

MATERIALES PARA EL DESARROLLO SUSTENTABLE

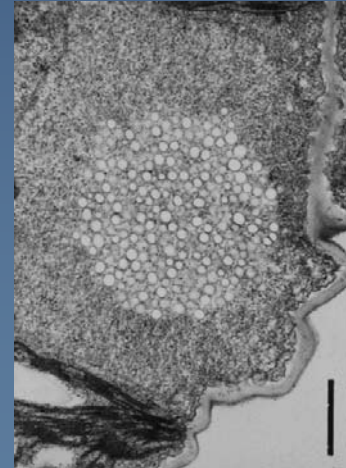
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Tecnología de Materiales
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patsy@inti.gov.ar

Bio Polymers or Biobased Polymers

Renewable
Resource-based



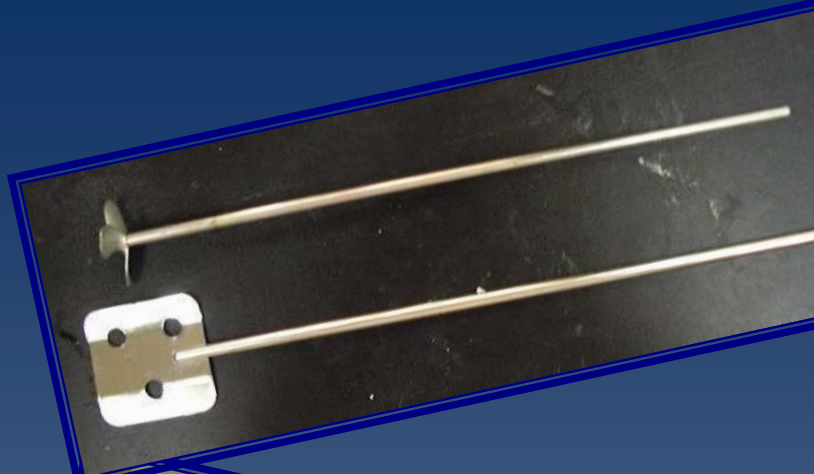
Microbial
synthesized





INTI

Plastisoc



COMPOSITE MATERIAL FROM COTTON SEED PROTEIN AND NATURAL FIBER



Protein Extraction from cottonseed pellets at Pilot Plant Scale (INTI-Cereales)

Pellets Production



Oil extraction (VICENTIN)

- Pressing (90°C)
- Hexane extraction (60 °C)
- Solvent elimination (90°C)
- Granulation (pellets)



SDP

Water

30 min, 30 °C
500 rpm
pH = 10 , TEA

Plastizacer

15 min
30 °C
500 rpm

Crosslinking agent

15 min
30 °C
500 rpm

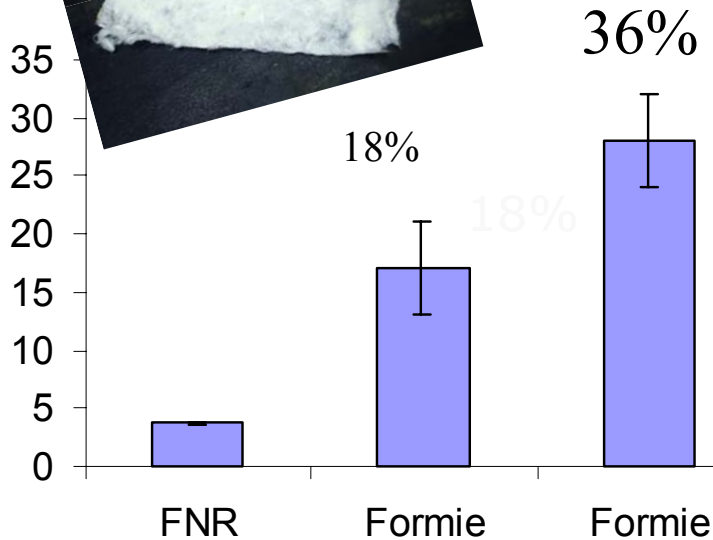
Degasification

Filmogenic Solution



Reinforced Formie Films Mechanical Properties

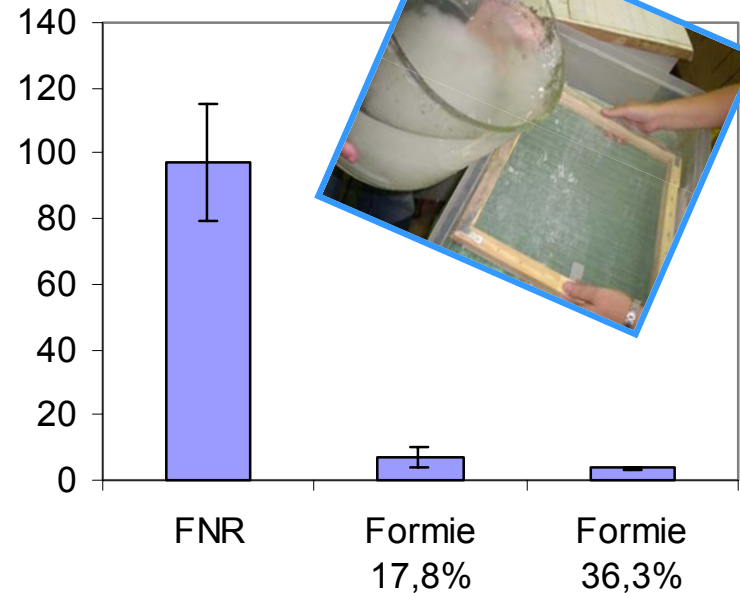
Maximum Tensile Strength (MPa)



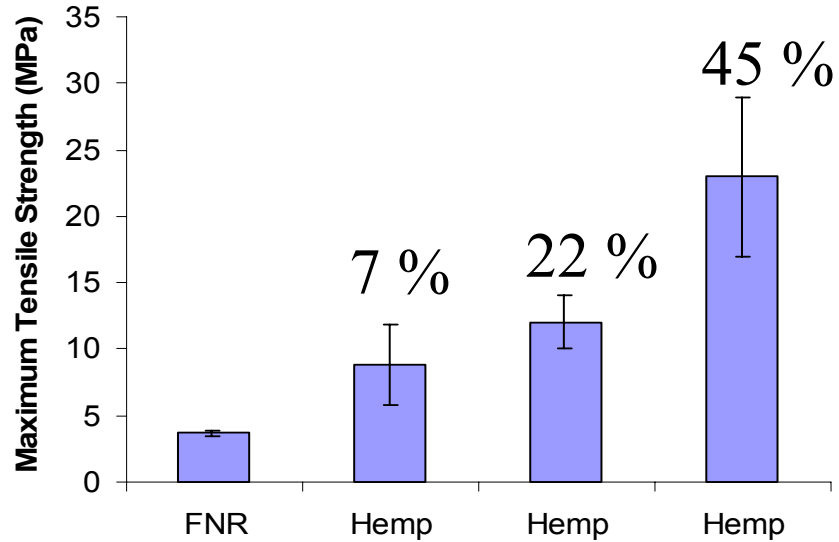
18 % fiber content
produce ~ 460% increase
in MTS
& 93% in % elongation lost

36% fiber content
produce ~ 750 % increase
in MTS
& 96% in % elongation lost

% Elongation



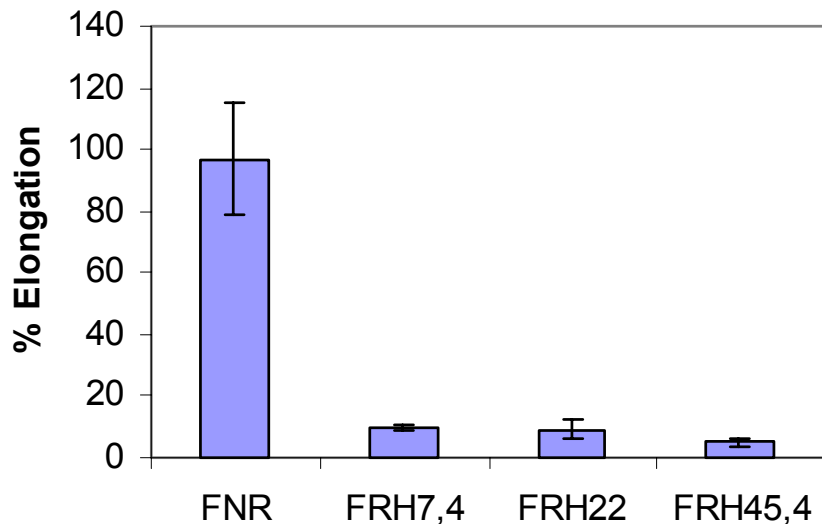
Reinforced Hemp Films Mechanical Properties



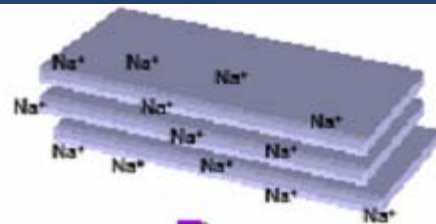
45% fiber content
produce ~ 621% increase in
MTS
& 95% in % elongation lost

