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Nanocomposites Coatings for Wood Flooring

Centre de recherche sur le bois

UNIVERSITÉ LAVAL

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Presentation Plan

- Introduction
- Objectives
- Experimental Part
  - Coating Formulation
  - Clay Dispersion
- Results
  - Clay Dispersion
  - UV Curing Analysis
  - Mechanical Properties
  - Optical Properties
- Future Work
- Conclusions

Introduction

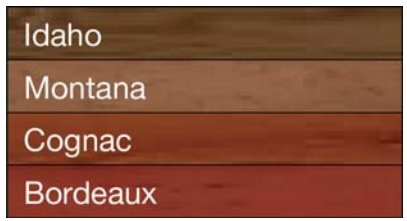
- The sales of floor covering (vinyl, rubber, carpet, wood and ceramics) in 2006 in the United States are evaluated to 24,18 billion dollars (wholesale) *(Floor Covering Weekly, 2006)*

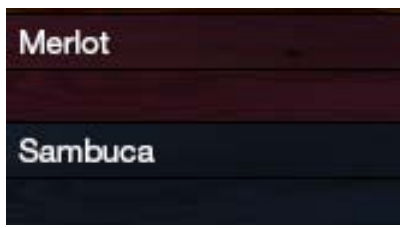
- The share of market of wood flooring represented 10,7 % (2,59 billion dollars) in 2006 *(Floor Covering Weekly, 2006)*

- The share of market for residential floor covering occupied by wood flooring represented 1,03 billion square feet in 2006 (decrease of 10,6 % compared to 2005) *(Floor Covering Weekly, 2006)*

Introduction

- Engineered Floors
- Different widths
- Introduction of exotic wood species
- New finishing products: new stains
- Pre-finished Floors





Source: www.miragefloors.com, www.armstrong.com, www.cocobolo.net, www.penningtonhardwoods.com

Our Objectives

Assess the potential for nanoparticles in UV-cured acrylate coatings for wood flooring.

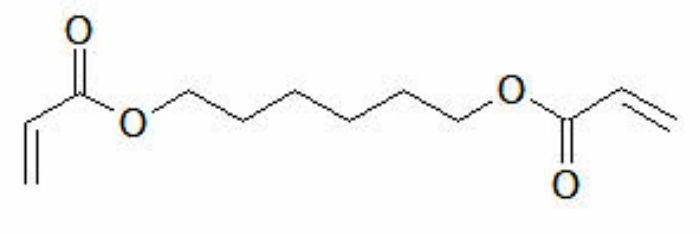
Specific objectives are:

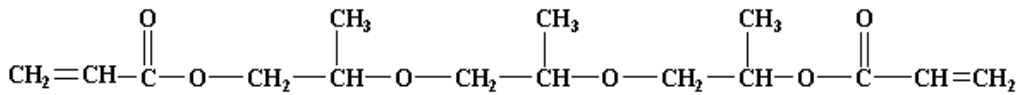
- Incorporate and disperse various nanoparticles in a typical acrylate formulation used for wood flooring.
- Study and image the dispersion of nanoparticles.
- Evaluate the kinetics and curing level of the various formulations.
- Evaluate the mechanical, optical and thermal properties and the stability of prepared formulations

Coatings Formulation

Aliphatic polyester based urethane hexaacrylate (CN 968, ~ 33-34 %)

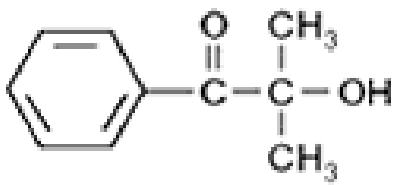
Difunctional bisphenol A based epoxy acrylate (CN 104A80, ~ 33-34 %)

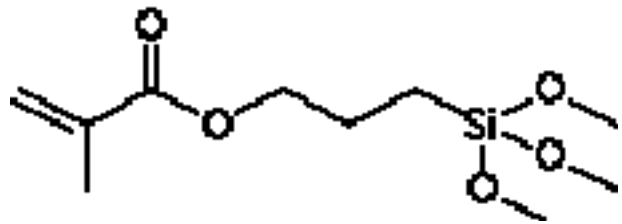




1,6-hexanediol diacrylate (HDDA, SR 238, ~ 14%)

Tripropylene glycol diacrylate (TRPGDA, SR 306, ~ 14%)



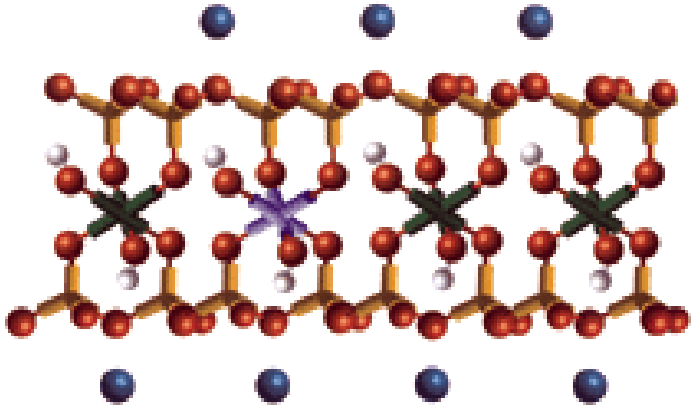


2-hydroxy-2-methyl-1-phenyl-1-propanone, Darocur 1173, Ciba Specialty Chemicals
4 %wt of acrylate reactives

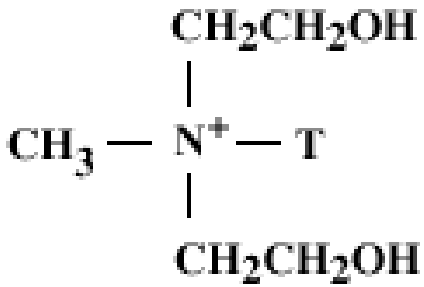
3-(trimethoxysilyl)propyl methacrylate Dynasylan MEMO, Degussa
1 %wt of nanoparticles

CLAY : montmorillonite

The selected clay is a montmorillonite



A organomodified montmorillonite was chosen, the **Cloisite 30B** from Southern Clay Products. The organic modifier is a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium salt. Tallow (T) is ~65% C18, ~30%C16, ~5%C14).



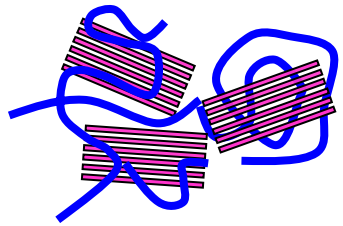
Cloisite 30B Dispersion

Clay dispersion was performed by four different dispersing equipments:

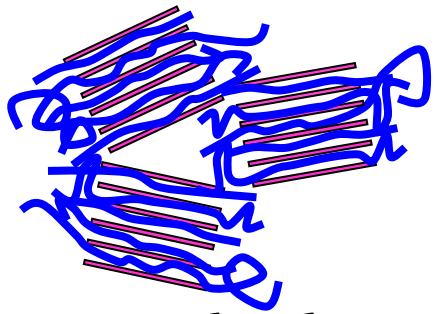
1. High speed mixer
2. Ball mill
3. Bead mill
4. Three roll mill

Shear

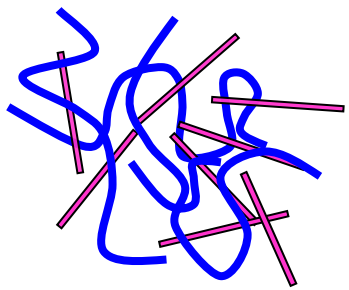
For each equipment, formulations were prepared with 1, 3 and 10 %wt of Cloisite 30B



Laminated



Intercalated



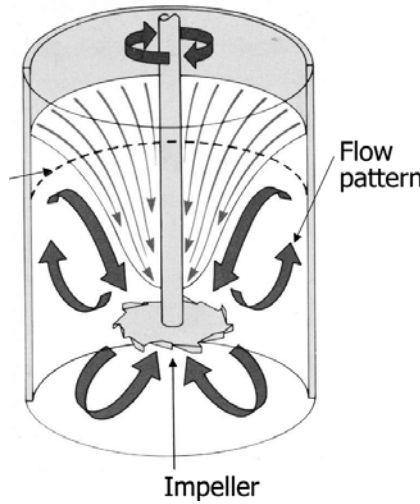
Exfoliated

Performance

Clay Dispersion

High speed mixing

- 30 minutes treatment, low shear equipment
- The obtention of a good dispersion is sometimes difficult to achieve, even at micrometric scale
- Frequently used in industry, very simple



« Ball milling »

- 2 hours treatment
- Long treatments times are often necessary in order to achieve a good dispersion
- Shear more important than for high speed mixer, but still low
- Frequently used in industry

Clay Dispersion

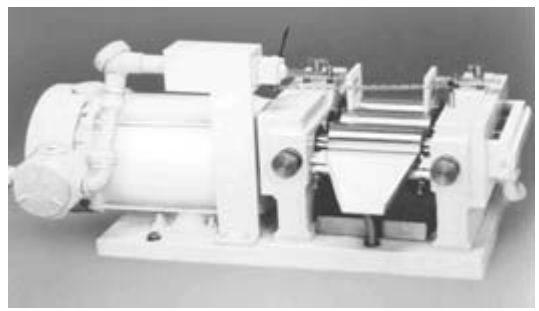
Bead milling

- 15 minutes treatment (5 min. at 2000 rpm, 5 min. at 3500 rpm and 5 min. at 5000 rpm)
- A spinning rotor inside the bead mill chamber activates the beads.
- Particles aggregates are broken by the high liquid and shear gradients and collision with the beads.
- Less used in industry

Bead mill

Three roll milling

- 2 or 3 passes, 30 minutes treatment
- The pressure between the rolls is important and it leads to a strong shear
- Less used in industry



Three roll mill

Clay Dispersion

Formulations Viscosity

- A good clay dispersion leads to a viscosity increase.
- These results suggest that three roll milling leads to a better clay dispersion.

