Ethylene-Acrylonitrile Copolymerization with Ni-Diimine/EASC/Clay Catalyst System

Sang-Young A. Shin, Joao B. P. Soares, Leonardo C. Simon

Department of Chemical Engineering

University of Waterloo

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Motivation

- Searching for a new surface modifier of clays

- Developing high performance thermoplastic elastomers
  - Product with properties similar to Therban®

Introduction

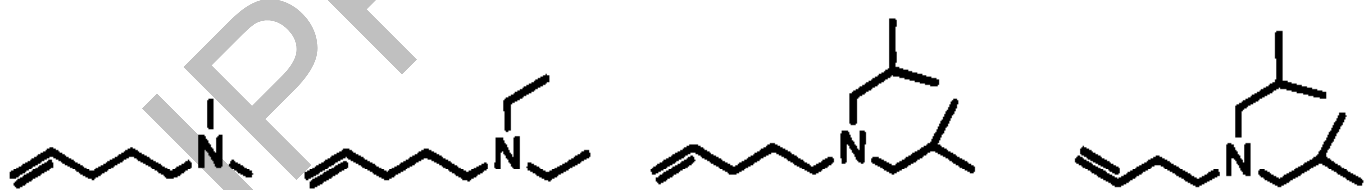
Polymerization Conditions for Polar Comonomers

- Comonomer should have at least two methylene spacers between the olefin and polar functional groups

- Tolerance to polar groups (approximately 1500 equiv. per metal center)

  3° Amines > Halides > Ethers > Ketenes > Esters > Water > Alcohols

Table 1. Amine Monomers Polymerized with $Cp^*_2ZrMe_2$ /Borate System



Activities [a] $(h \cdot c[M])^{-1}$	9	155	619	151

a. Activity = mol of monomer/mol of Zr·c[monomer]·h

Stehling,et al., *Macromolecules.*, **1998**, 31,2019

Part 1: Ethylene/Acrylonitrile Copolymer with α-Diimine-[N,N] Nickel Dichloride/EASC System

- **Nitrile group of acrylonitrile can coordinate metal active center in Ethylene/Acrylonitrile copolymerization.**
- **Late transition metal catalysts are tolerant for polar comonomer.**
- **Pretreatment acrylonitrile with alkyl aluminum.**
- **EASC as a co-catalyst for ethylene/acrylonitrile copolymerization.**

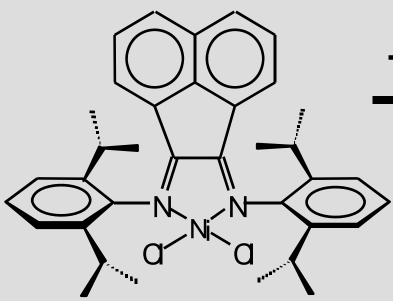
Catalysts for Ethylene/Acrylonitrile Copolymer

Purging with N_2/Solvent →

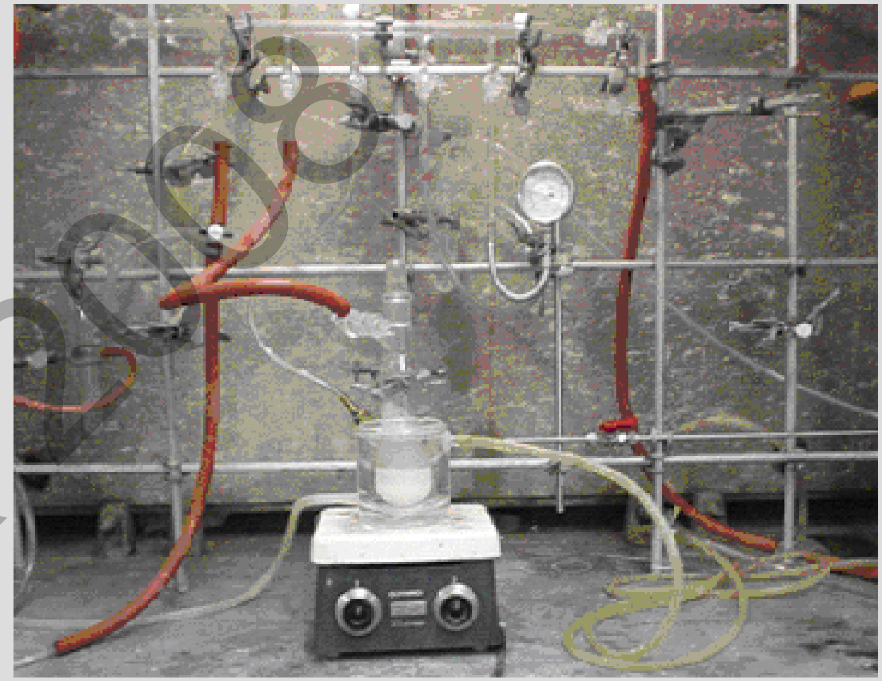
Ethylene →

EASC/CAT →

TIBA/Acrylonitrile →



1,4-bis(2,6-diisopropylphenyl)
-acenaphthenediimine-dichloronickel (II)



- Ethylene and acrylate copolymer was reported by Pd-diimine catalyst system by Brookheart Group.