22% fiber content
produce ~ 320% increase
in MTS
& 91% in % elongation lost

7% fiber content
produce ~ 240% increase
in MTS
& 90% in % elongation lost



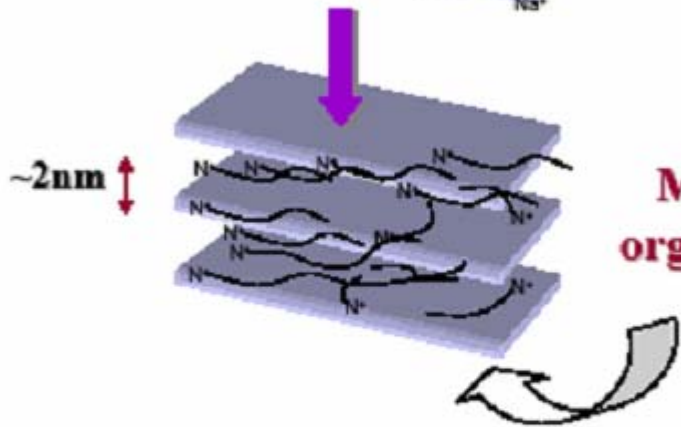
Nanocomposites are a new class of materials filled with nanometers size mineral particles instead of conventional scale fillers



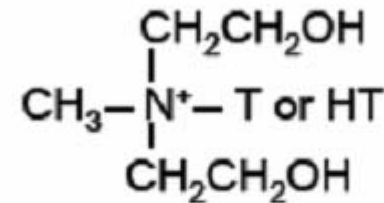
Na⁺-Montmorillonite

+

Modification with ammonium cation



Modified organophilic MMT



**Where T is Tallow
(~65% C18; ~30% C16; ~5% C14)**

Onium ion modification

**bis(2-hydroxyethyl)methyl
Hydrogenated Tallow Ammonium**

Source: <http://www.nanocor.com/>

Source: <http://www.nanoclay.com/data/30B.htm>

Wheat Gluten Protein - Montmorillonite Nanocomposite (MMT-Na⁺)

left: 0 % MMT-Na⁺;
right: 5% MMT-Na⁺;



| | Tensile Strength (MPa) | % Strain at Break | Young Modulus (MPa) |
|--------------------------------------|-------------------------|-------------------|---------------------|
| SC gluten 0 % MMT-Na ⁺ | 6.8 ± 1.5 ^a | 63 (20) | 442 (114) |
| SC gluten 5% MMT-Na ⁺ | 10.6 ± 0.8 ^b | 45.4 (6) | 617 (116) |

Water Vapour Permeability (WVP at 50% RH)

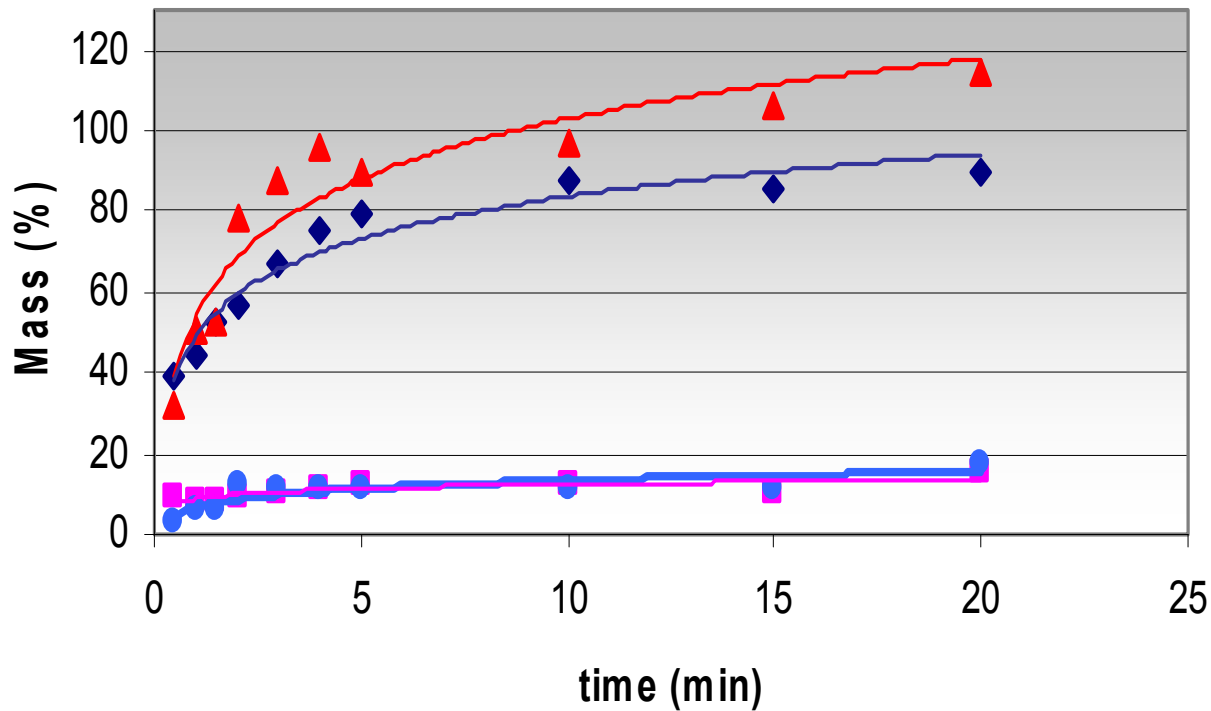
| | Thickness (μm) | WVT (g/s*m*Pa) |
|--------------------------------------|----------------|-----------------|
| SC gluten 0 % MMT-Na ⁺ | 188 | 3,75E-11 |
| SC gluten 5% MMT-Na ⁺ | 184 | 1,72E-11 |