Formulations Stability (Freeze-thaw stability)

- A good clay dispersion leads to a good stability.
- These results suggest that bead milling leads to a better dispersion.

Small Angle X-ray Diffraction

- Disappearance of the d_{001} peak suggests an exfoliated structure.
- No peak was observed for formulations prepared with 1 %wt of clay.

Atomic Force Microscopy (AFM)

Transmission Electron Microscopy (TEM)

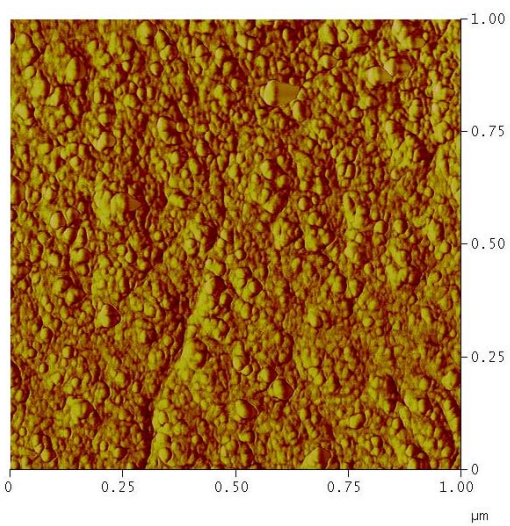
Results - Atomic Force Microscopy (AFM)

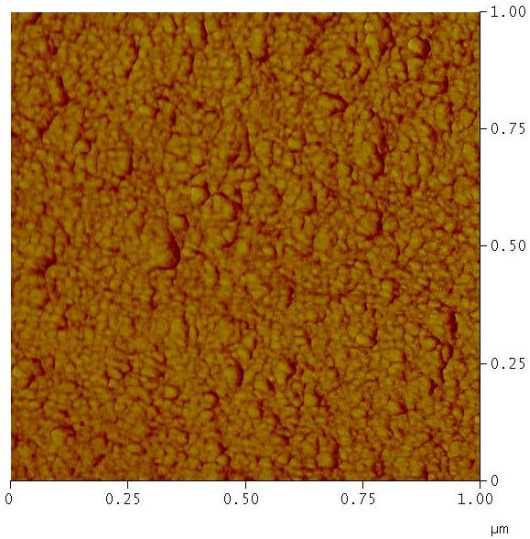
Images of 1 µm x 1 µm

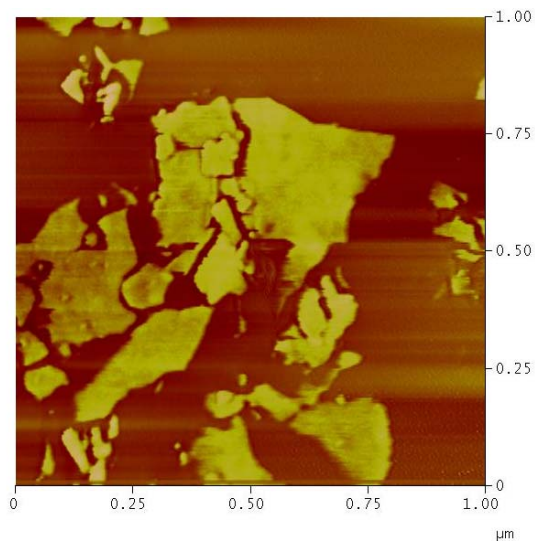
Nanoscope III multimode AFM (Digital Instruments (DI)), tapping mode

1 %wt of clay Three roll mill	3 %wt of clay Three roll mill	10 %wt of clay Three roll mill

1 µm



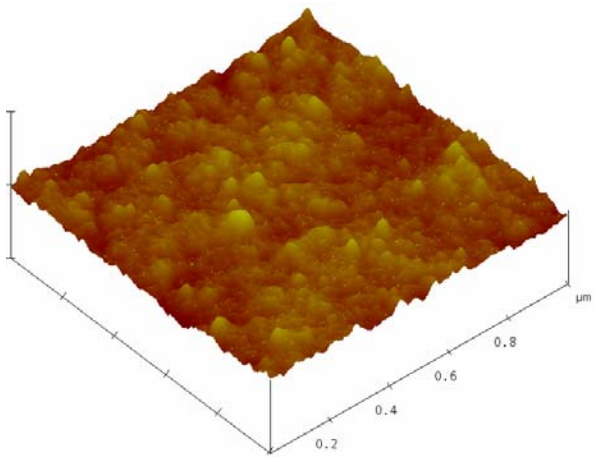


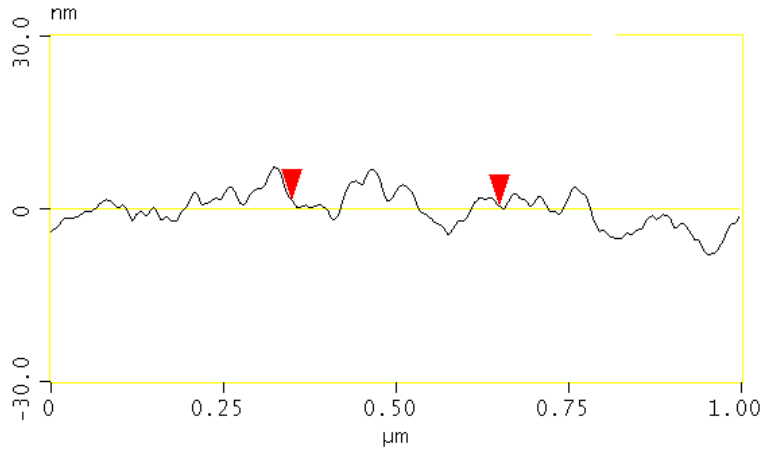


Results - Atomic Force Microscopy (AFM)

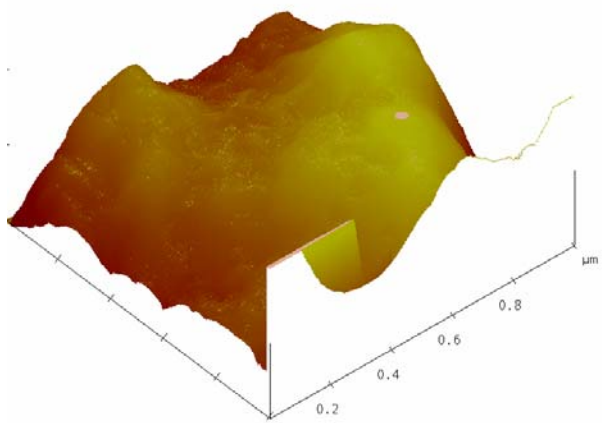
Height images of the formulations prepared with:
(a) 3%wt by bead milling (b) 3%wt by high speed mixing

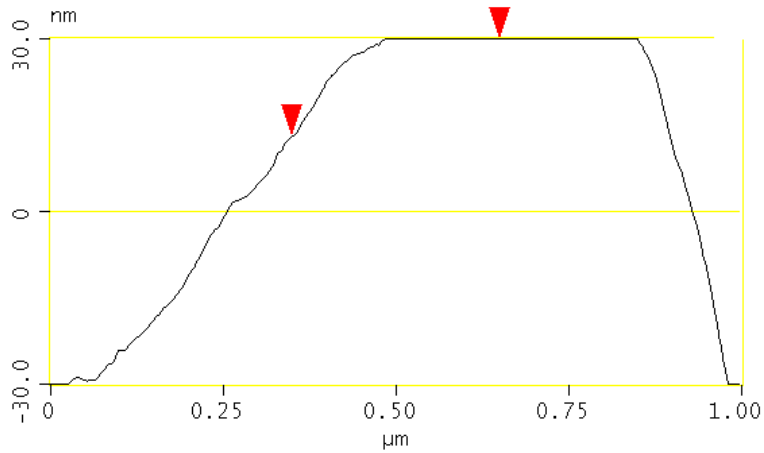
(a)