  Johnson, L.K.; Mecking, S.; Brookhart, M. J. Am. Chem. Soc., 1996, 118, 267.

Copolymerization of Ethylene and Acrylonitrile

No.	M	C	[C] (mol/L)	Time (hr.)	Yield (g)	Mw (kg/mol)	PDI
1	C_2H_4	-	-	1	2.1	233	3.2
2	C_2H_4	C_2H_3CN	0.06	1	2.0	247	3.4
3	C_2H_4	C_2H_3CN	0.36	1	0.32	364	2.8
4	C_2H_4	C_2H_3CN	0.48	1	0.30	295	2.4
5	C_2H_4	C_2H_3CN	0.60	1	0.32	249	2.2
6	C_2H_4	C_2H_3CN	0.73	1	0.32	277	2.2

Catalyst :(diimine)$NiCl_2$/EASC system
M: monomer(ethylene); C: comonomer (acrylonitrile with tri-isobutilaluminum)
Experimental conditions: solvent: 25 mL;
[**1**] = 4.25μmol/L, [Al]/[**1**] = 43, temperature = 25^{o}C ;
$P_{ethylene}$ = atmospheric.
All samples were dried in the oven at 80 °C for 24 hrs.

Functional Groups in Ethylene/Acrylonitrile Copolymer, Xylene Soluble, Xylene Insoluble Fractions