Nanocomposite Guten /Montmorillonite- Na⁺ present

56 % increase in TS

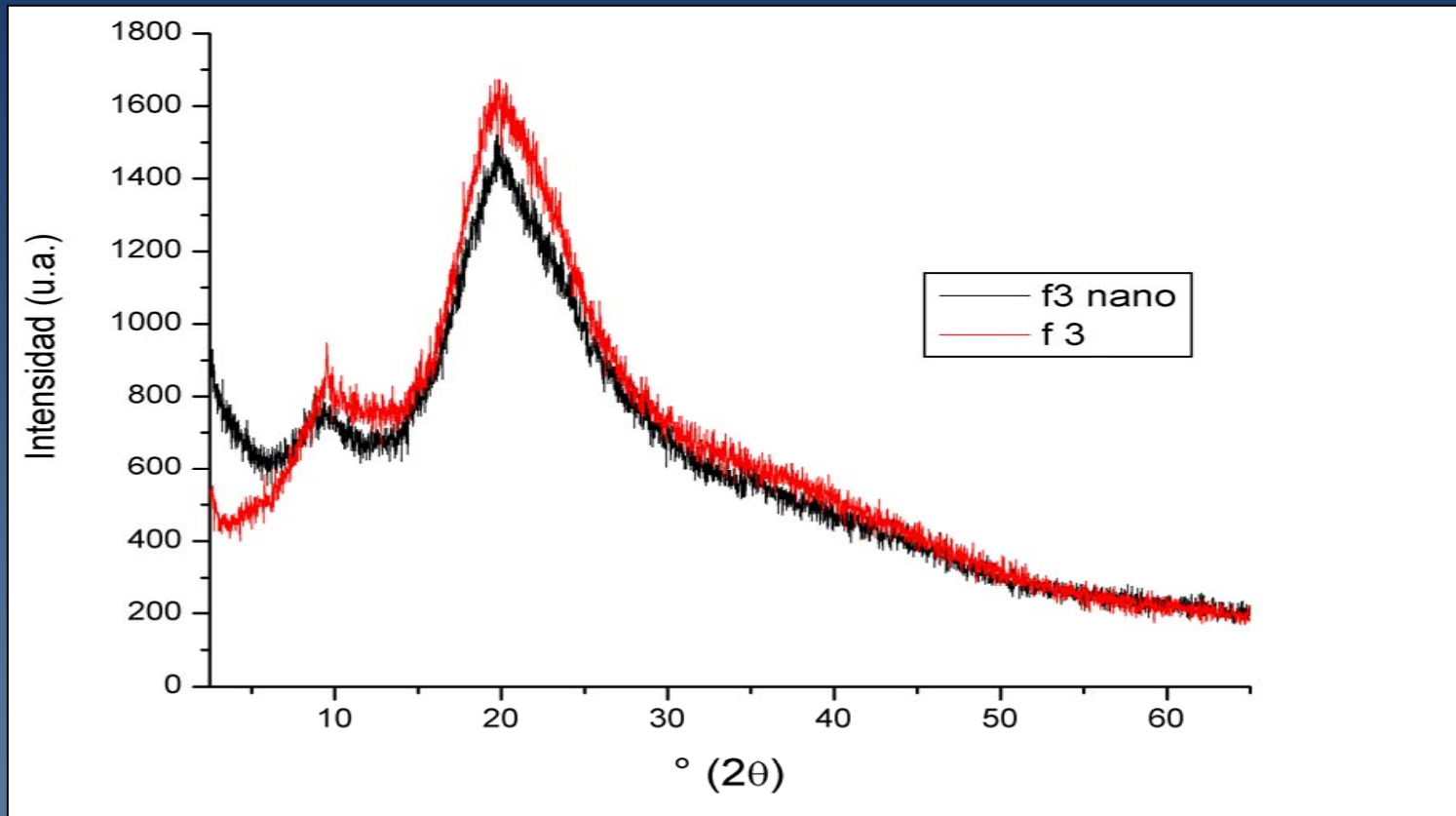
54% reduction in WVT

Water up take



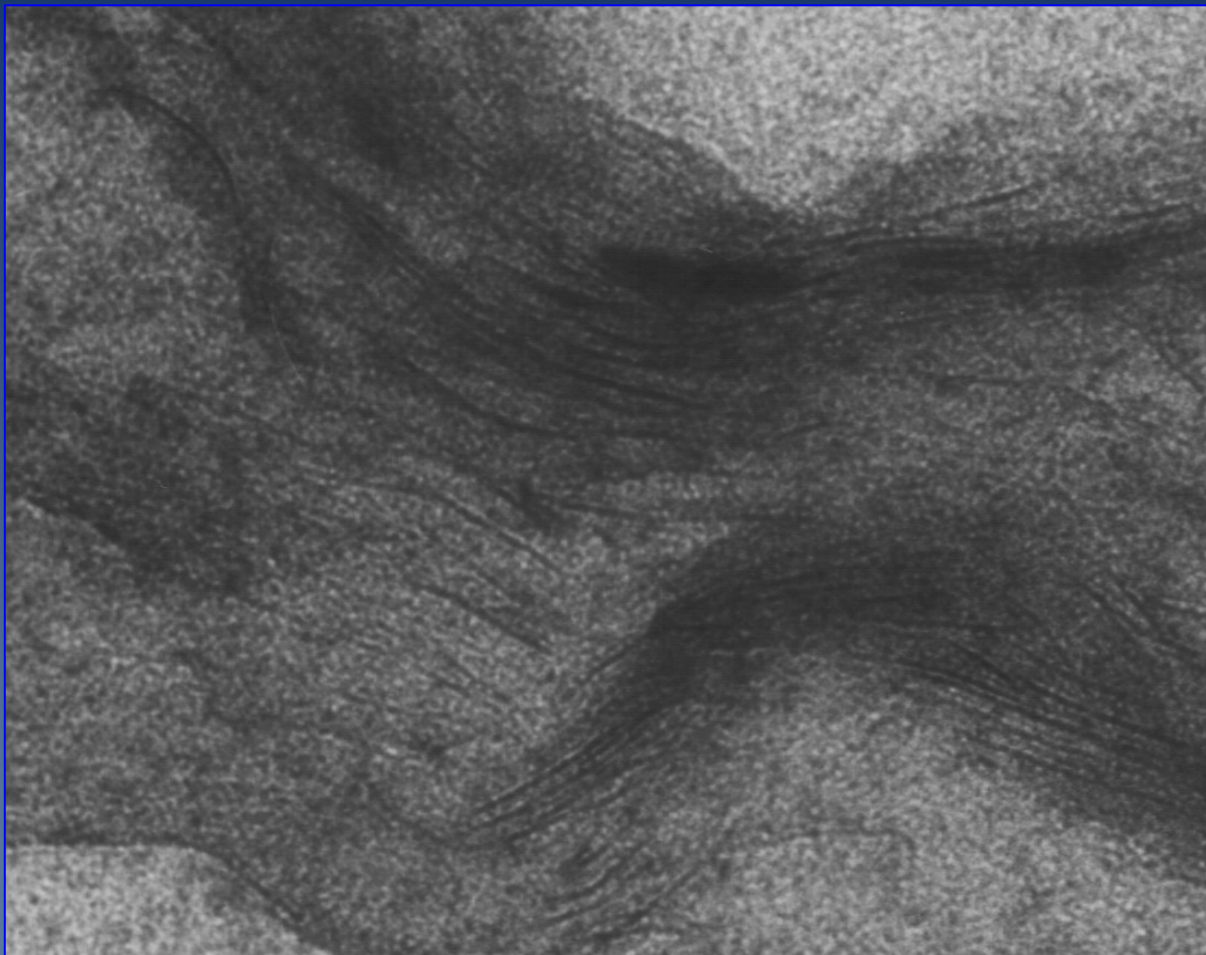
- ◆ WG N Water abs
- WG N Soluble
- ▲ WG Water abs
- WG Soluble

XRD pattern for WG and WG-MMT-Na (5%) composite



Diffraction pattern showed a similar pattern to that of WG without MMT-Na indicating that sufficient intercalation/exfoliation was achieved in these nanocomposites.

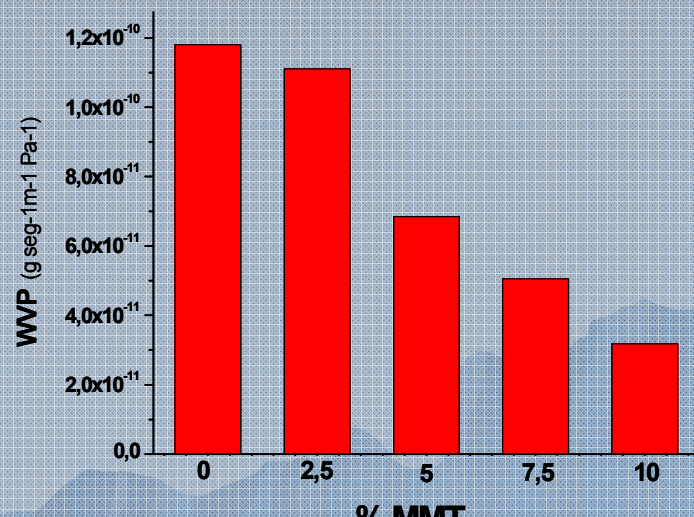
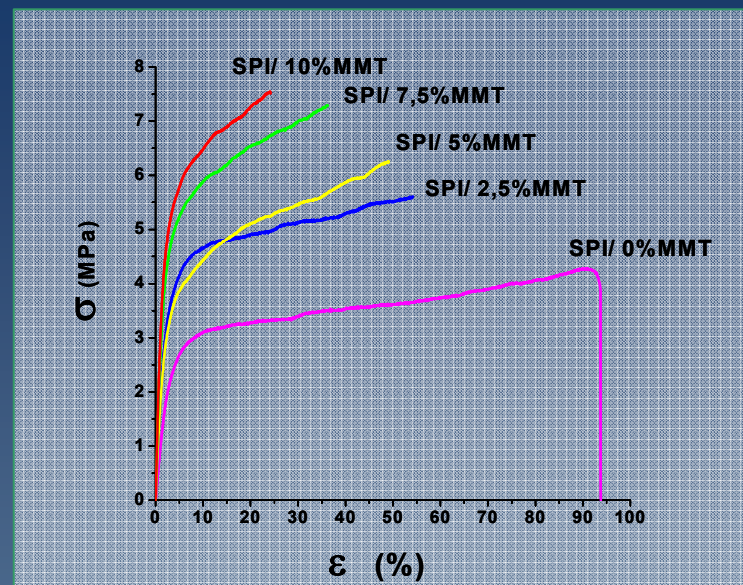
TEM images for WG-MMT-Na (5%)



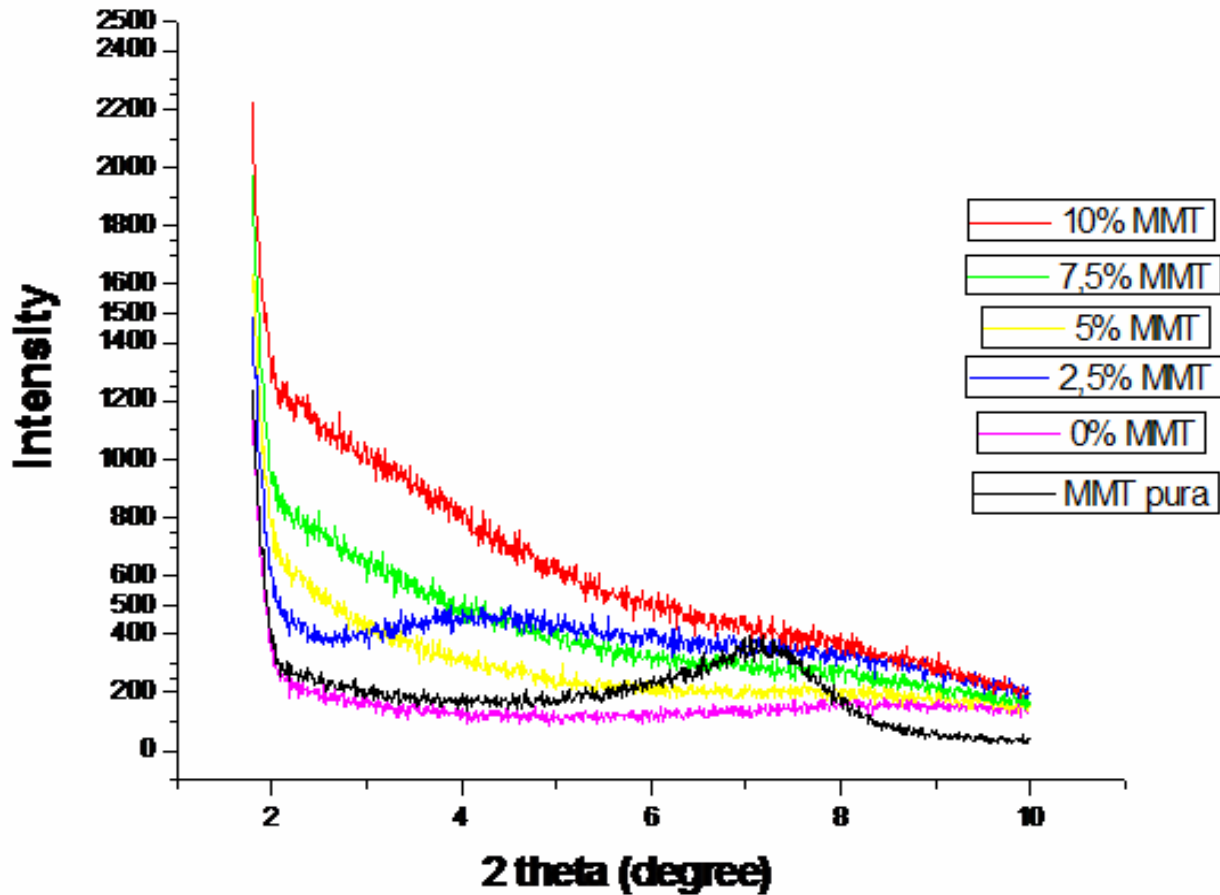
1mm = 3.9 nm

SOY PROTEIN –MONTMORILLONITE NANOCOMPOSITE (MMT-Na+)