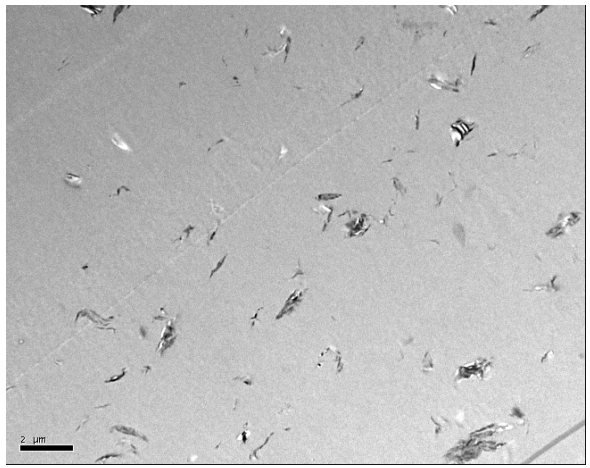
(b)



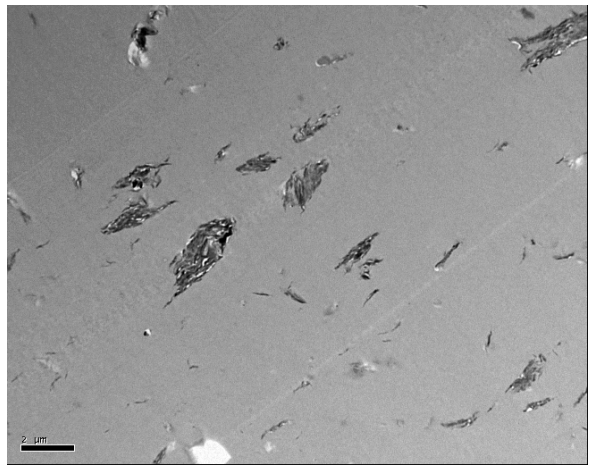


Results - Transmission electron microscopy

Formulations with 1 %wt of clay

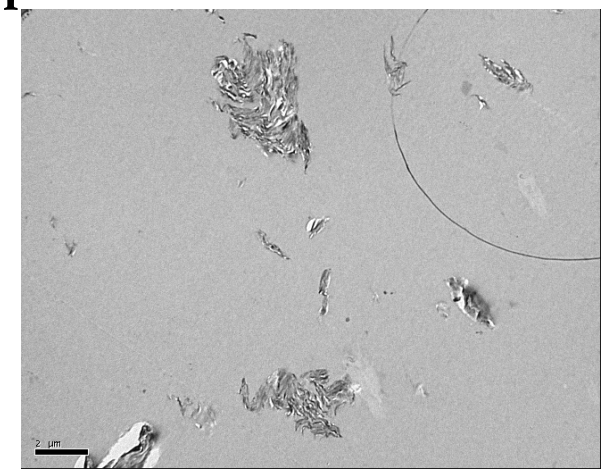


Three roll mill

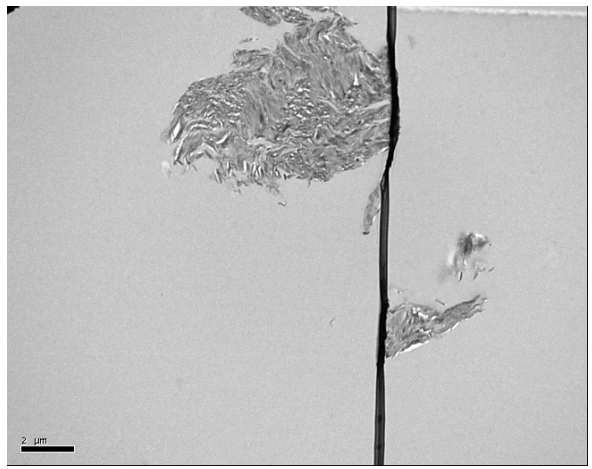


Bead mill

2 µm



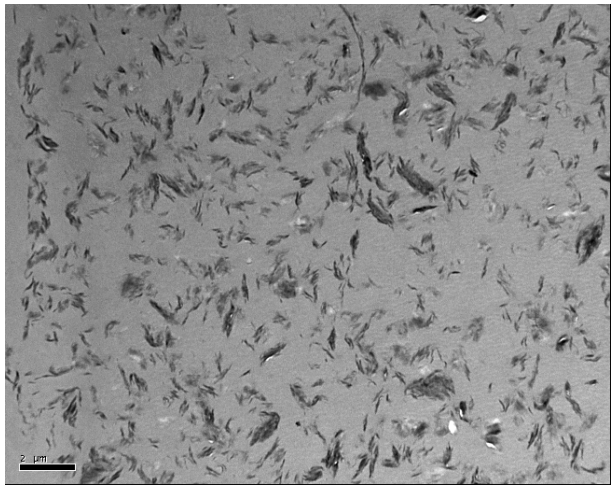
Ball mill



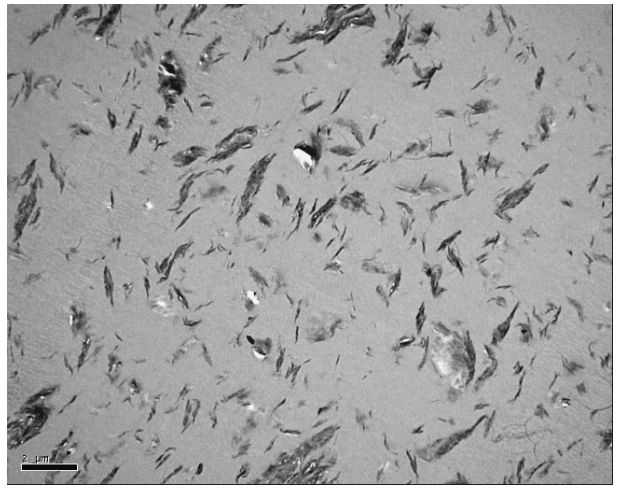
High speed mixer

Results - Transmission Electron Microscopy

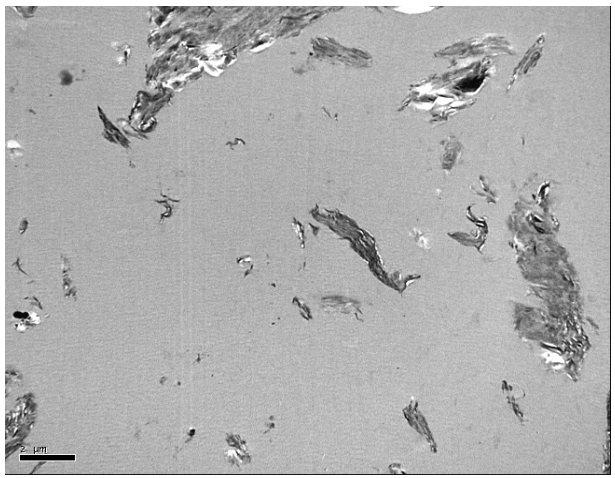
Formulations with 10 %wt of clay



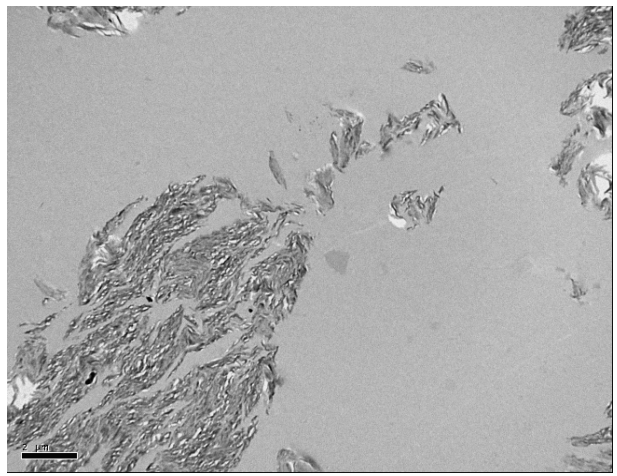
Three roll mill



Bead mill



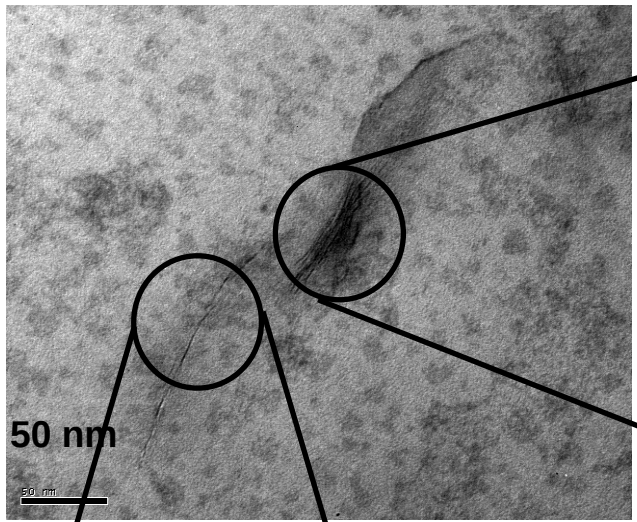
Ball mill



High speed mixer

Results - Transmission Electron Microscopy

Formulation prepared by bead milling with 1%wt of clay



Laminated platelets

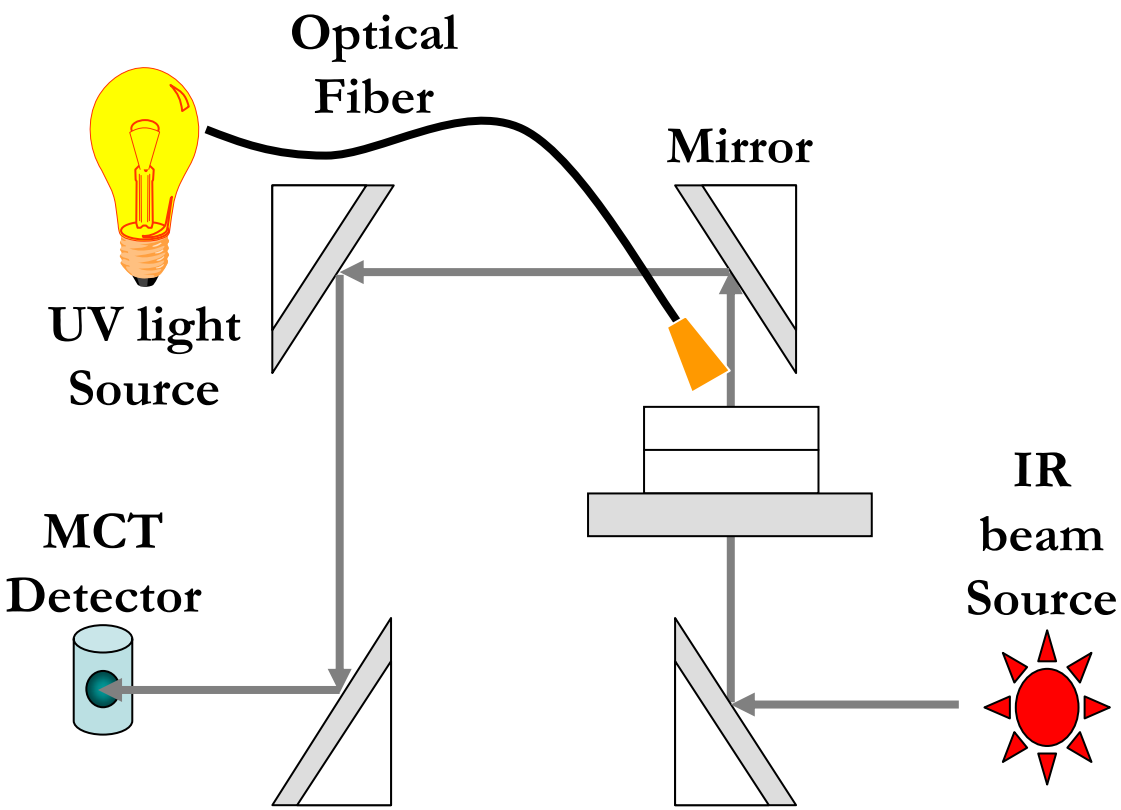
