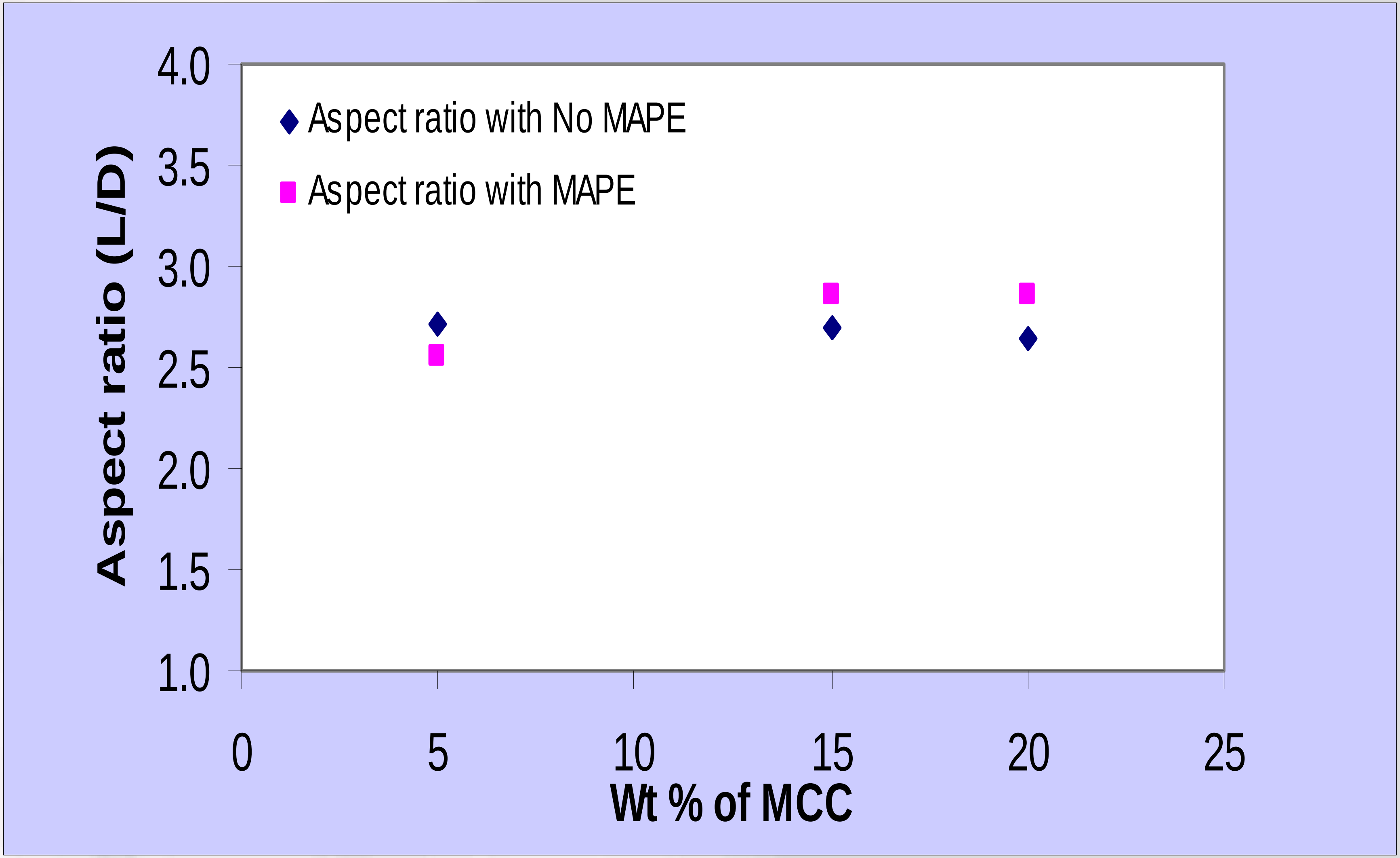
- **Diameter – 4nm**
- **Length – 120 – 160 nm**
- **Aspect ratio – 30-40**