INTI-Plásticos
CIDCA-CONICE



XRD pattern for Soy and Soy-MMT-Na composite



0 % MMT



5 % MMT



10 % MMT

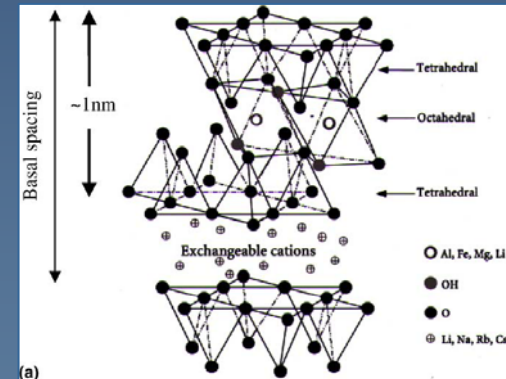
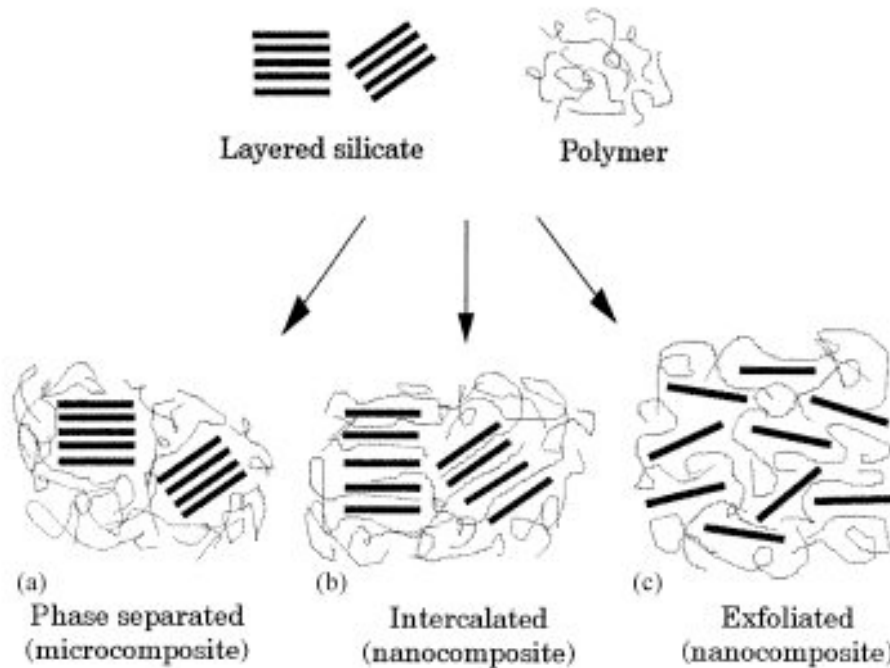


100.000 x

200.000 x

Nanoclays effects on protein composite films

- Increase mechanical properties
 - Decrease water sensitivity
- Decrease water vapour permeability



Polycaprolactone Nanocomposites (PCL-MMT)

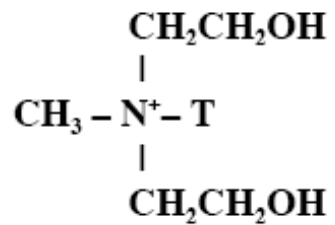
Study of the influence of Montmorillonite structure in the PCL nanocomposite properties

Commercial grade poly (ϵ -caprolactone) FB 100 was supplied by Solvay Chemical (Perstorp caprolactones), mean Molecular Weight $>100,000$; melting Point 58°C - 60°C .

Clay minerals were "CloisiteTM Na⁺" (native montmorillonite) and "CloisiteTM 30B" (organic modified montmorillonite)(Southern Clay Products). Cloisite 30 B is a natural montmorillonite modified with a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium (Figure 1). The modifier concentration was 90 meq/100g clay. Clay moisture content was < 2 wt. % and its specific gravity was 1.98g/cc.

Interlayer spacing $d(001)$ was 1.85 nm.

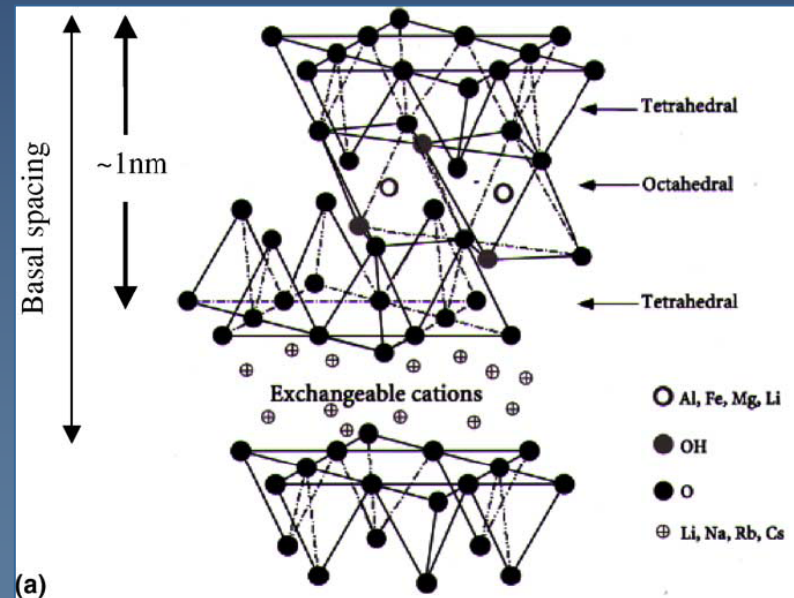




Where T is Tallow (~65% C18; ~30% C16; ~5% C14)

Anion: Chloride

Cloisite 30B



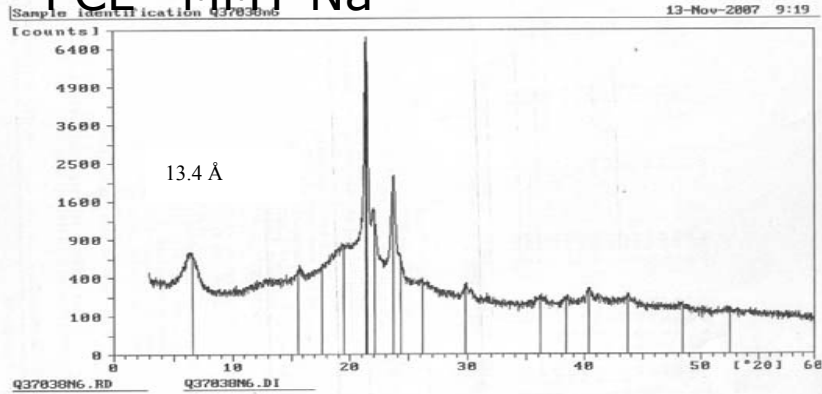
COMPOSITE PREPARATION

PCL/montmorillonite (PCL-MMT Na and PCL-MMT 30B) were prepared by melt intercalation in Brabender Plasticorder mixing chamber 30 cm³ , at 100 °C, 90 rpm for 10 min.

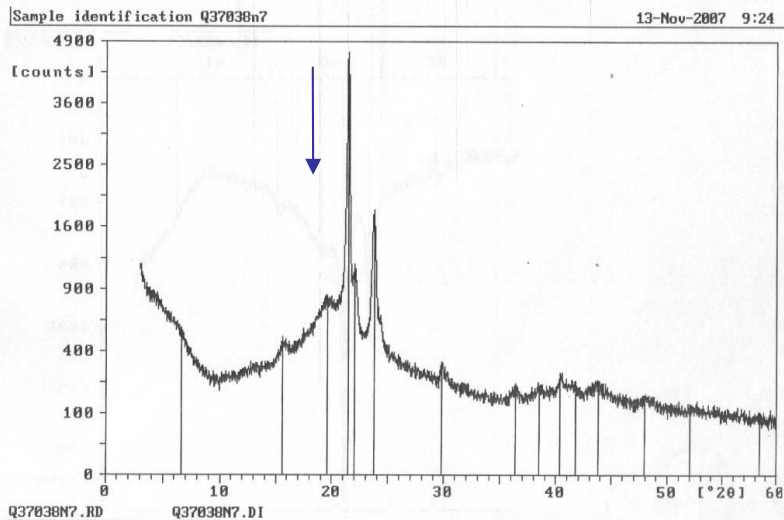
The collect molten materials were compression-molded into 0,4 mm-thick plates by hot pressing at 100 °C for 2 min., and then 2 min under 50 bar. The nanocomposites contained 5% of MMT.

Analysis of clay dispersion and intercalation/exfoliation in the nanocomposite material.