(c) Xylene-soluble fraction

- **Nitrile groups**
- **Attenuated vinyl groups**

(b) Xylene-insoluble fraction

- **Nitrile groups**
- **vinyl groups**
- **PAN structure**

(a) Ethylene/acrylonitrile copolymer

- **Nitrile groups**

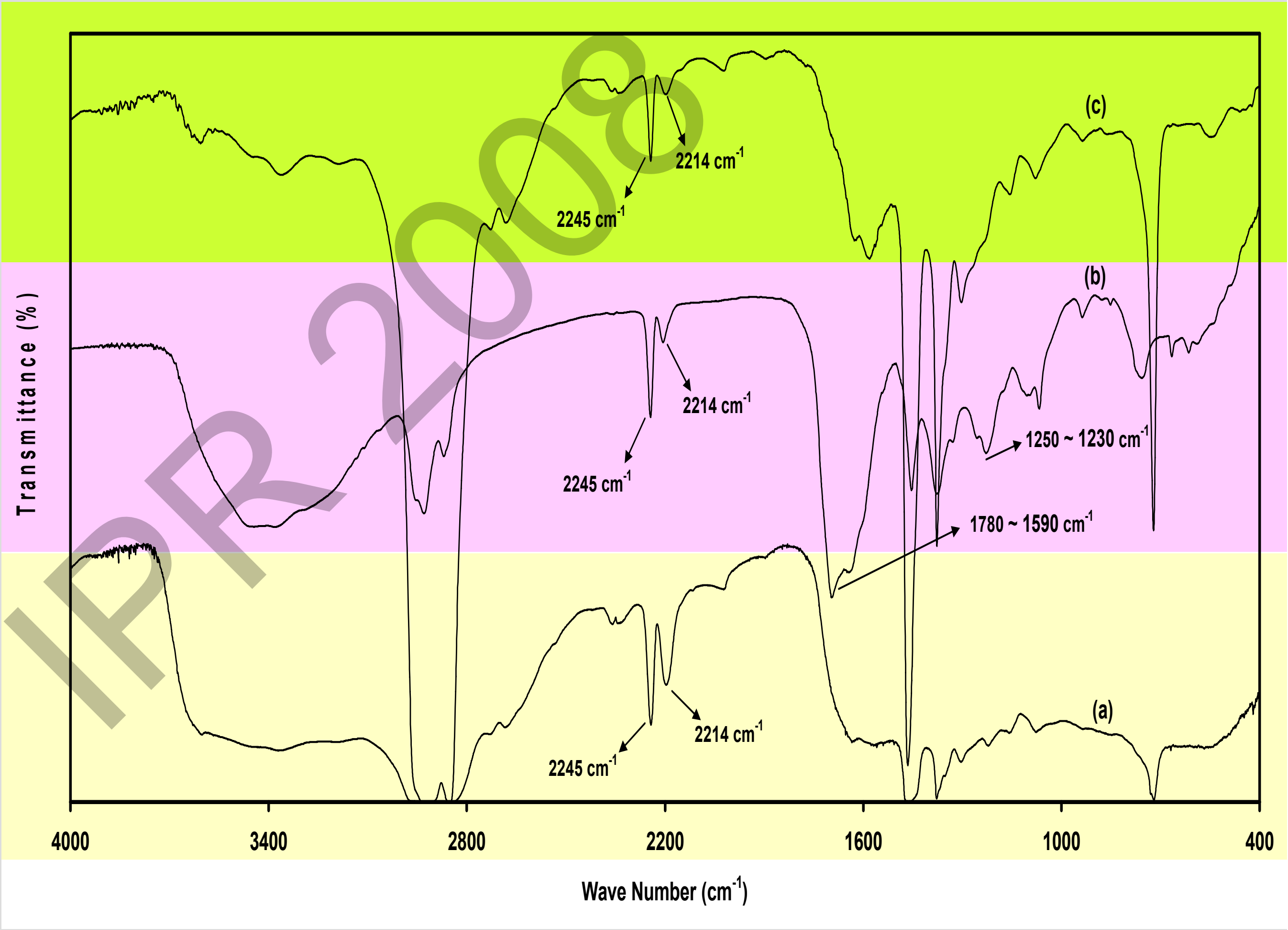
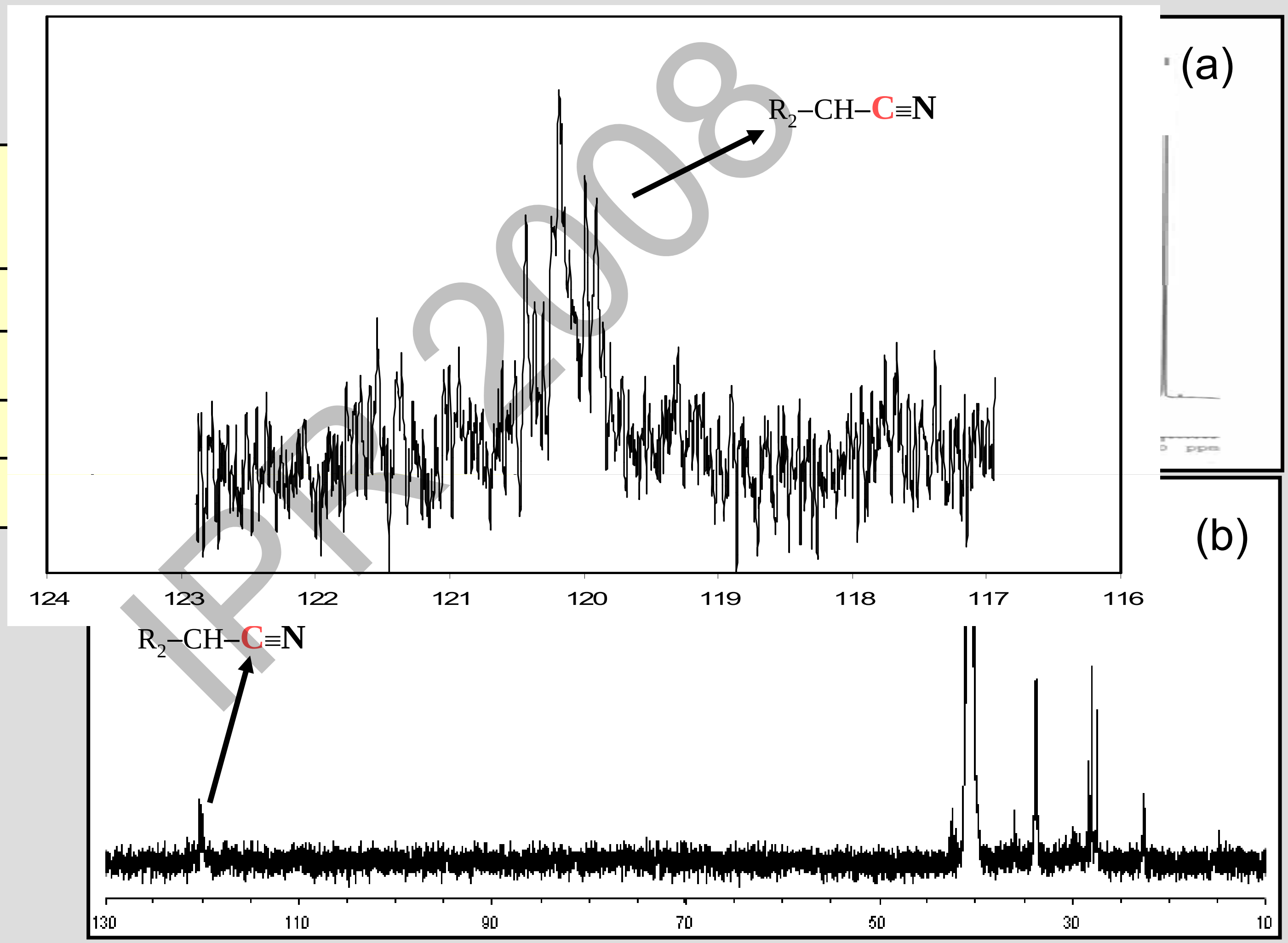