Single platelet

Dispersion Conclusions

- **Small X-ray diffraction experiments** were first performed but it was difficult to conclude on the dispersion efficiency based on these experiments
- Dispersion was evaluated by **AFM** and **TEM**
- We found that three roll milling leads to the best dispersion, followed by bead milling, ball milling and last high speed mixing

- **Does the clay dispersion affects the curing of the formulations ???**

Real-Time Infrared Spectroscopy



Infrared Spectrophotometer : Perkin-Elmer 781

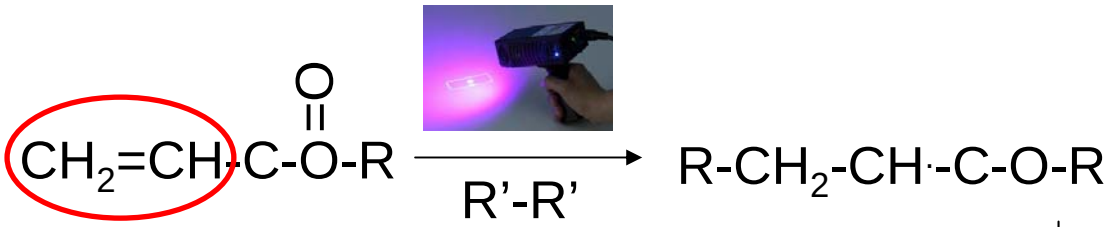
Exposition time : one thousand seconds

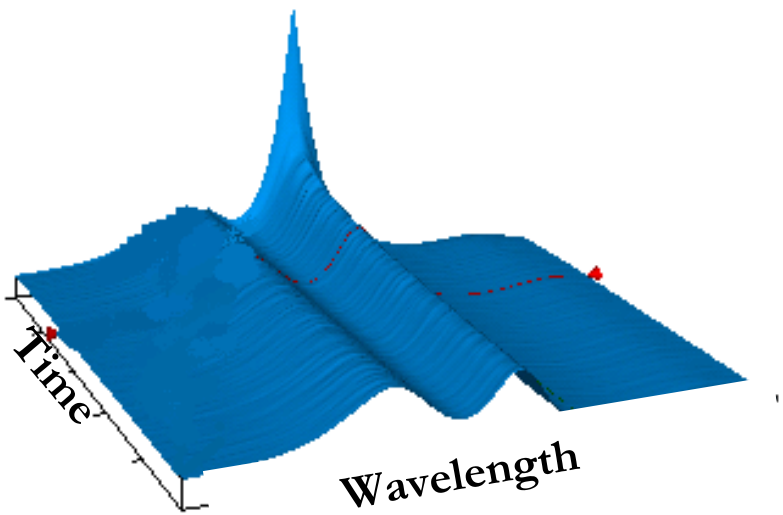
UV Lamp: a medium pressure mercury (HOYA-SCHOTT-UV-200) via a fiber optic light pipe.

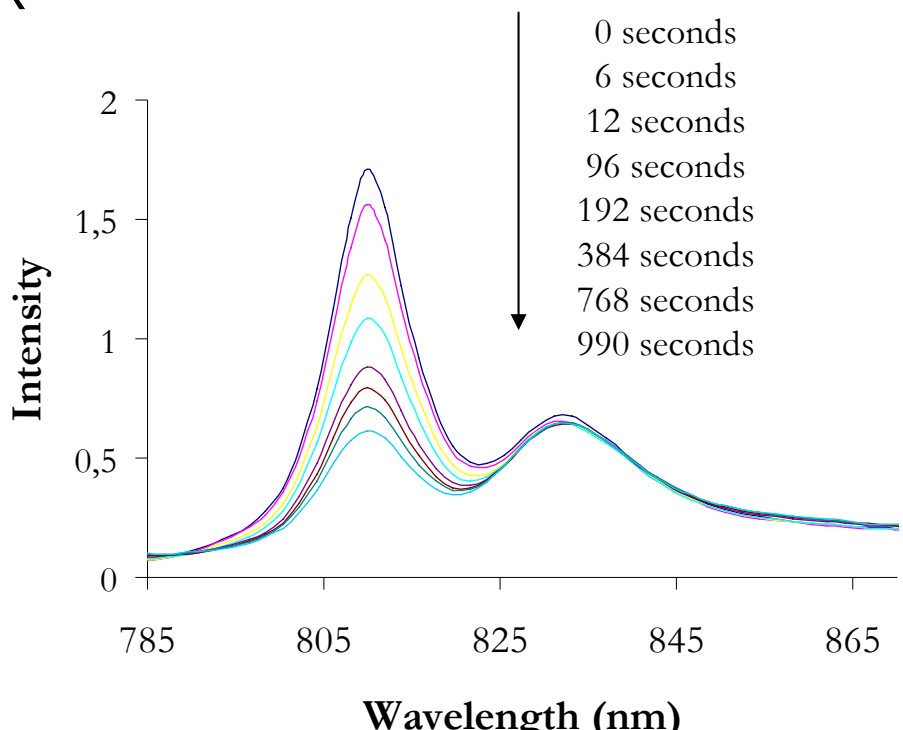
Light intensity: 18.7 mW/cm^2.