PCL - MMT Na



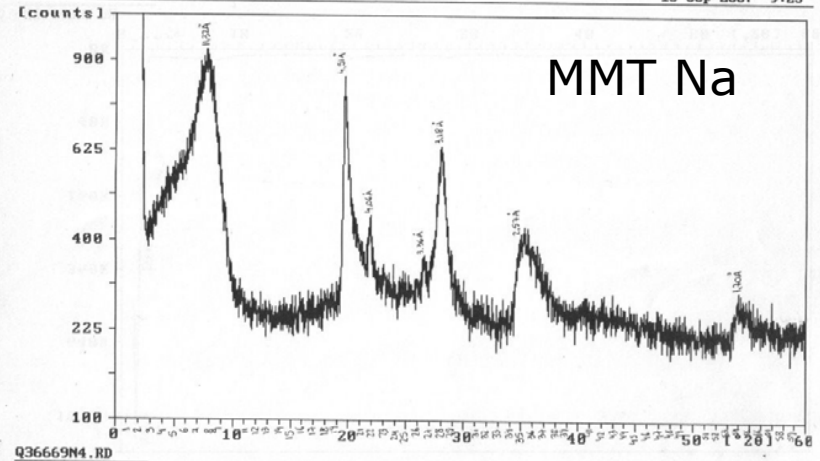
PCL - MMT 30B



PCL+30B

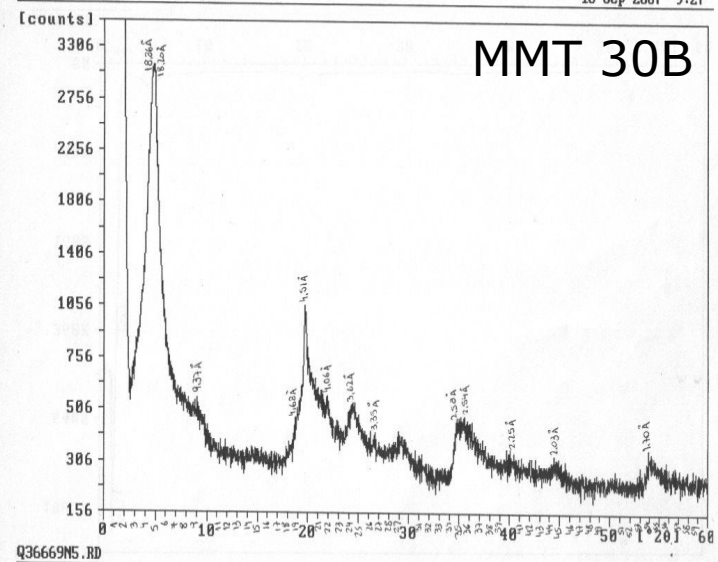
Sample identification: Q36669n4

18-Sep-2007 9:25



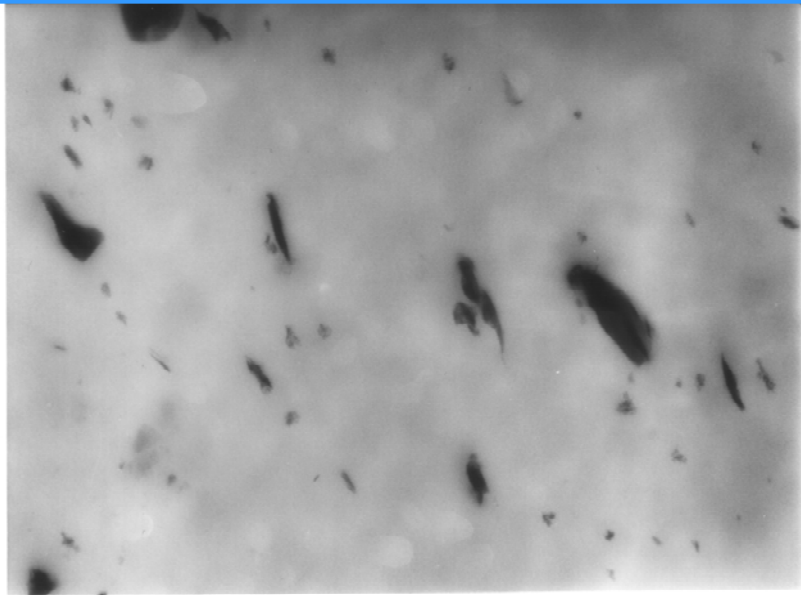
Sample identification: Q36669n5

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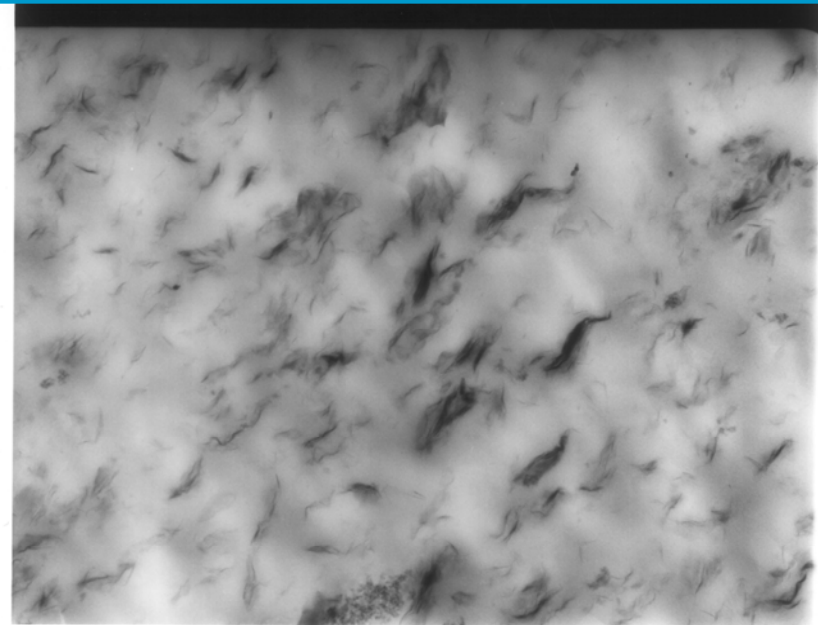


TEM Polycaprolactone Nanocomposites (PCL-MMT)

1 mm= 0.6 μm



PCL-MMT Na

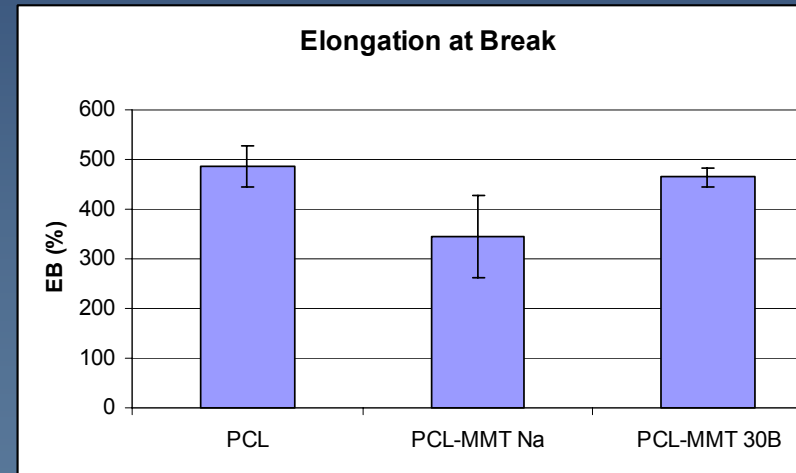
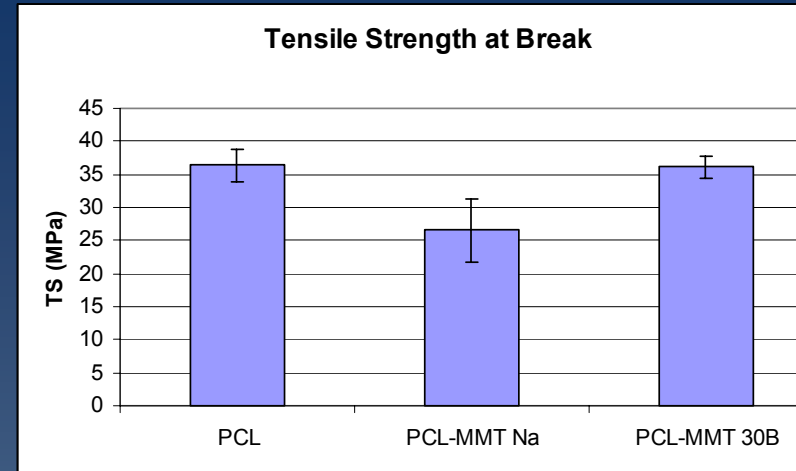


PCL-MMT 30B



Mechanical Properties

| | Young modulus (MPa) | Tensile Strength at break (MPa) | Elong. at break (%) |
|-----------------|---------------------|---------------------------------|---------------------|
| PCL | 414 | 36,4 | 486 |
| PCL – MMT Na 5% | 504 | 26,6 | 345 |
| PCL-MMT 30B 5% | 473 | 36,1 | 464 |



No difference between tensile strength for PCL and PCL-MMT 30 B, but lower value was found for PCL-MMT Na. The same trend is observed for the elongation at break. These results agree with the intercalation/exfoliation structure for PCL-MMT 30 B observed by TEM and XRD.

Comparative Burning Characteristics of Solid Plastics in a Vertical Position

The nanocomposite burning behaviour was studied by vertical burning test, adapted from UL 94

The procedure consists of subjecting a set of specimens of identical composition and geometry to a standard test flame for two 10s flame applications.

The after flame time is recorded after the first flame application (t_1). After the second flame application, the after flame time is recorded (t_2).

Information is also recorded out whether or not flaming material drips from the specimen and total flame time for a particular specimen set.