Figure 1. FT-IR spectra of ethylene/acrylonitrile copolymer sample 3

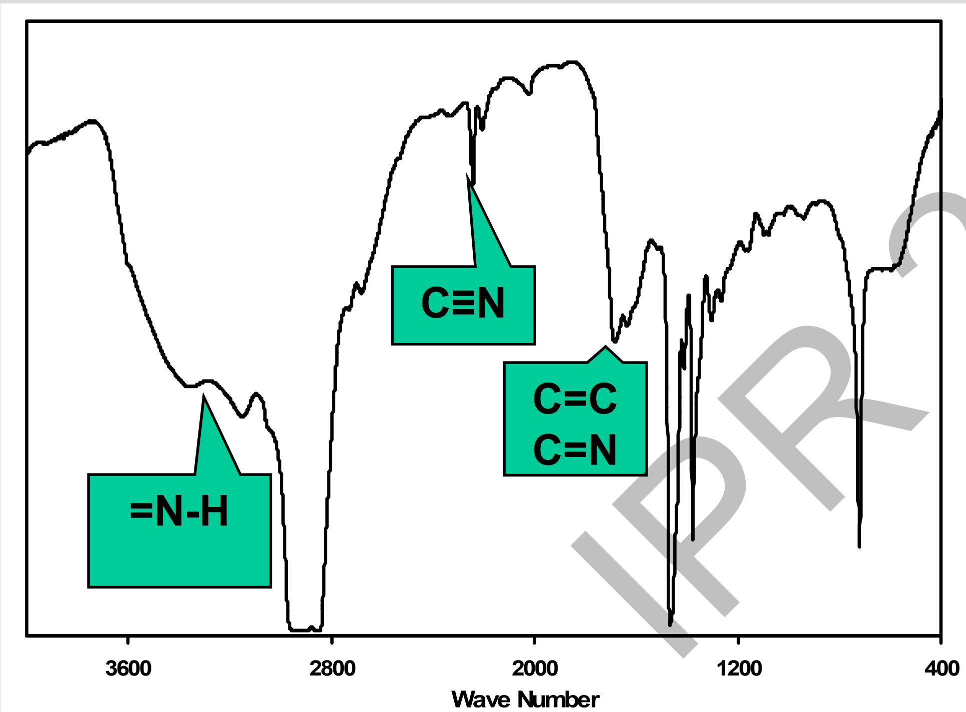
^{1}H, ^{13}C NMR spectra ; Xylene insoluble part polymer after 24 hours extraction.