# Flexural Strength (MOR)



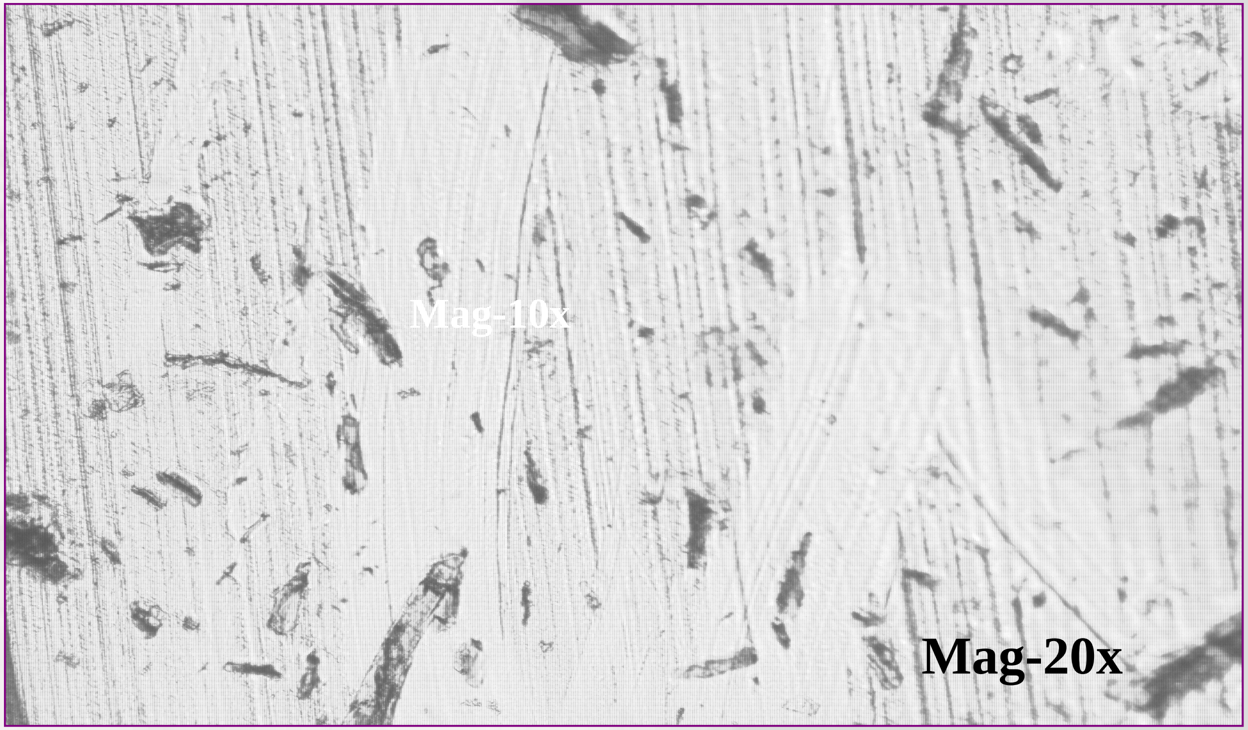
# Flexural Stiffness






- **Low aspect ratio due to agglomeration**

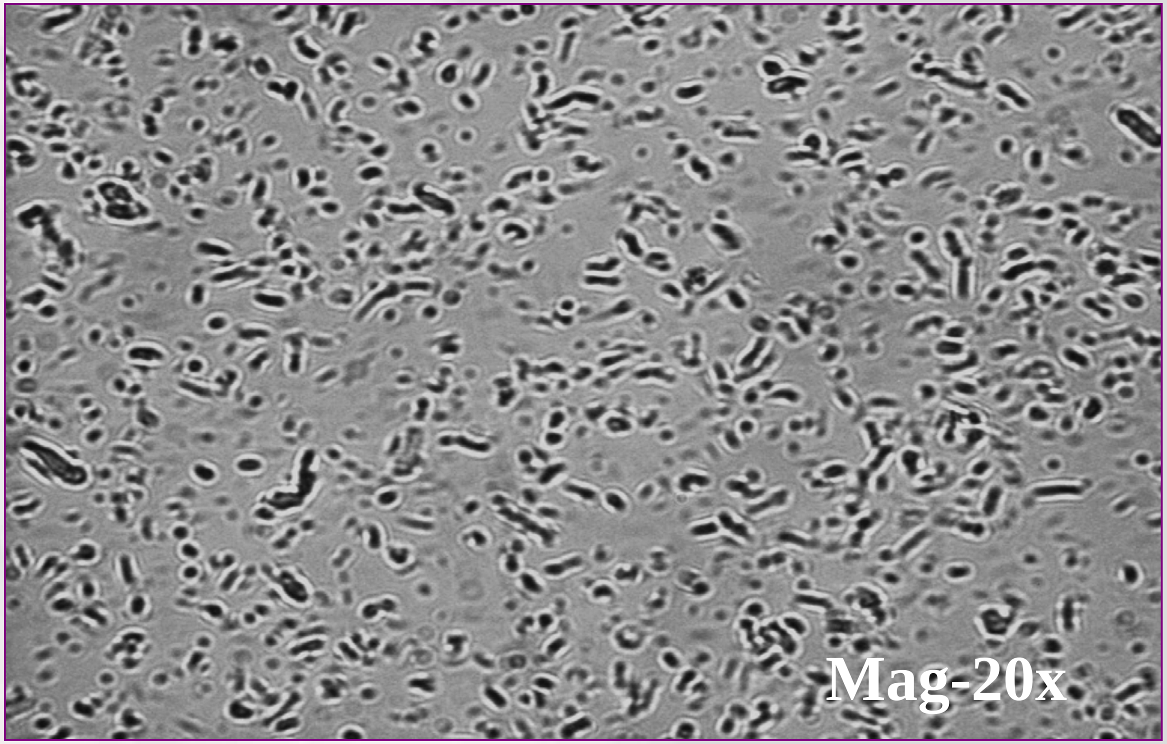
# Light Microscopy Image of the Cross Section Perpendicular to the Length of the Samples