Real-Time Infrared Spectroscopy

The degree of conversion of the UV-exposed sample was evaluated by infrared spectroscopy through the decrease of the IR band at 812 cm^{-1} or 1625 cm^{-1} of the acrylate double bond.

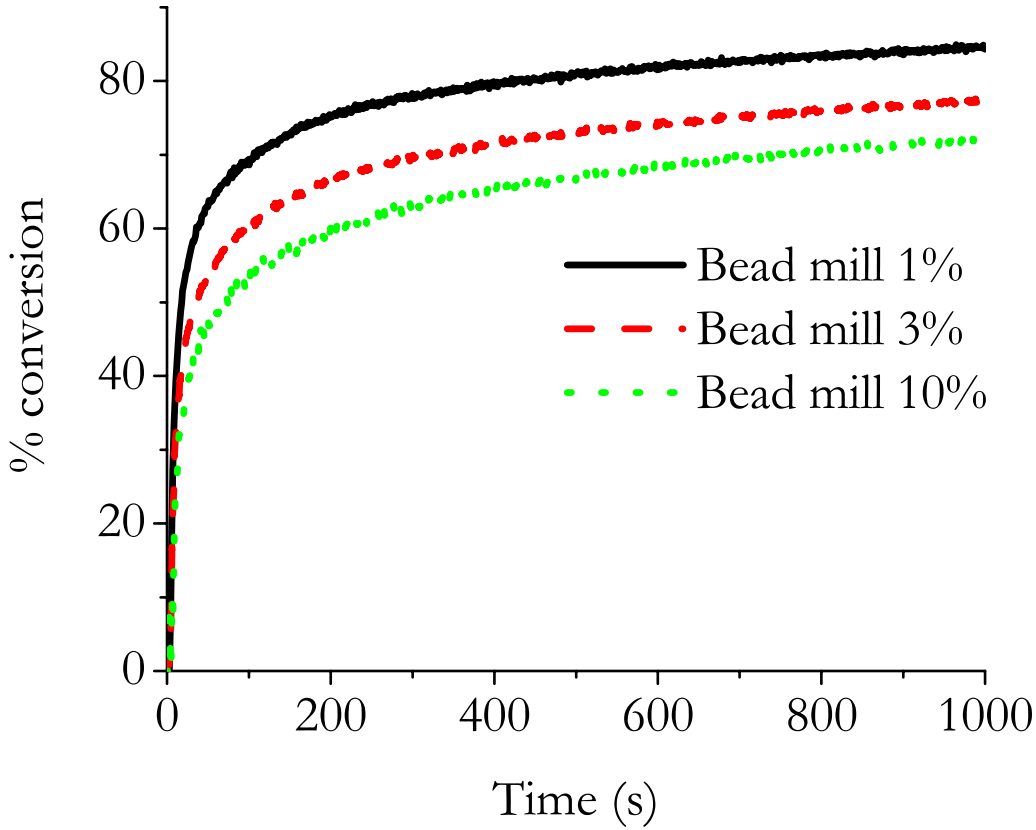


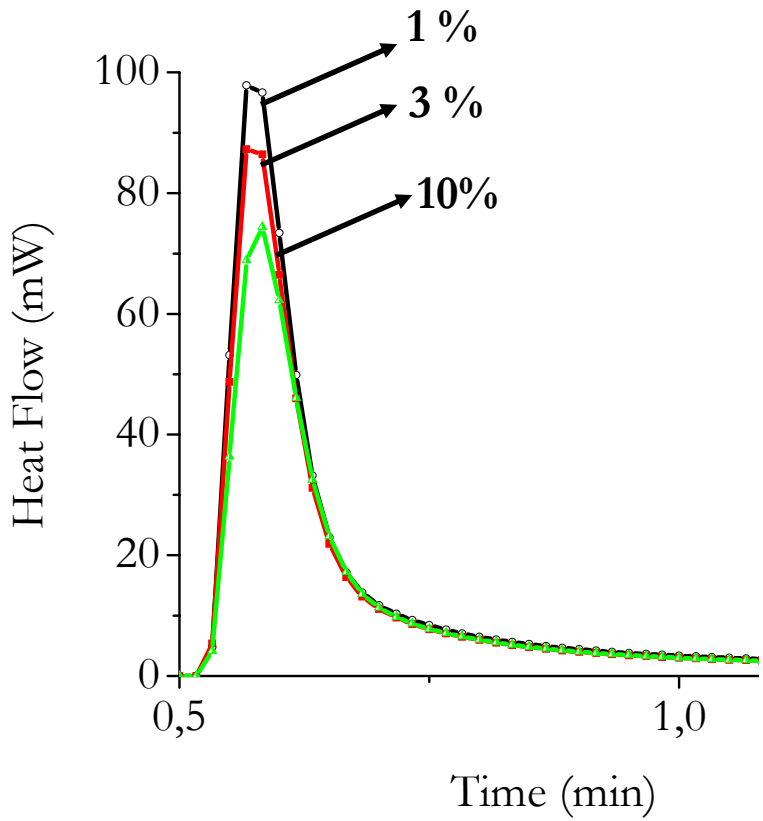




Real-Time Infrared Spectroscopy – Loading Comparison

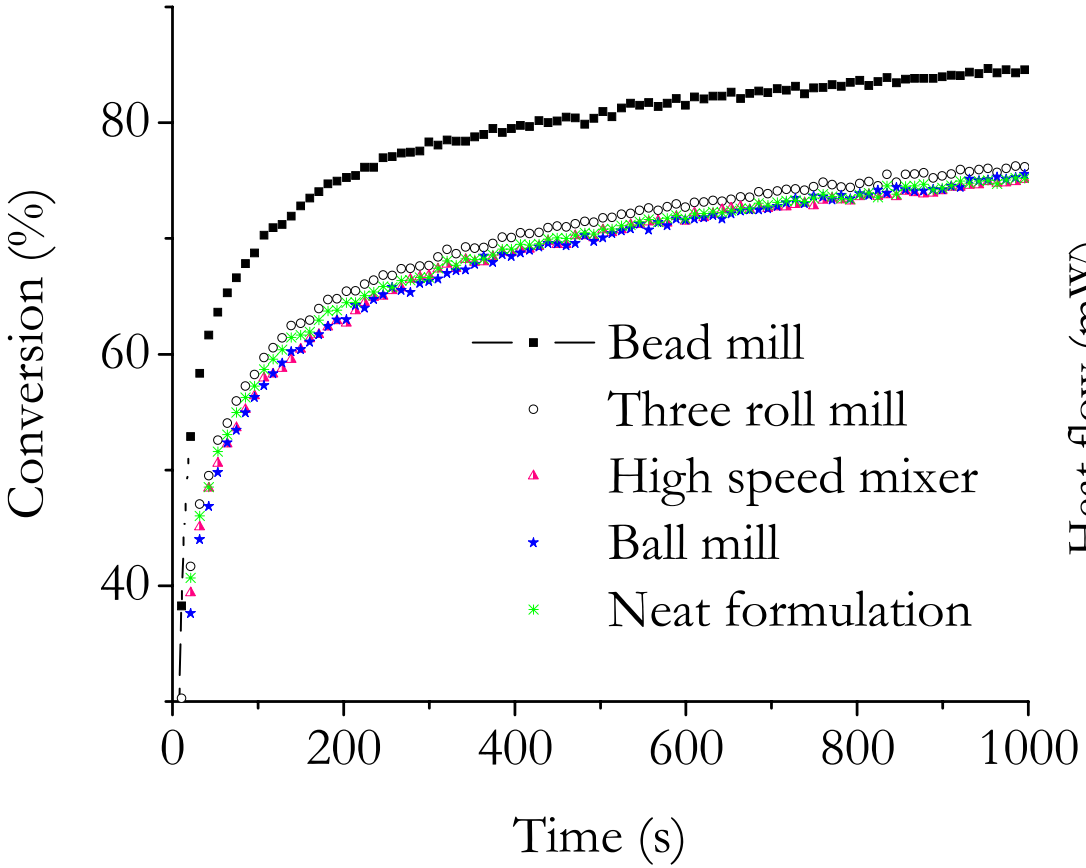
Conversion profiles for the bead milled formulations prepared with 1, 3 and 10 %wt of clay