No.	Assignment[c]
3	CH_3-CH(R)–C≡N
4	CH_3–CH(C=N)–)
1	R–CH_2–C≡N
2	R_2–CH–C≡N

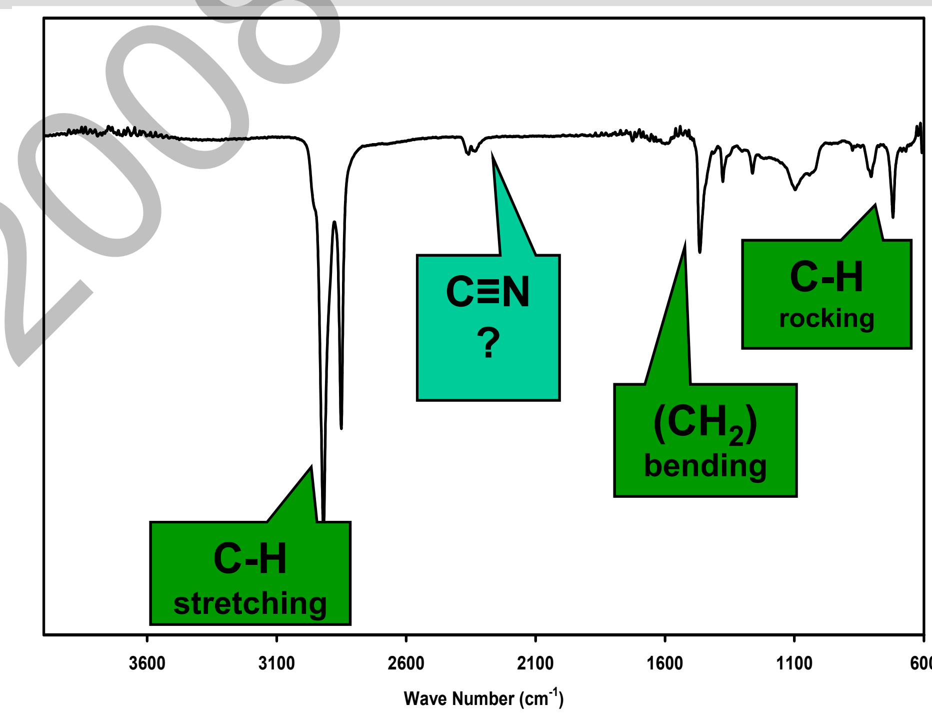


Transmission and ATR FT-IR spectra of Ethylene/Acrylonitrile Copolymer

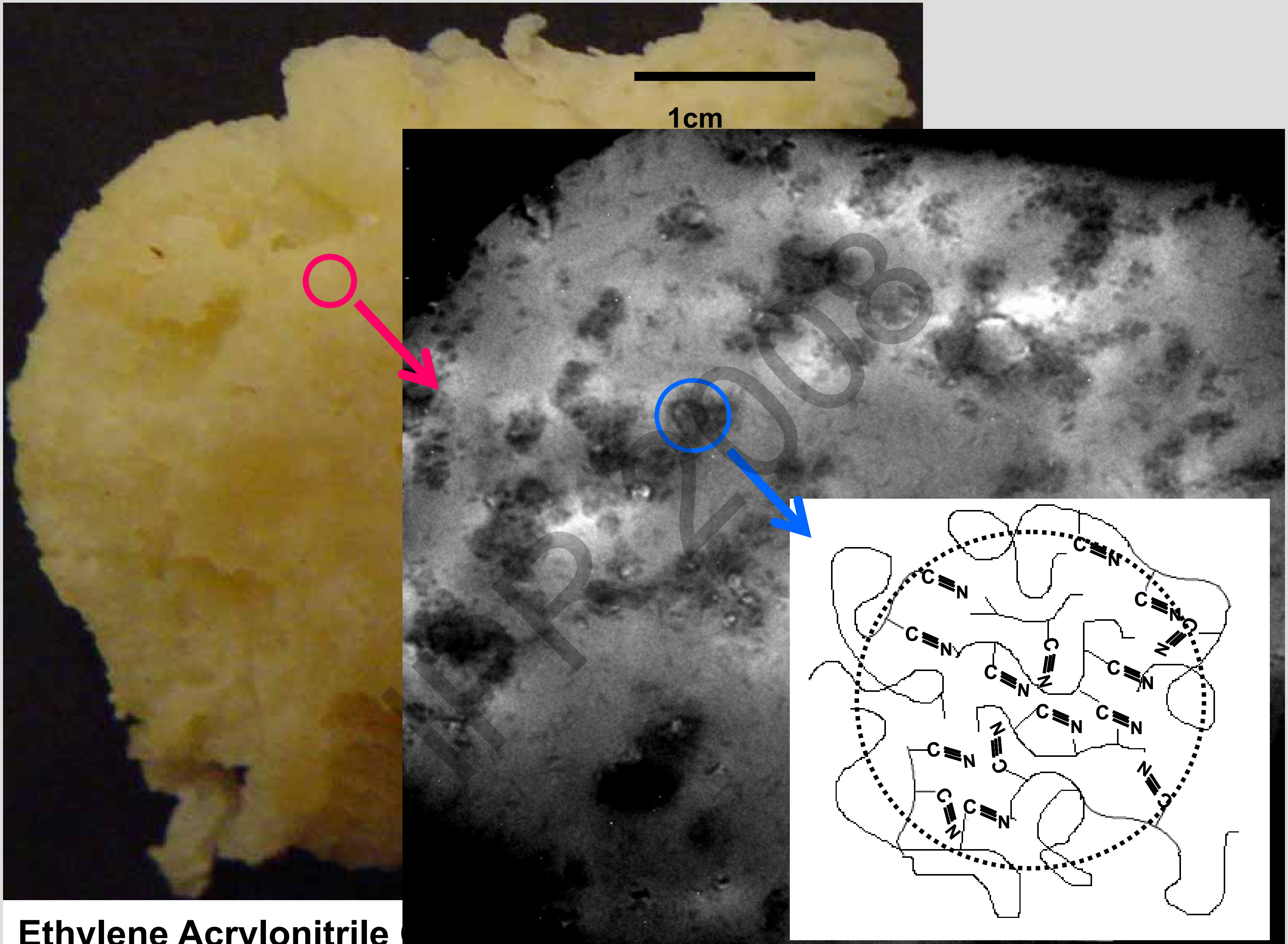
Transmission



ATR



* ATR :Attenuated total reflection infrared



Ethylene Acrylonitrile (

TEM, microtomed section of sample (No.6 in Table 1)
(80 nm thickness)