**Agglomerated cellulose fibers in**

**5%NCC-HDPE composite**

# Light Microscopy Image of the Cross Section Perpendicular to the Length of the Samples




**Dispersed cellulose fibers in 5 % MCC-AKD—PMDI-HDPE sample**

# THERMAL ANALYSIS

## Differential Scanning Calorimetry/ Thermal Gravimetric Analysis

# Polymer Crystallization

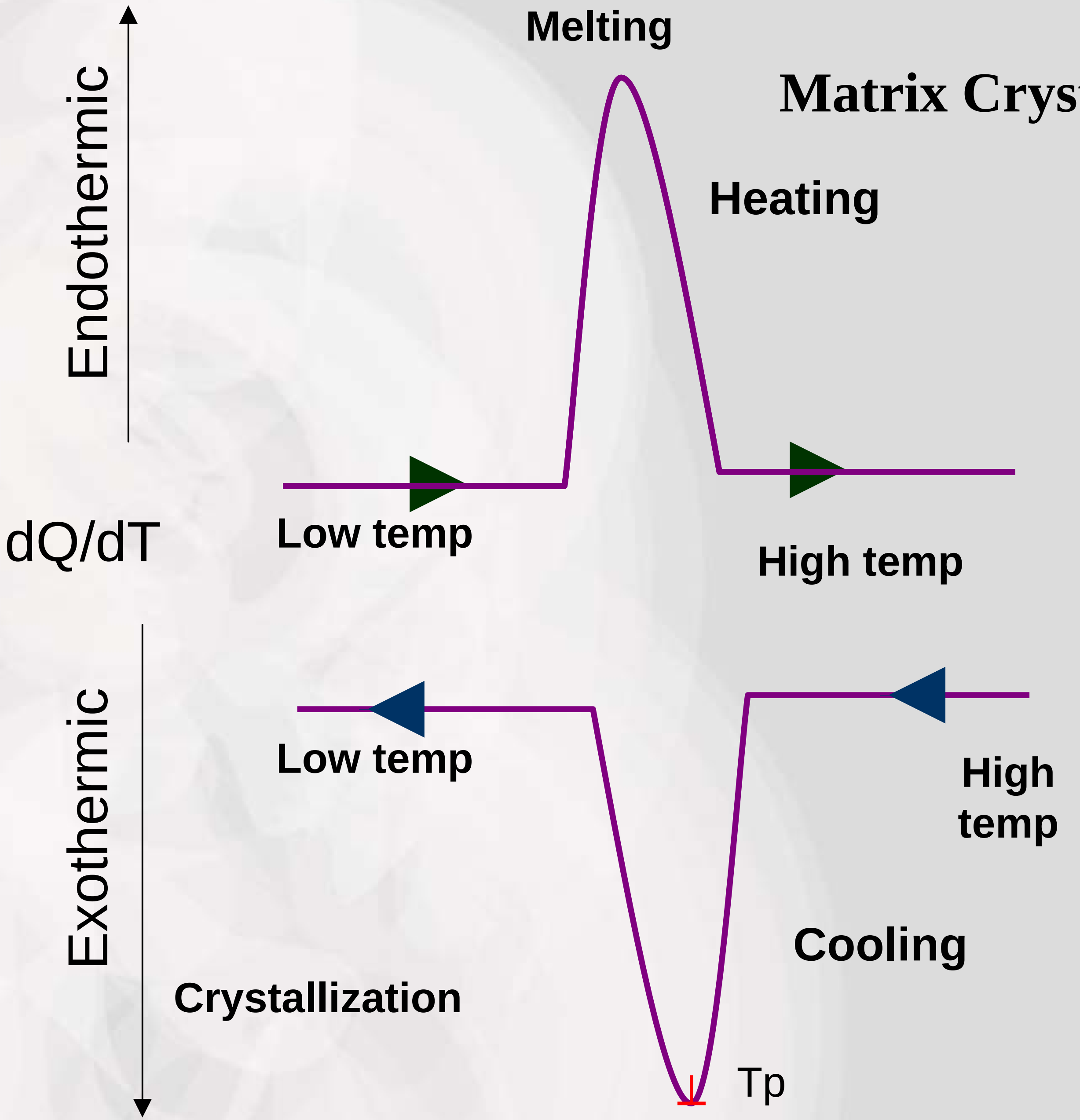
- **Isothermal Crystallization**
  - **Constant temperature process**
  - **Avrami, Ozawa,Kissinger**
- **Non- Isothermal crystallization**
  - **Constant cooling rate process**
  - **Simulates real processing conditions**
  - **Modified Avrami, Kissinger**