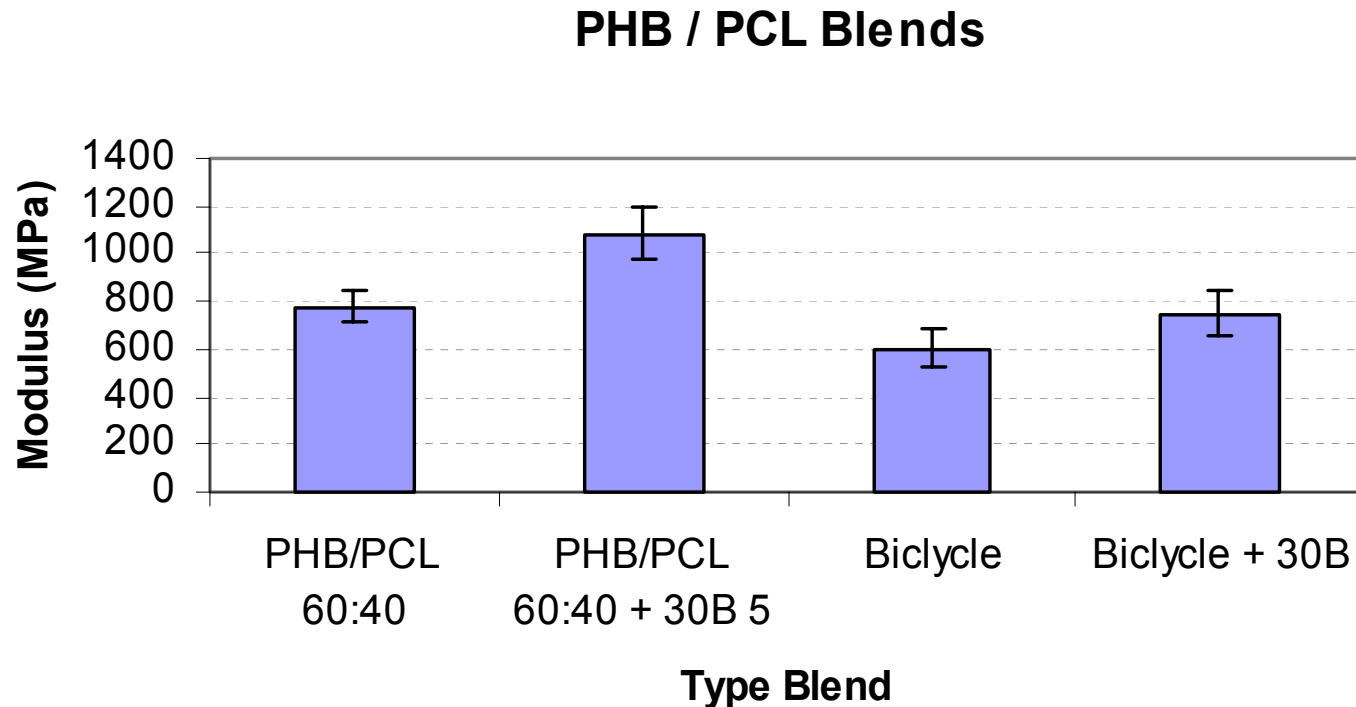
- The different burning characteristics found for PCL- MMT 30 B compare to PCL and PCL-MMT Na could be due to clay intercalated/exfoliated and percolated in the PCL matrix.
- This interaction provides physical integrity to the material burning, avoiding a configuration in which dripping of flaming material could occur, which constitutes an additional fire propagation to surrounding materials

Nanocomposites PCL / PHB /MMT 30 B

Preliminary evaluation of the effect of organic modified MMT 30B on one particular composition of PHB/PCL blend, similar to the composition of a commercial PHB/PCL blend, was done.

PCL FB 100 was supplied by Solvay Chemical
PCL/PHB 40/60 blends and Biocycle (Industrial PHB S.A.
(Brazil) nanocomposites (5% MMT-30B) were prepared in
Brabender Plasticorder mixer at 170° C/80 rpm/ 10 minutes.

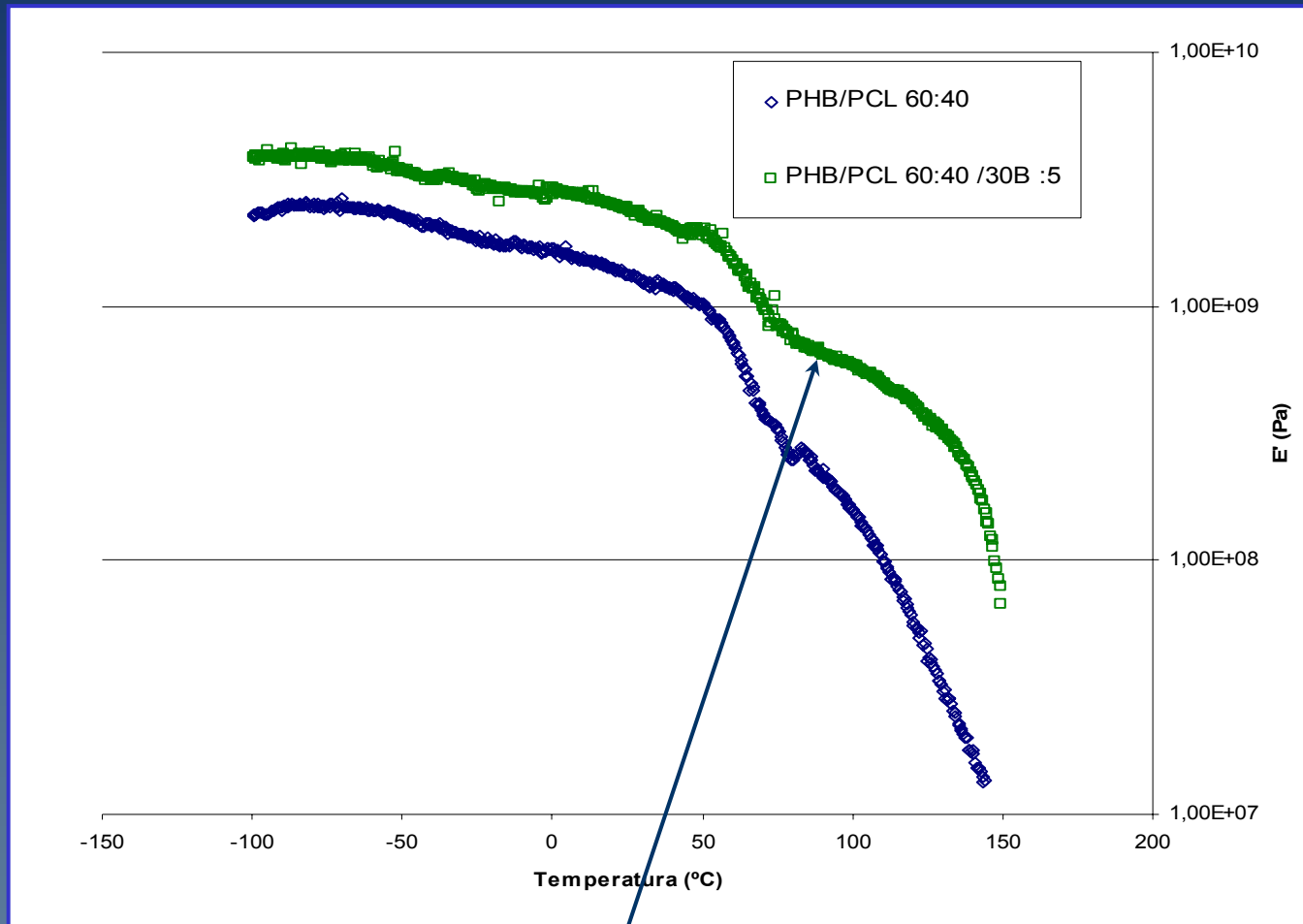
Mechanical Properties



A 38 % increase in modulus was observed for the nanocomposite PCL/PHB (40/60)-MMT 30 B.
For the commercial polymer Biocycle nanocomposite a 24 % increase in modulus was observed.



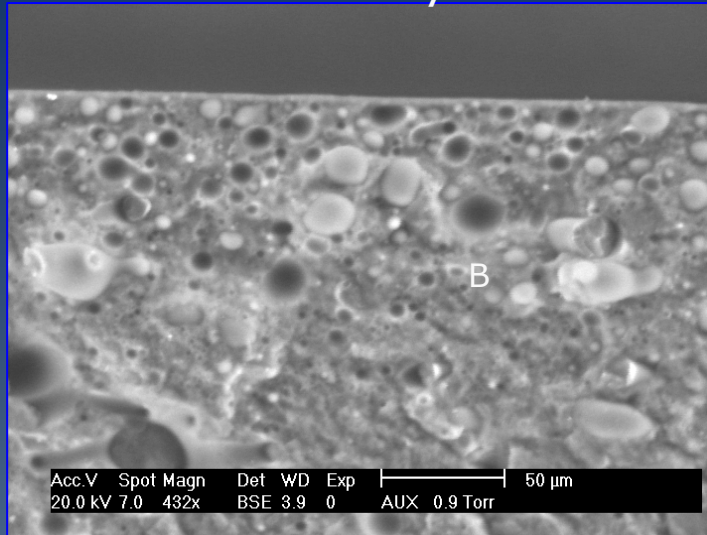
DMTA of PCL/PHB (40/60) blend and nanocomposite