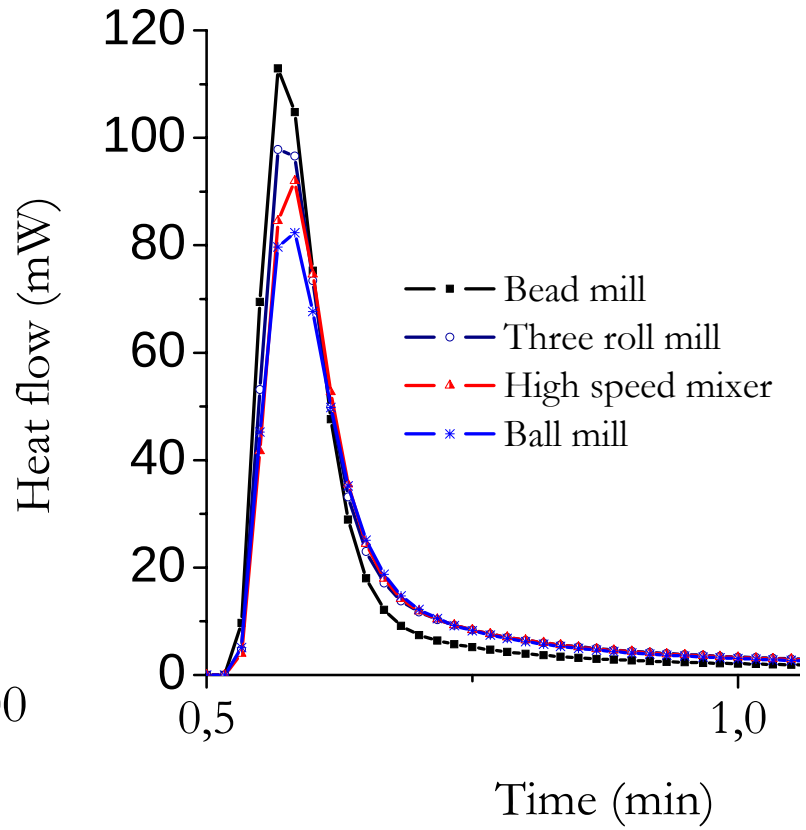




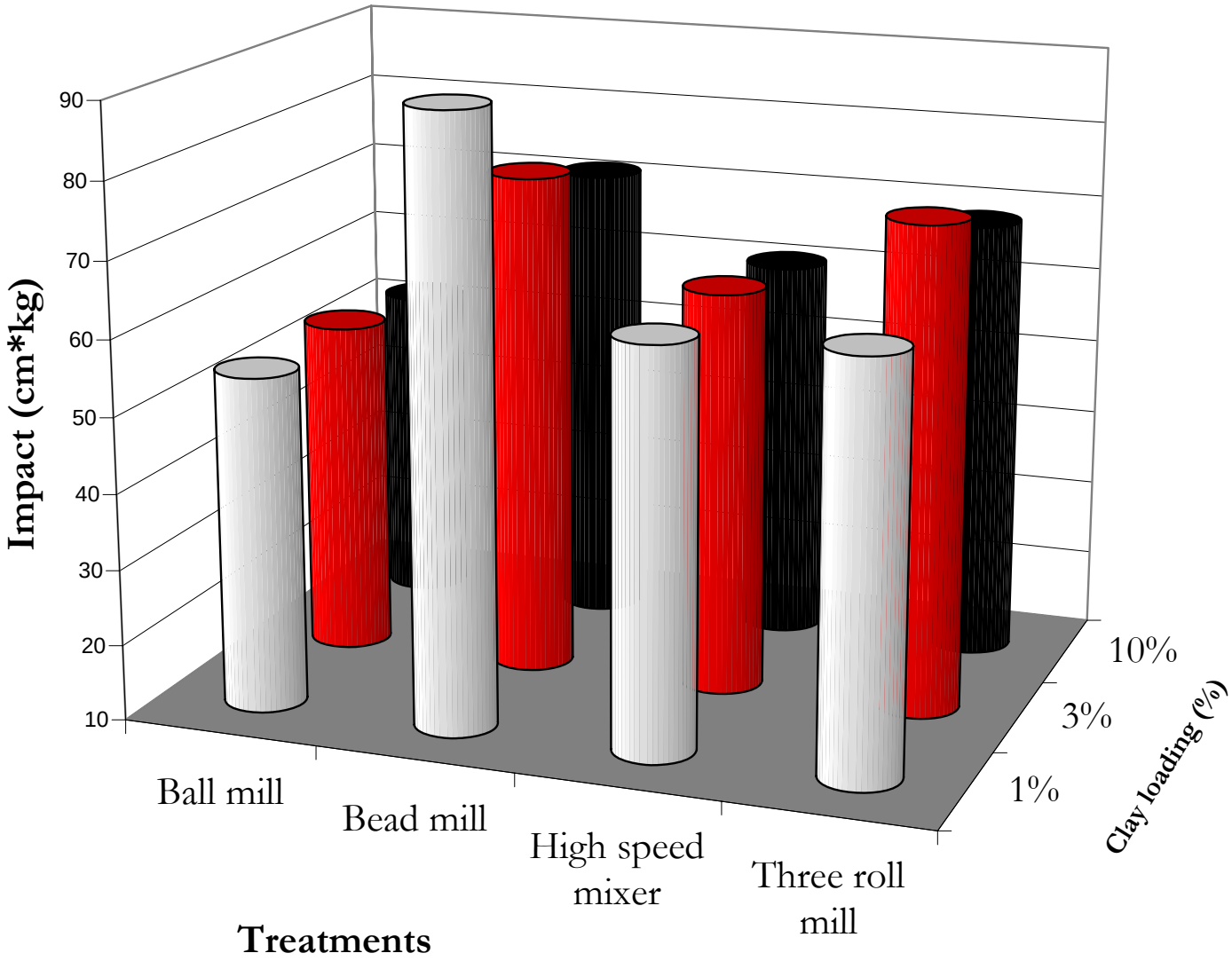
Real-Time Infrared Spectroscopy – Treatment Comparison

Conversion profiles for the formulations prepared with 1%wt of clay for the different treatments