# Kissinger Method – Activation Energy ($E_a$)

$$d\left(\ln \varphi/T_p^2\right)/d(1/T_p) = -\Delta E/R$$

**$\varphi$– Cooling rate (°k/min)**
**$T_p$ – Crystallization peak temperature (k)**
**$\Delta$E – Activation energy (kJ/mole)**
**R- Universal gas constant (= 8.314 j/mol k)**

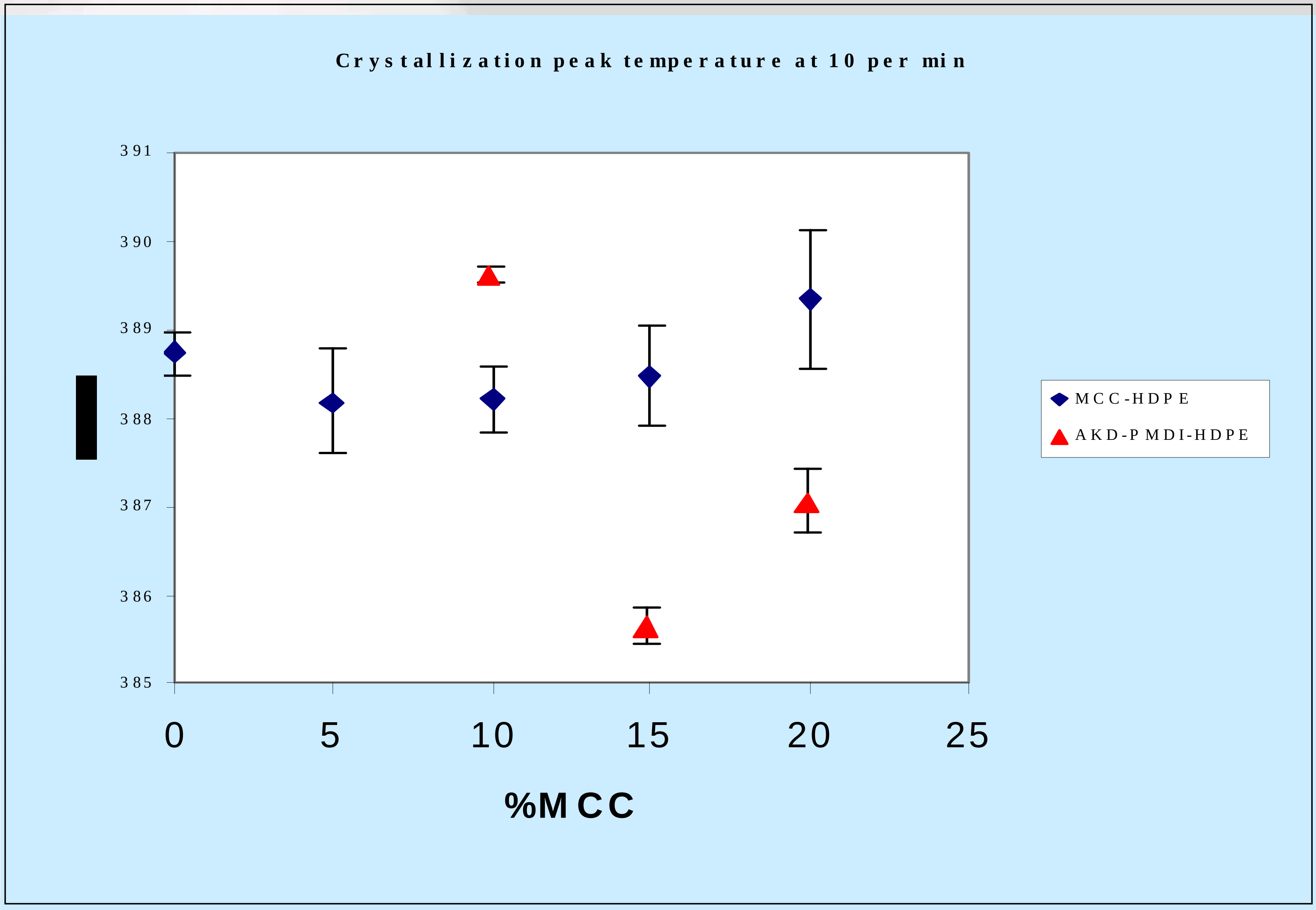
Matrix Crystallinity= $\Delta H_c / \Delta H^o_c$