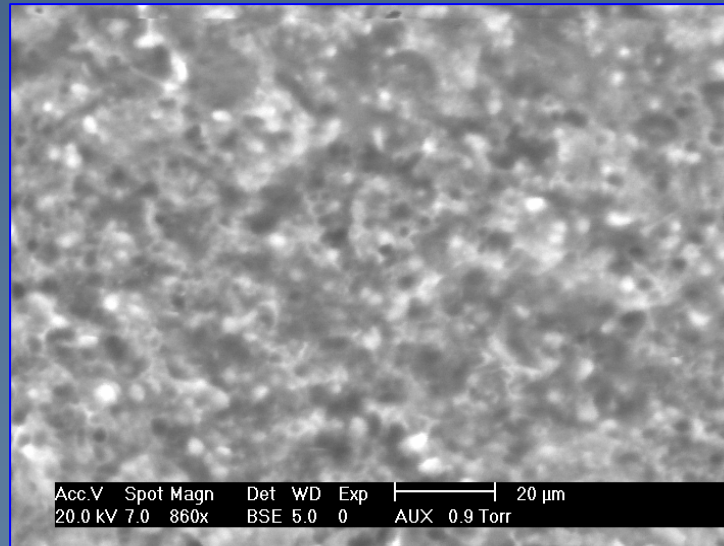
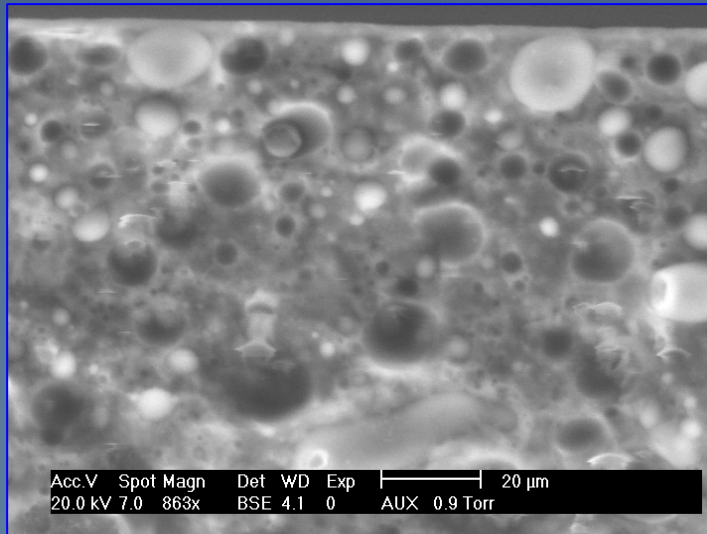
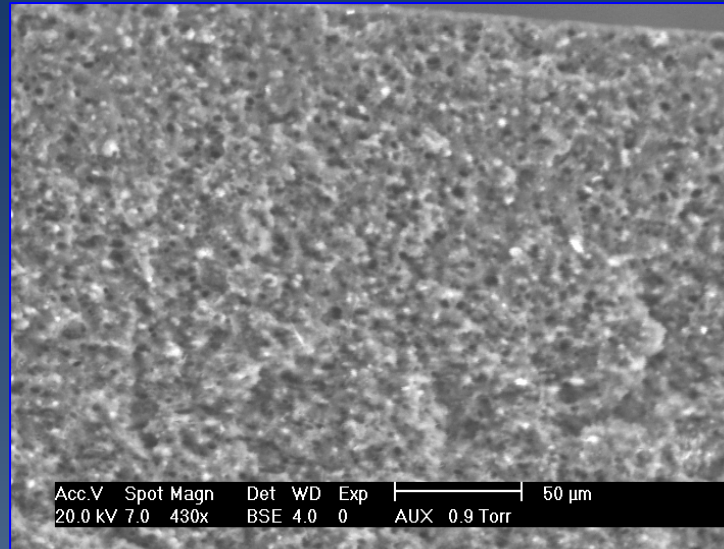
MMT 30 B allows the use of this composite blend in temperature range where the PCL/PHB (40/60) blend has already a constant decay in modulus value.

SEM PHB/PCL 40/60 blend and PCL/PHB –MMT 30 B

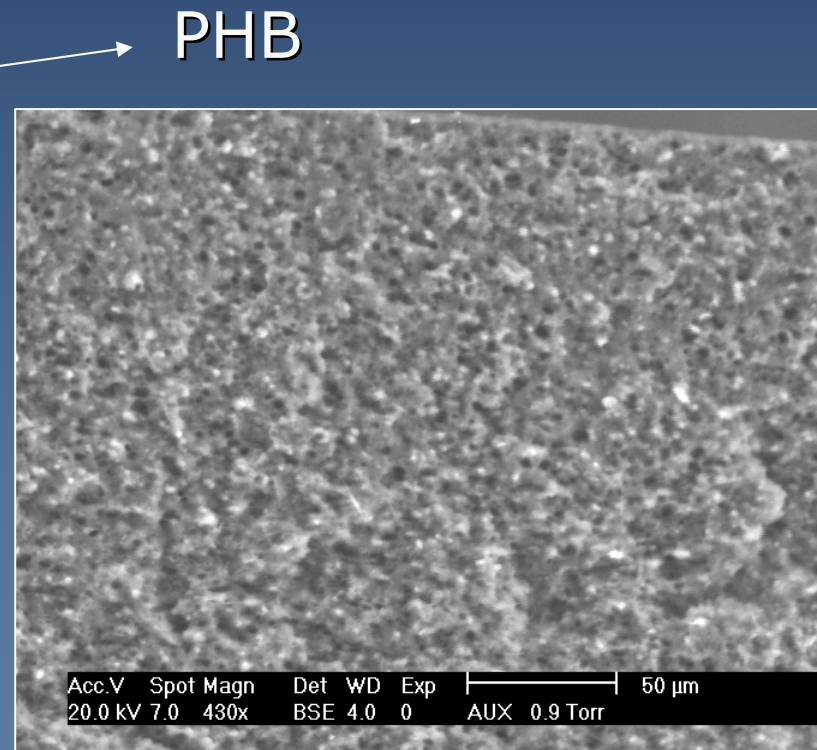
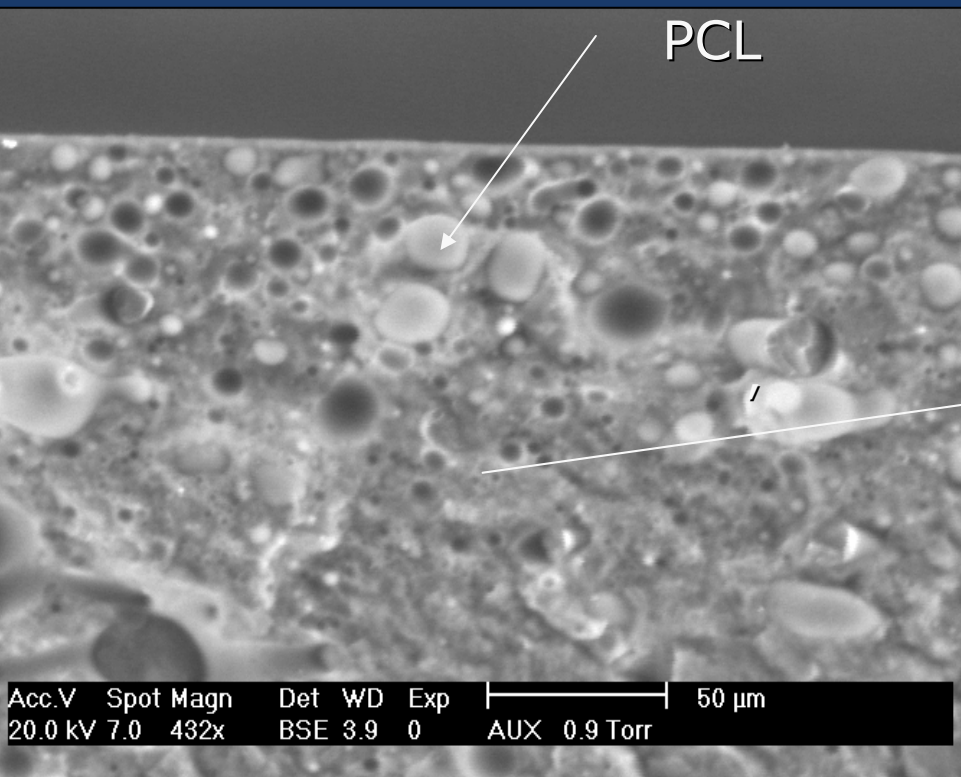
Without clay