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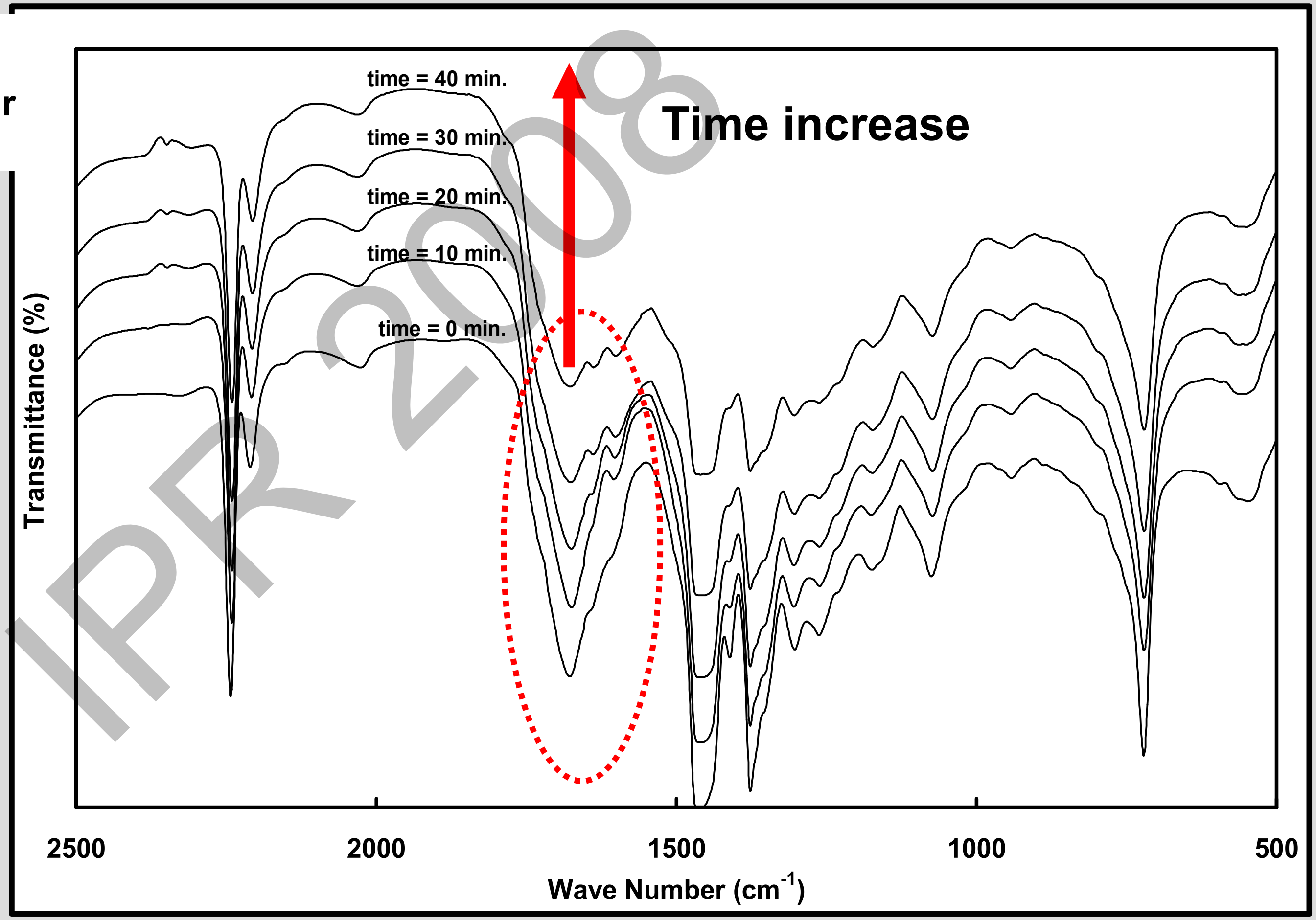
Thermal Behavior of Ethylene/Acrylonitrile Copolymer

➢ **FT-IR Spectra** ;
ethylene/acrylonitrile copolymer
(In the heating block at 160 °C)



Thermal Behavior of Xylene Insoluble Fraction

(PAN Rich Part)