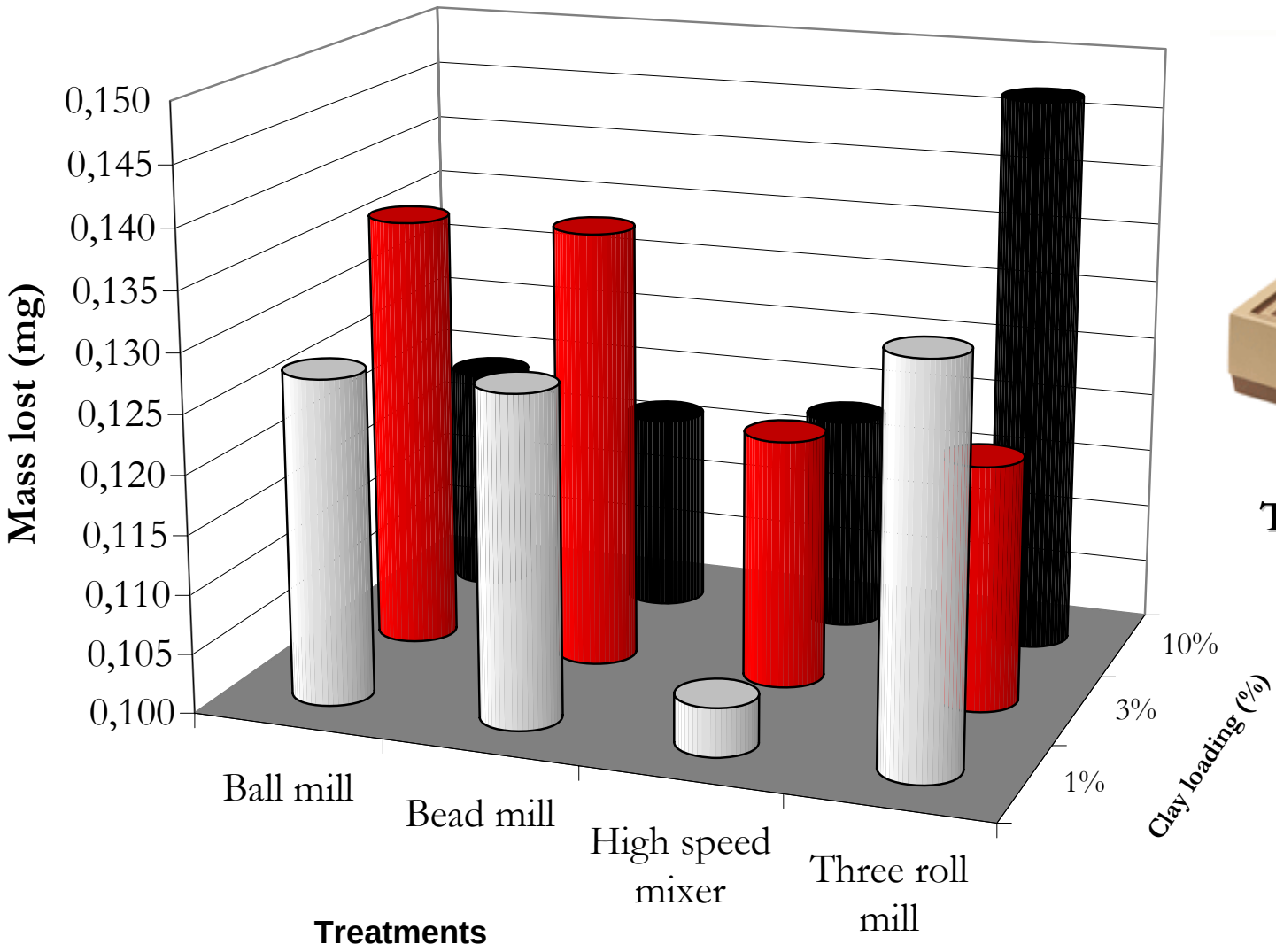


Mechanical Properties – Impact Resistance



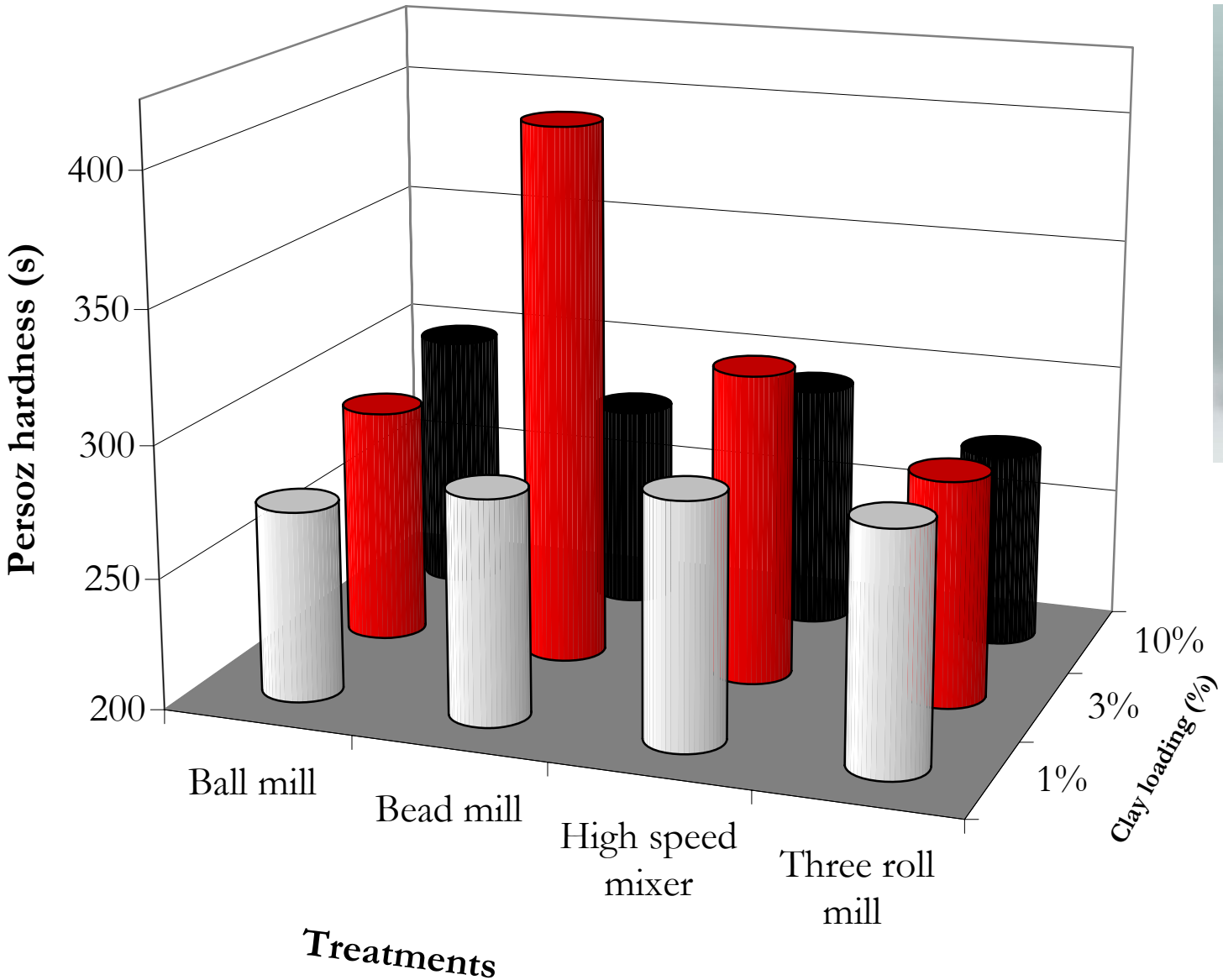
Impact tester

Mechanical Properties - Abrasion Resistance



Taber Abraser

Mechanical Properties - Hardness

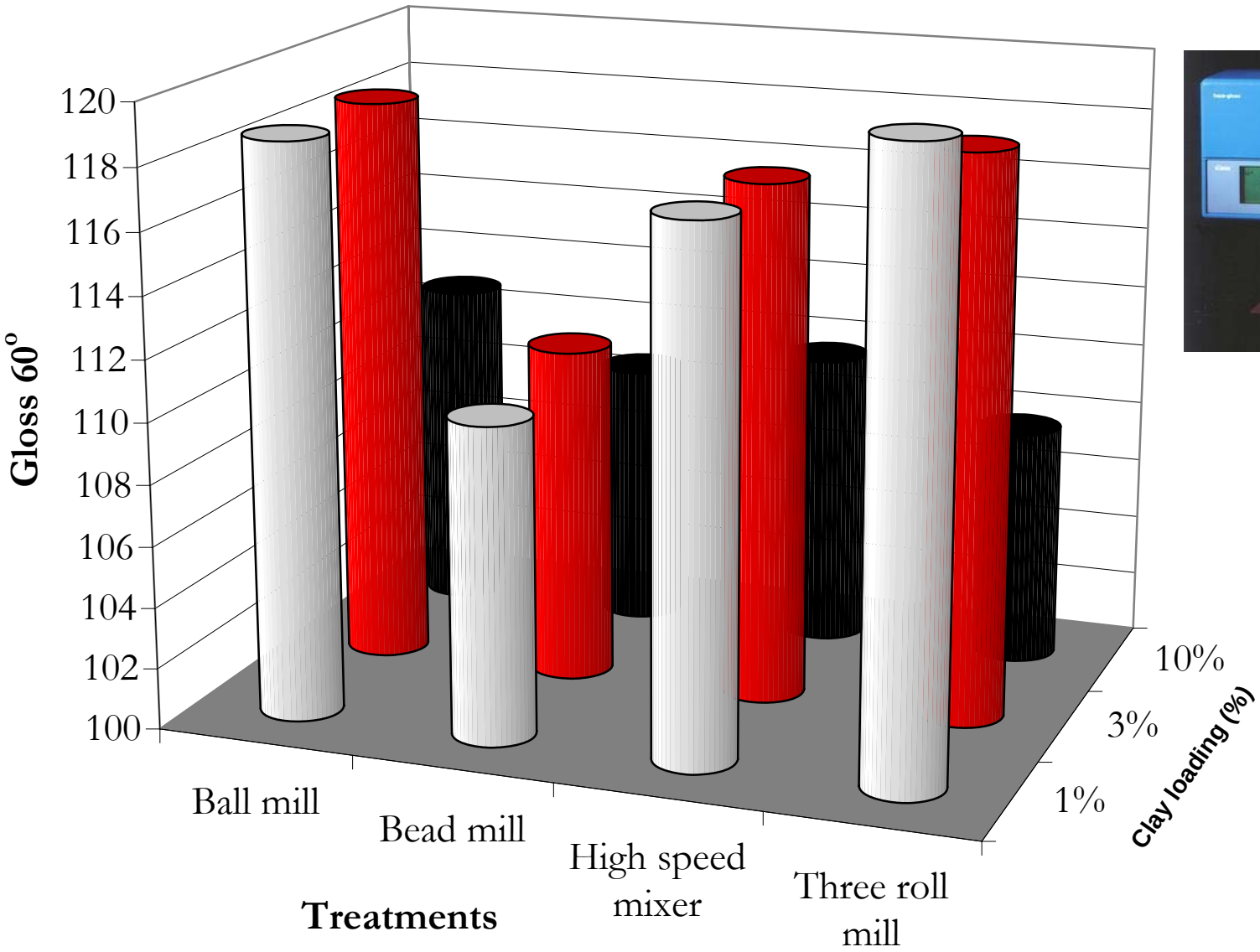


Pendulum

Summary- Mechanical Properties

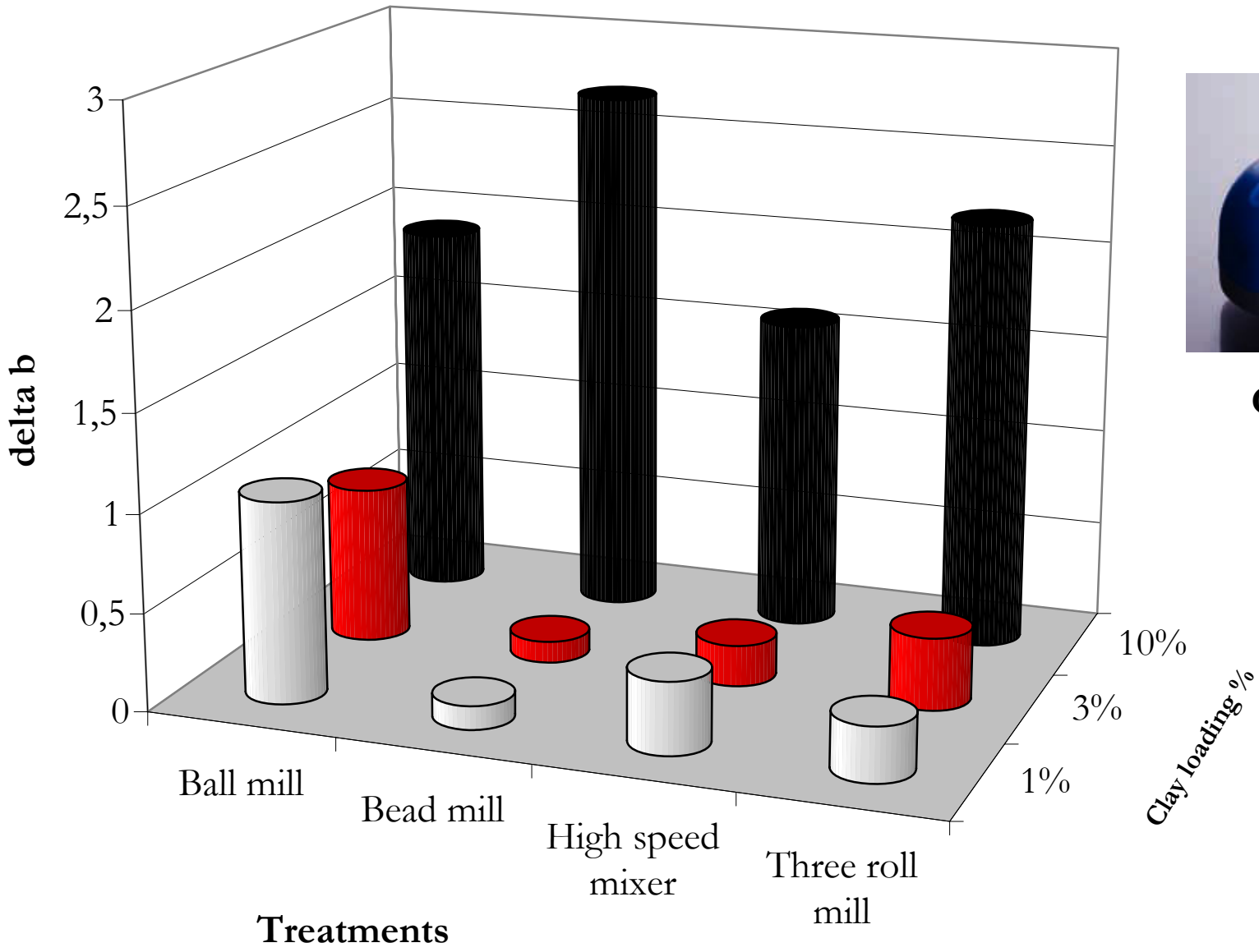
Formulations	Hardness	Abrasion	Impact	Reverse Impact
Ball mill 1%	—	⇑	⇓	⇓
Ball mill 3%	—	—	⇓	—
Ball mill 10%	—	⇑	⇓	—
Bead mill 1%	—	⇑	⇑	⇑
Bead mill 3 %	⇑	—	—	⇑
Bead mill 10%	—	⇑	—	—
High speed mixer 1%	—	⇑	⇓	—
High speed mixer 3%	⇑	⇑	⇓	—
High speed mixer 10%	—	⇑	⇓	—
Three roll mill 1%	—	—	⇓	—
Three roll mill 3%	—	⇑	—	—
Three roll mill 10%	—	—	—	—

Optical Properties - Gloss



Haze-gloss

Optical Properties – Color (b component)