5% MMT 30

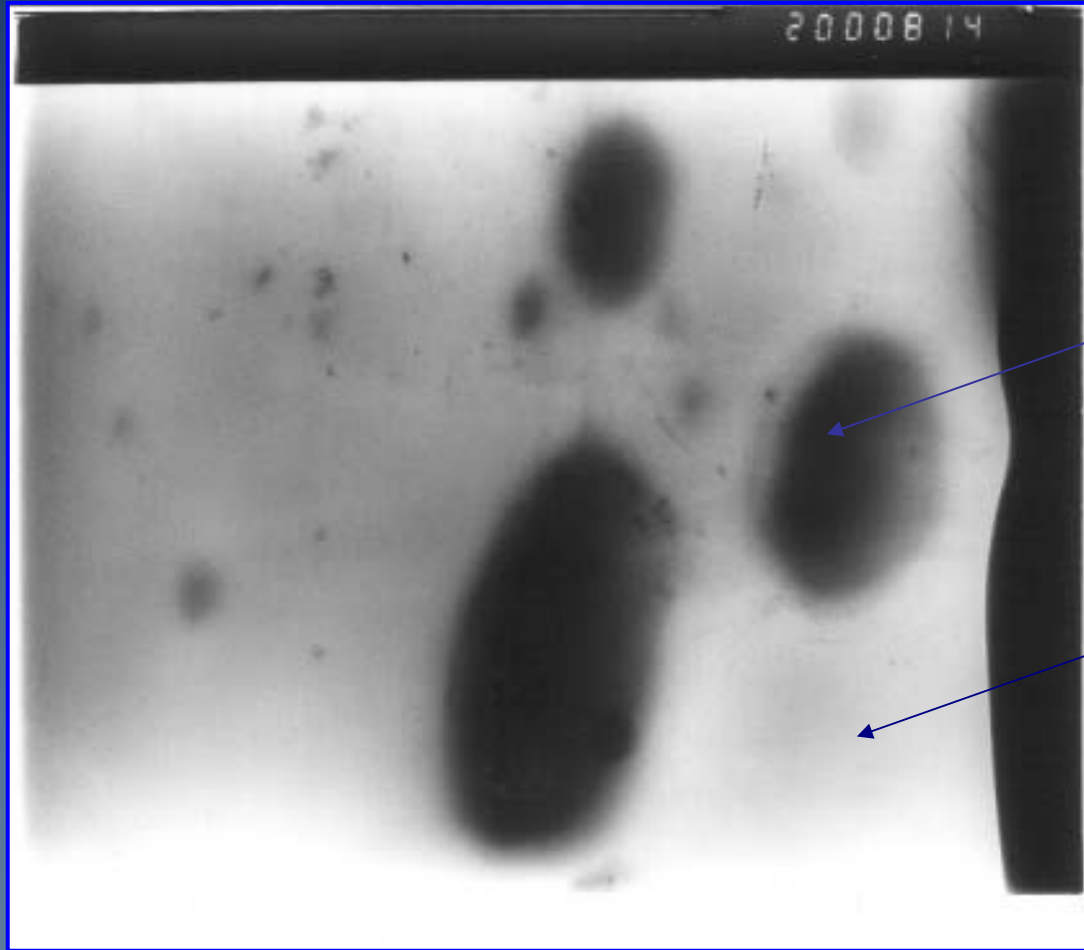


SEM images PCL/PHB 40/60, PCL/PHB40/60–MMT 30 B



PCL disperse phase domain size decreases drastically when nanoclay is incorporated due to the localization of the clay in the interfacial region (TEM)

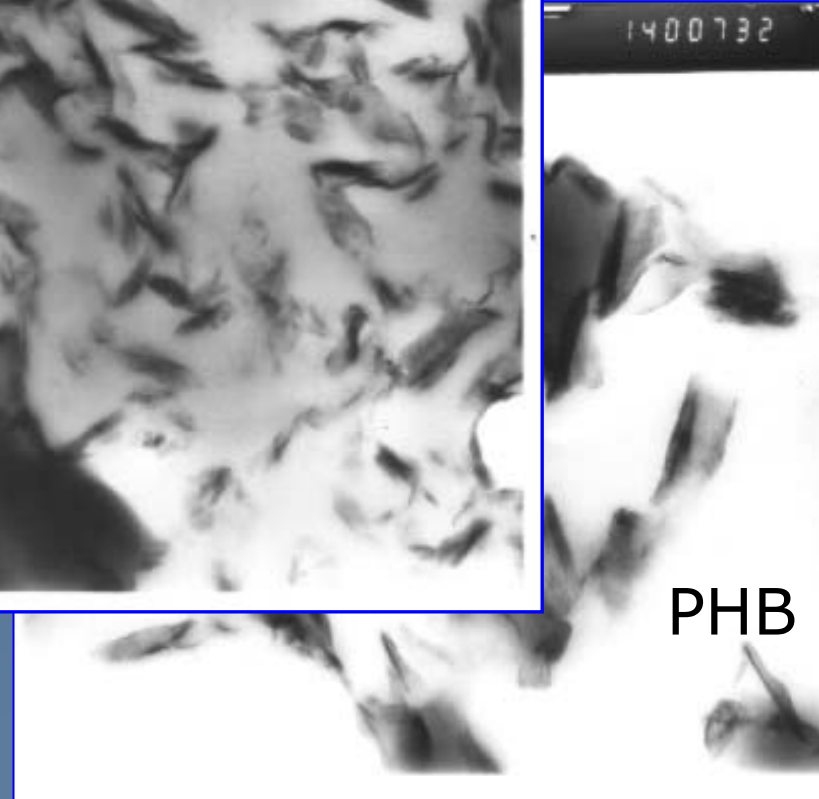
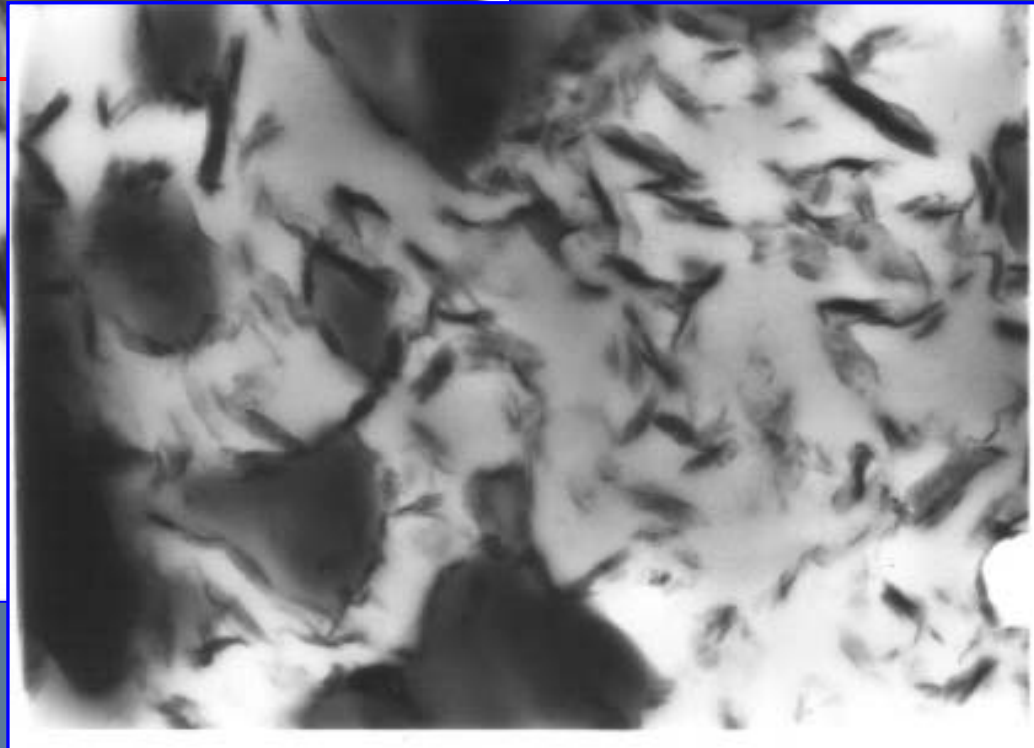
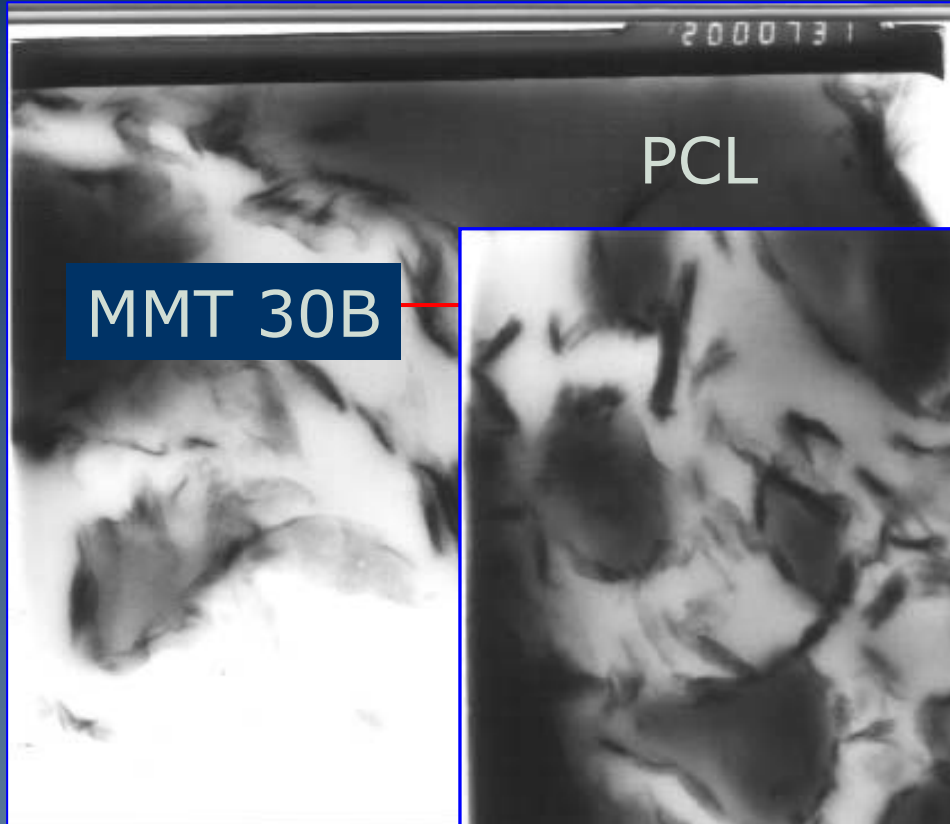
TEM image of PCL/PHB (40/60) blend



PCL

PHB

TEM images PCL/PHB40/60–MMT 30 B



- PCL/PHB 40/60, PCL/PHB40/60–MMT 30 B and Biocycle nanocomposite SEM images show that the disperse phase domain size decreases drastically when the MMT 30 B is incorporated, in both materials.

This behavior is due to the localization of the clay in the interfacial region, as it was confirmed by TEM images.

PCL/PHB (40/60) nanocomposite 38 % increase in modulus compare to PCL/PHB (40/60) blend.