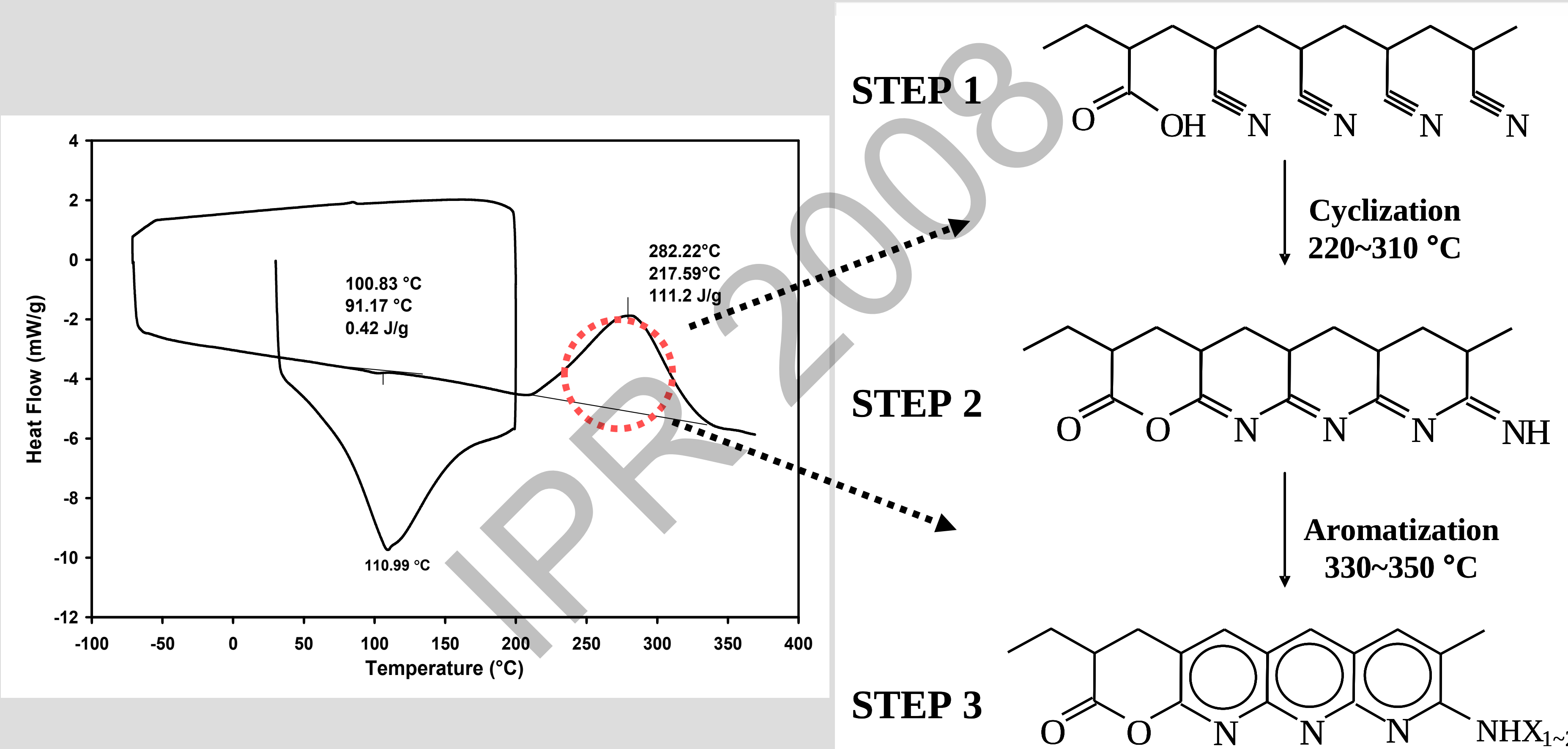
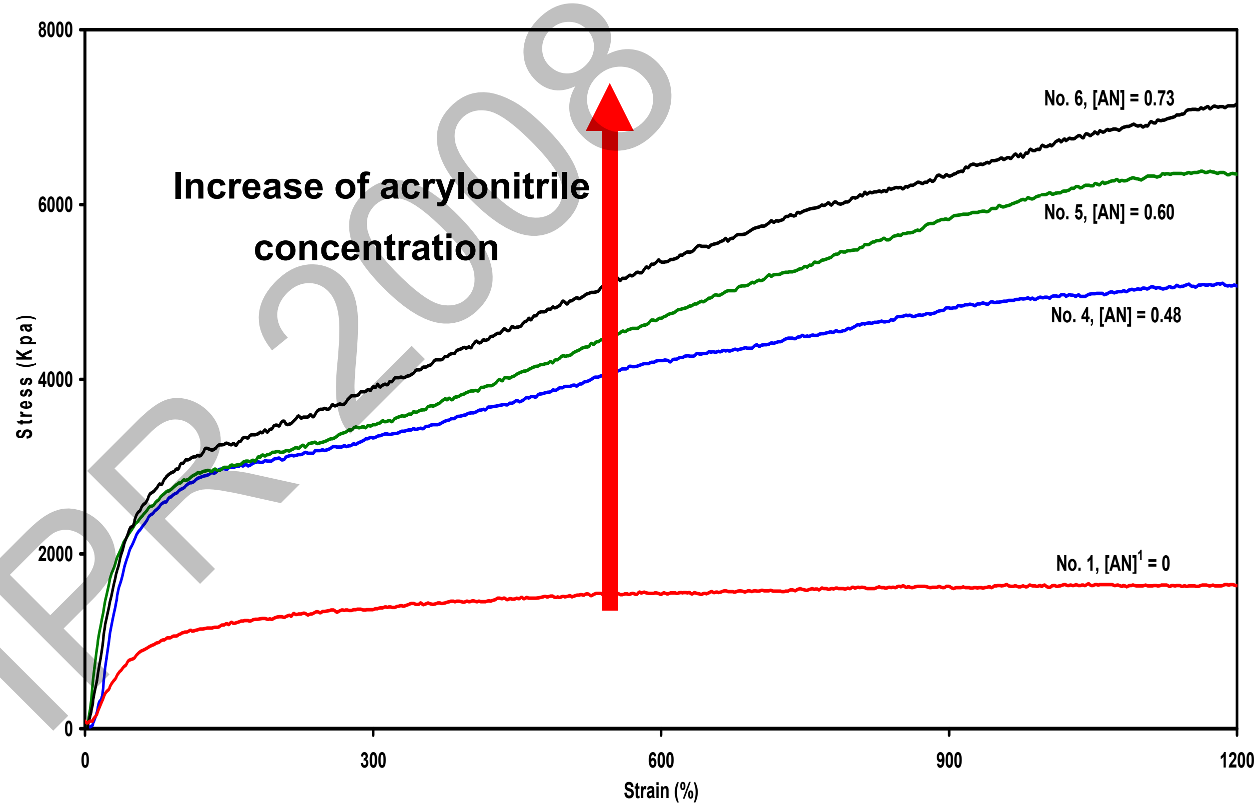


Figure 4-16. Proposed mechanism for cyclization and aromatization of nitrile and acid groups during thermal treatment of ethylene/acrylonitrile copolymers.

Stress-Strain Curves of Ethylene/Acrylonitrile Copolymer

- **Stress-Strain Curves ;**
  Tensile properties are increased as the increase of initial loading of acrylonitrile concentrations



•**Sample Dimension : width- 6.5 mm, Height - 0.2 mm, Pressed film**
•**[AN] ; mol/L**

Conclusion

- **Successful synthesis of Ethylene/acrylonitrile copolymer.**
- **Presence of PAN structure was confirmed by**
  - **FT-IR, ^{1}H-NMR, ^{13}C-NMR**
- **Nano-phase distribution of PAN domains in PE matrix was observed by**
  - **TEM**
- **Improved physical properties were confirmed by**
  - **Tensile tests.**

Part 2: Ethylene In-Situ Polymerization with a Catalyst Supported on Clay Modified with Acrylonitrile

- Intercalation and exfoliation of clay with acrylonitrile.