Colorimeter

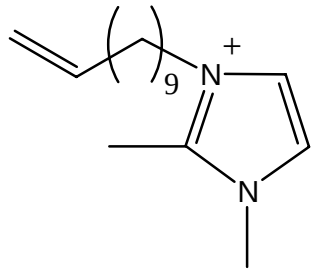
Conclusions

- Three roll milled and bead milled formulations present a good clay dispersion
- Strong aggregates are present in the formulations prepared by high speed mixing and ball milling
- Curing is more efficient for bead milled formulations even though the three roll milled formulations present a better clay dispersion
- Formulations prepared by bead milling lead to better mechanical properties
- Optical properties remain good at low clay loading

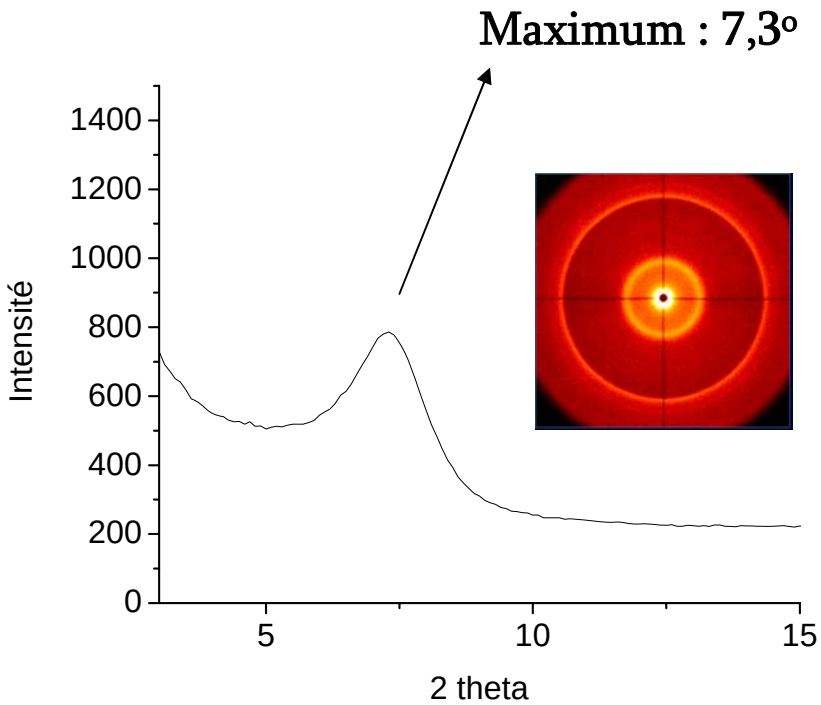
Future Work

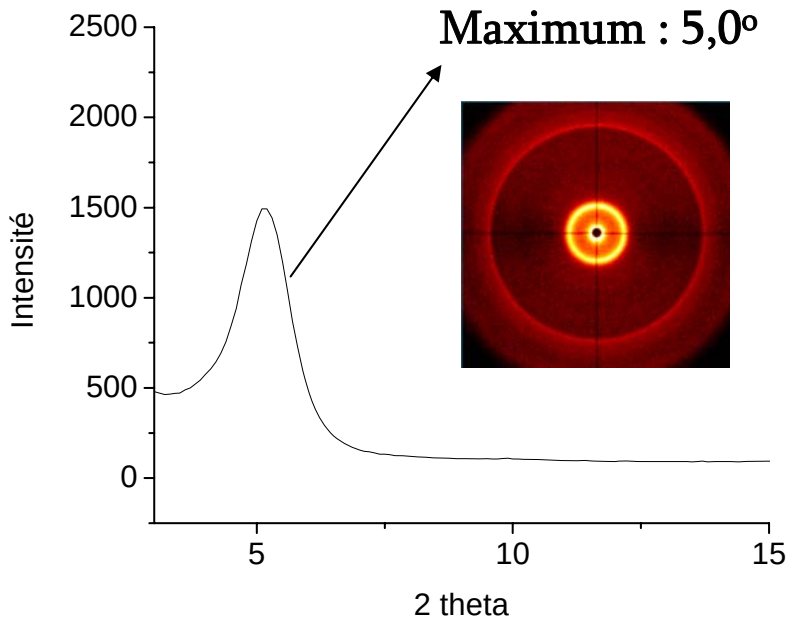
Natural Clay modification

X-ray Diffraction : d_{001} peak goes from 7.3° to 4



1, 2-dimethyl-3-undecene imidazolium bromide





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