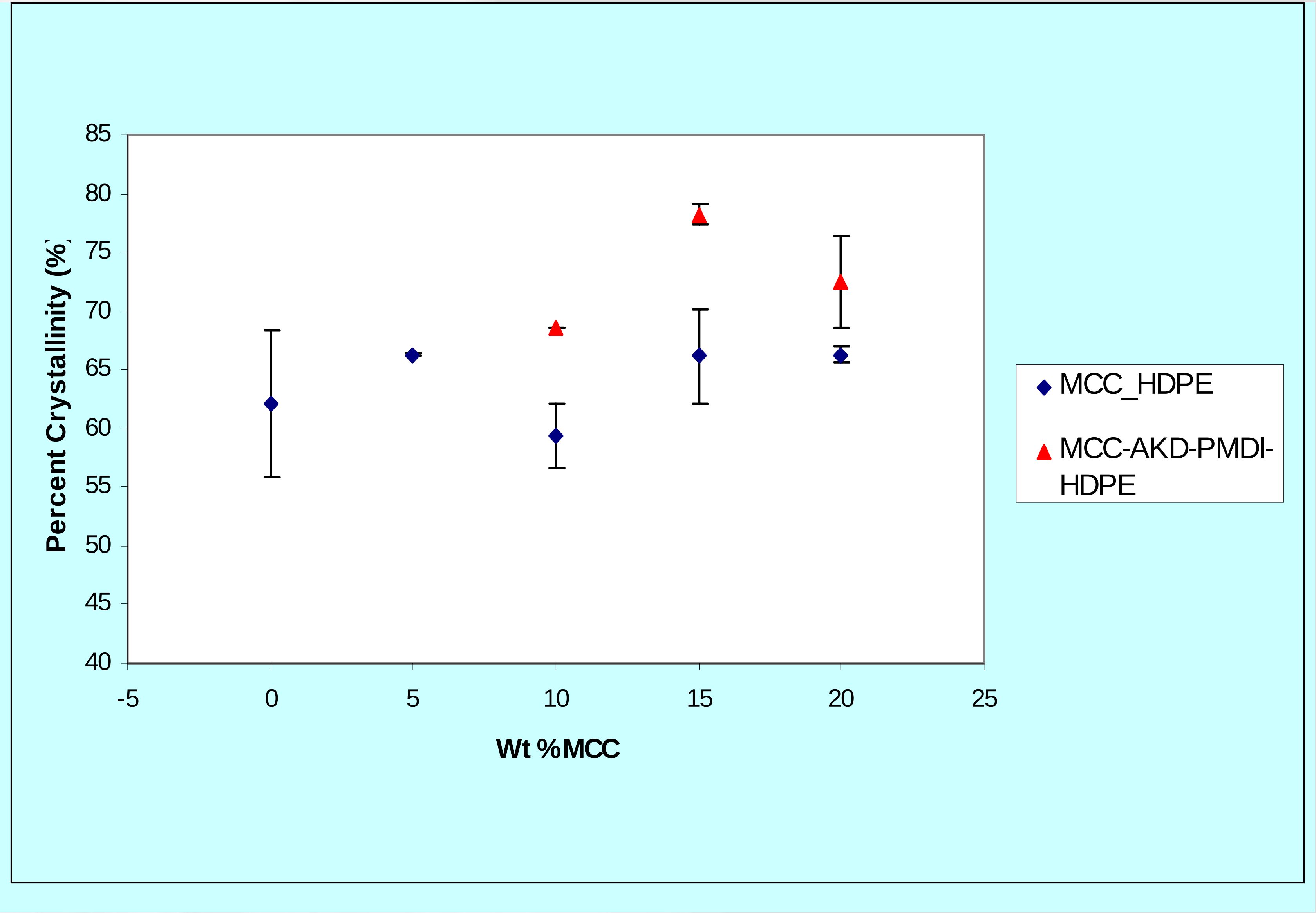
# RESULTS

# Thermal Analysis

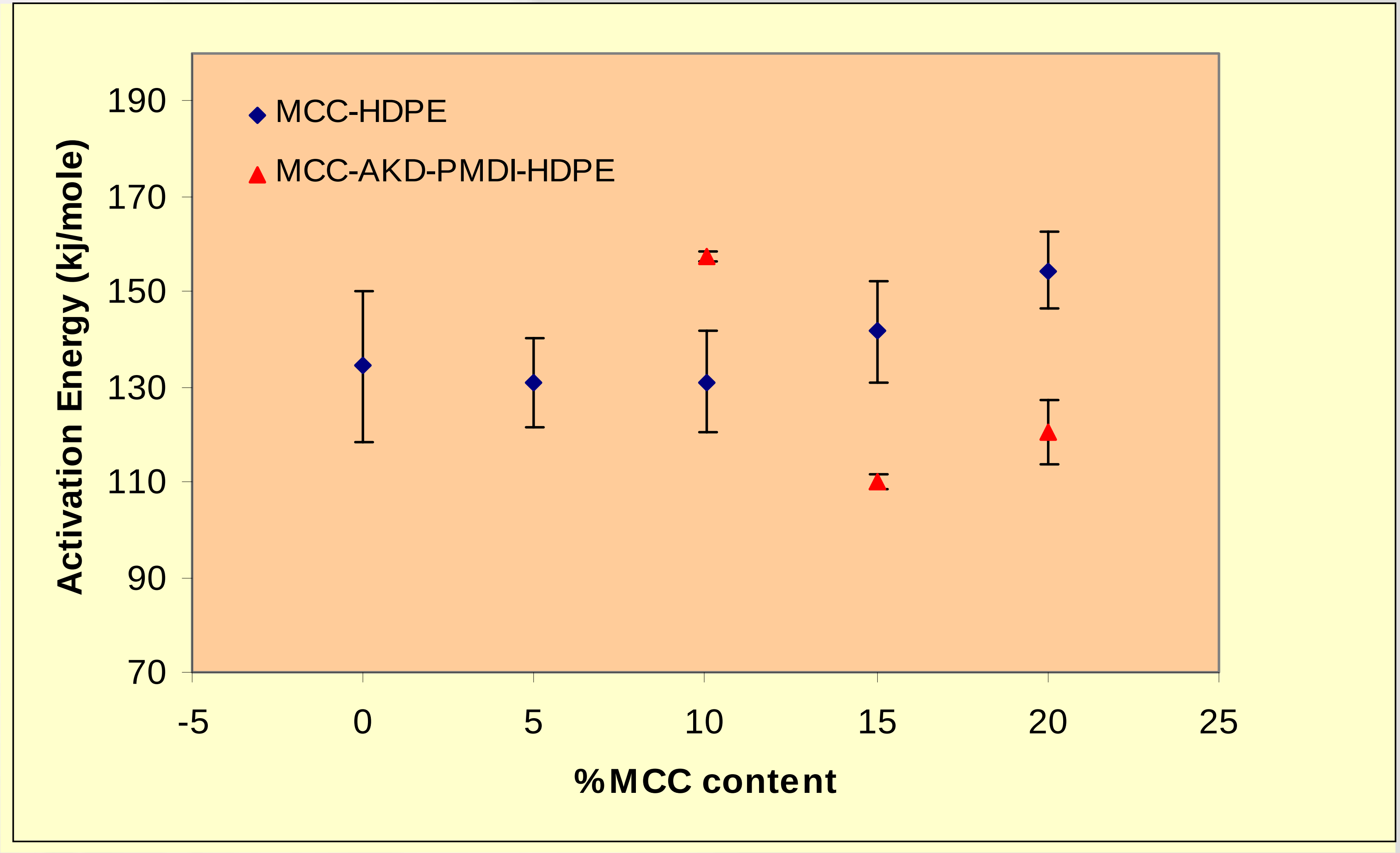
# Crystallization Peak Temperature



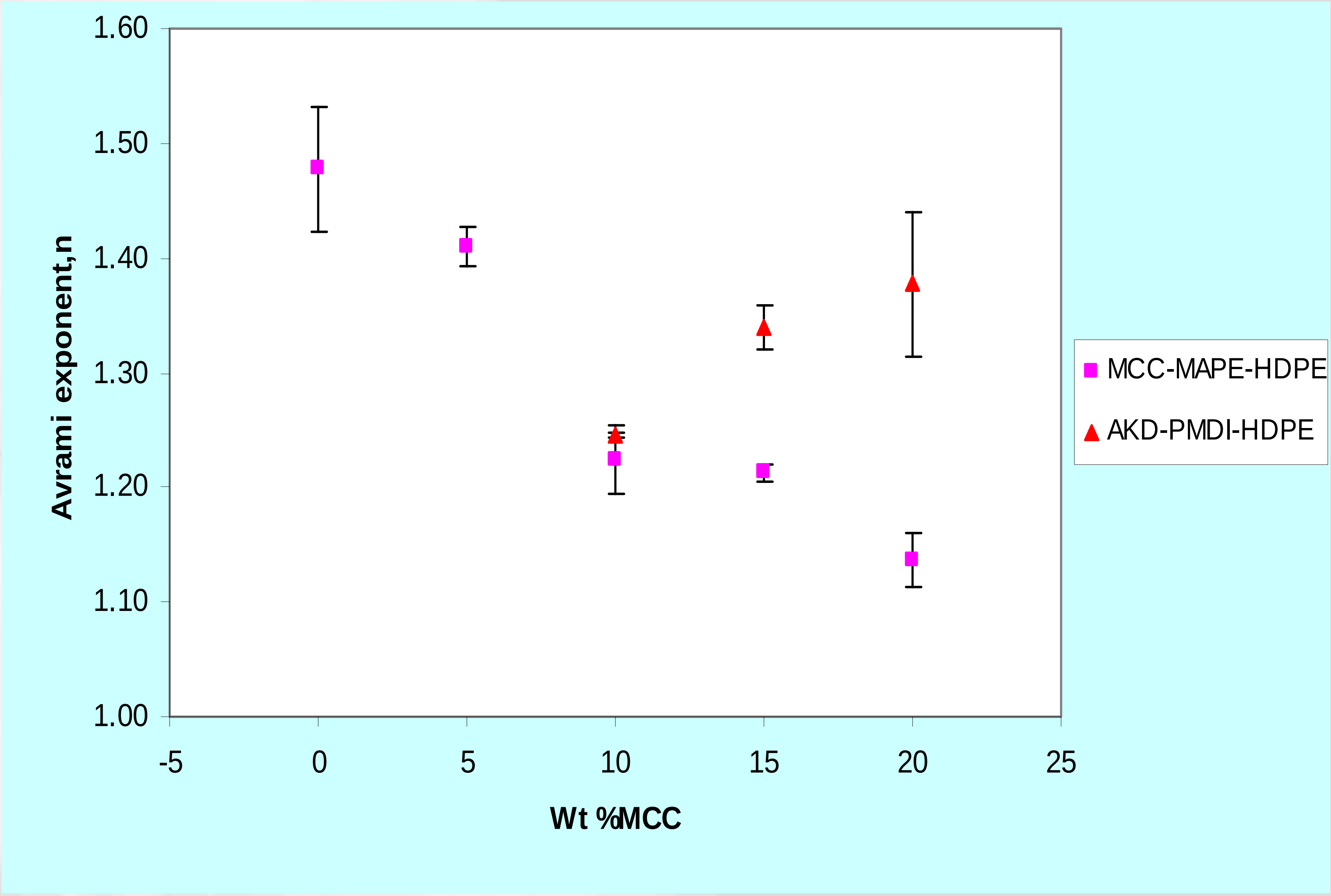
# Percent Matrix Crystallinity



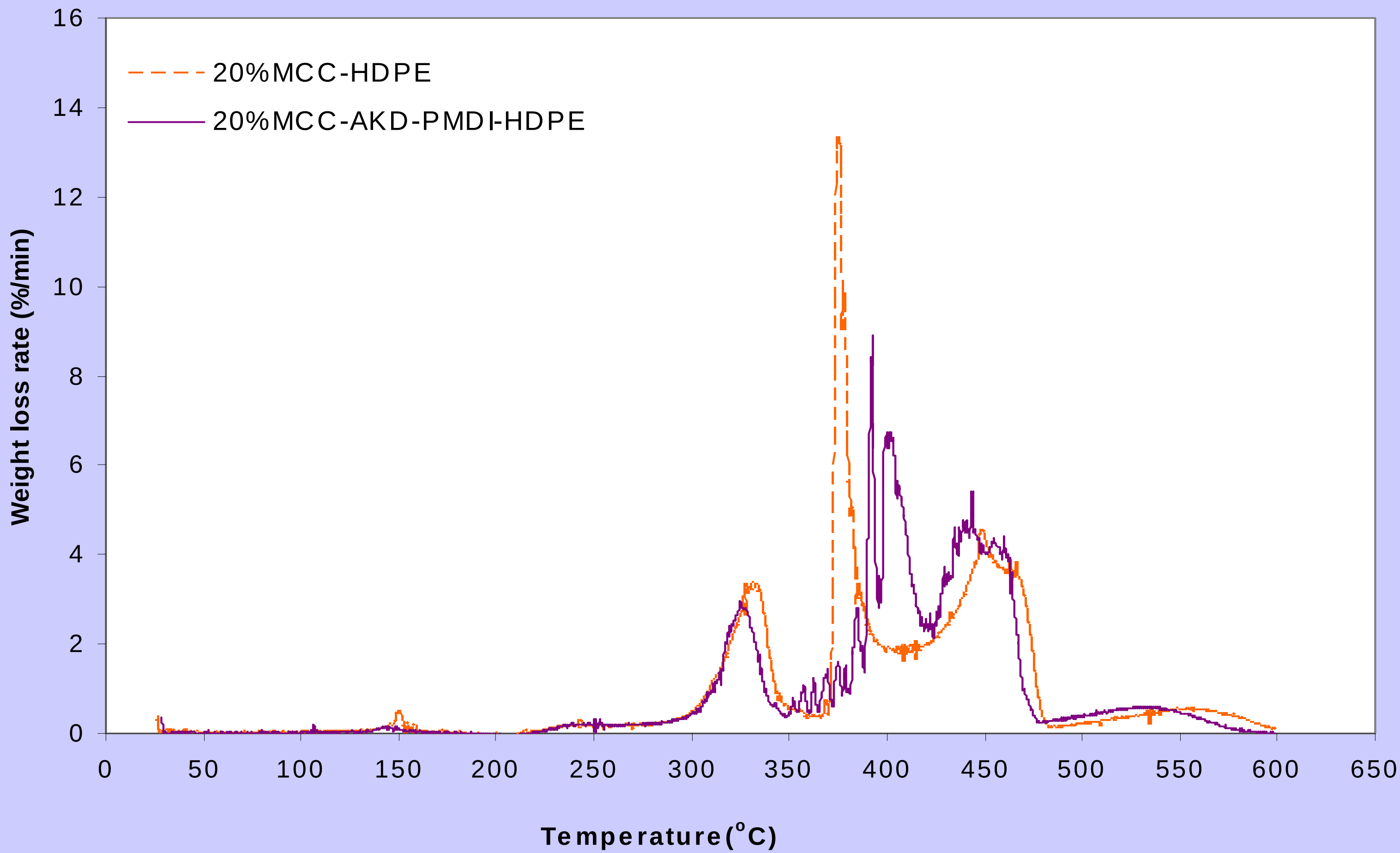
# Activation Energy



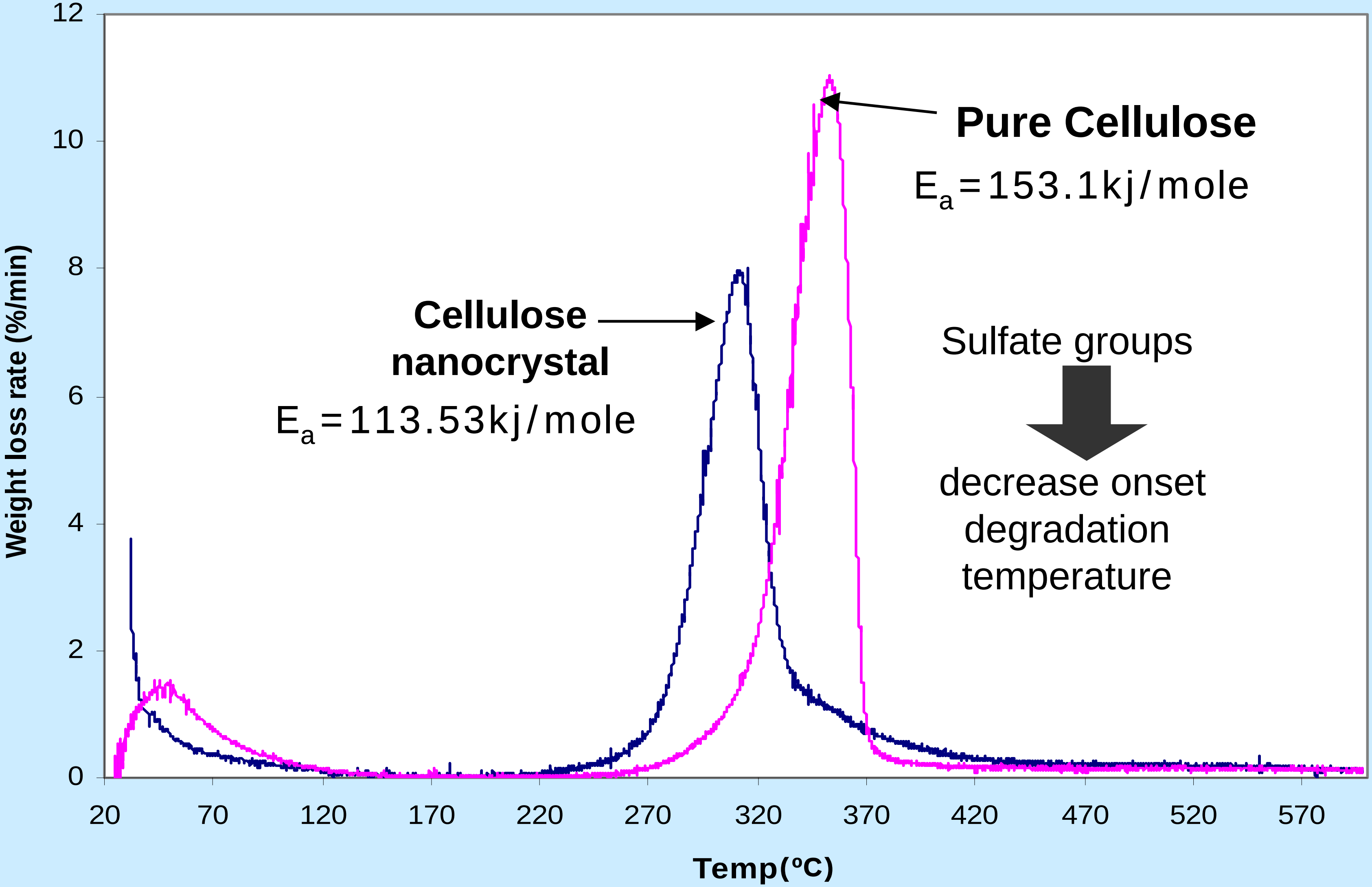
# Avrami Exponent



# Derivative Thermogravimetric (DTG) Curves



# Derivative Thermogravimetric (DTG) Curves



# Conclusions

- Coupling agents increase strength.
- Fillers alter nucleation behavior
- PMDI-AKD increases crystallinity.
- PMDI-AKD changes the activation energy and peak crystallization temperature
- Degradation behavior of the composite is not altered in the presence of compatabilizer.
- Grafted sulfate groups decreases the activation energy and onset degradation temperature
- The concept of compatabilizer systems can be extended to nanocomposites

# Acknowledgements

- This project was funded by a grant from the USDA National Research Initiative Competitive Grants Program
- Advisors
    - Dr.John Simonsen
    - Dr.Ralph Busch
- Committee members
    - Dr.Joe Karchesy
    - Dr.Sundar V.Atre
    - Dr.Jeffrey K.Stone
- Thanks to my colleagues in my group and to folks in WSE dept