- In-situ copolymerization of ethylene and acrylonitrile on the clay surface.

- Strong interfacial interaction between clay surface and PE matrices through introduction of chemical bonds.

- Enhanced mechanical properties with PE-acrylonitrile/clay polymer composite.

Commercial Applications

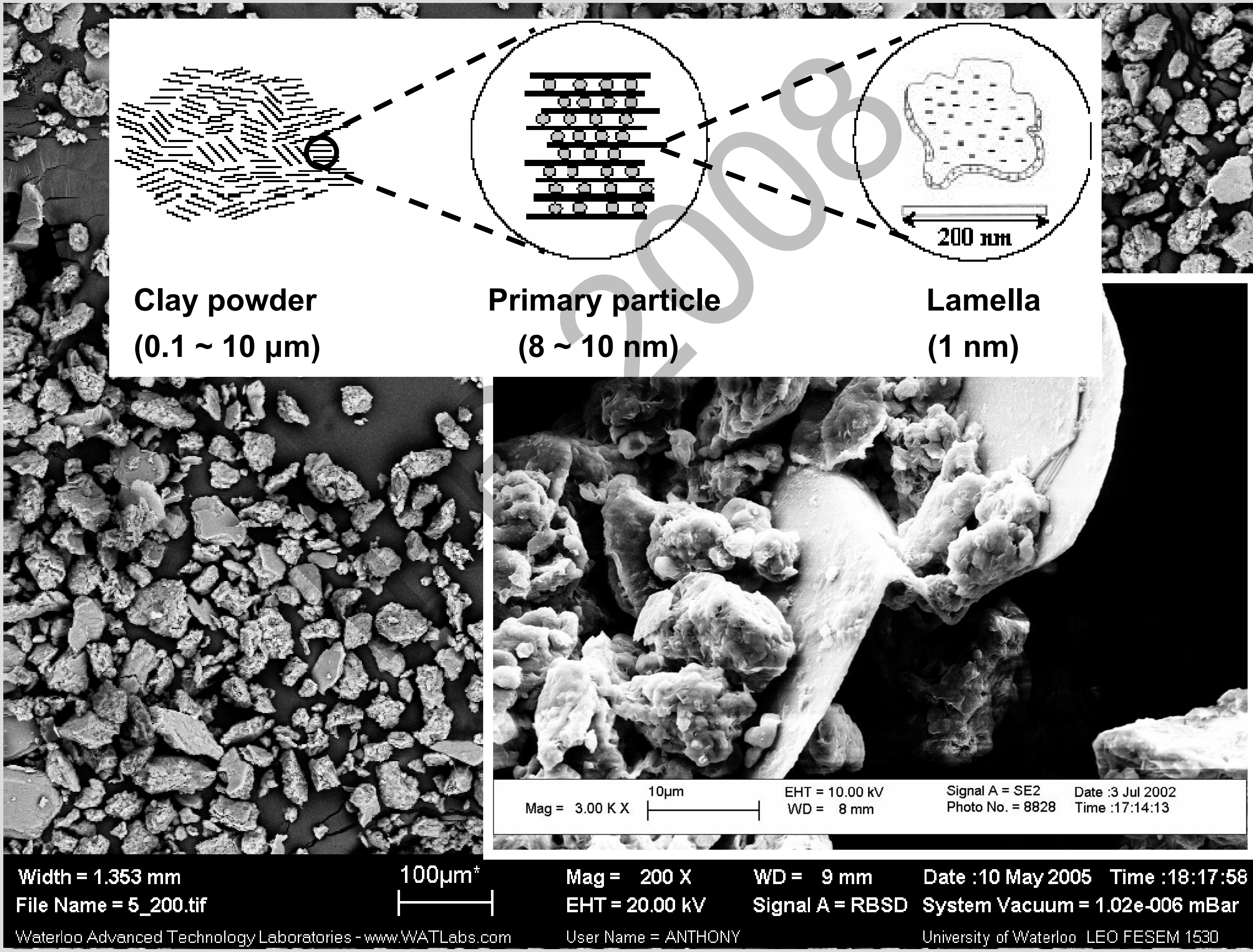
Clay Nanocomposites

- **Timing belt covers of automotive engines**
  - **Standard is glass fiber reinforced nylon or PP**
  - **Injection molded nylon 6 nanocomposite used in Toyota's automotive engine parts**
  - **Exhibited good rigidity and excellent thermal stability with a 25% weight reduction**

- **Step- assists on vans/ trucks**
  - **Thermoplastic olefin (TPO) nanocomposite used on 2002 GM mid- size vans**
  - **Nanocomposites are stiffer, lighter, less brittle in cold temperatures and more easily recyclable**
  - **Cost the same as conventional TPOs, with no new tooling required**

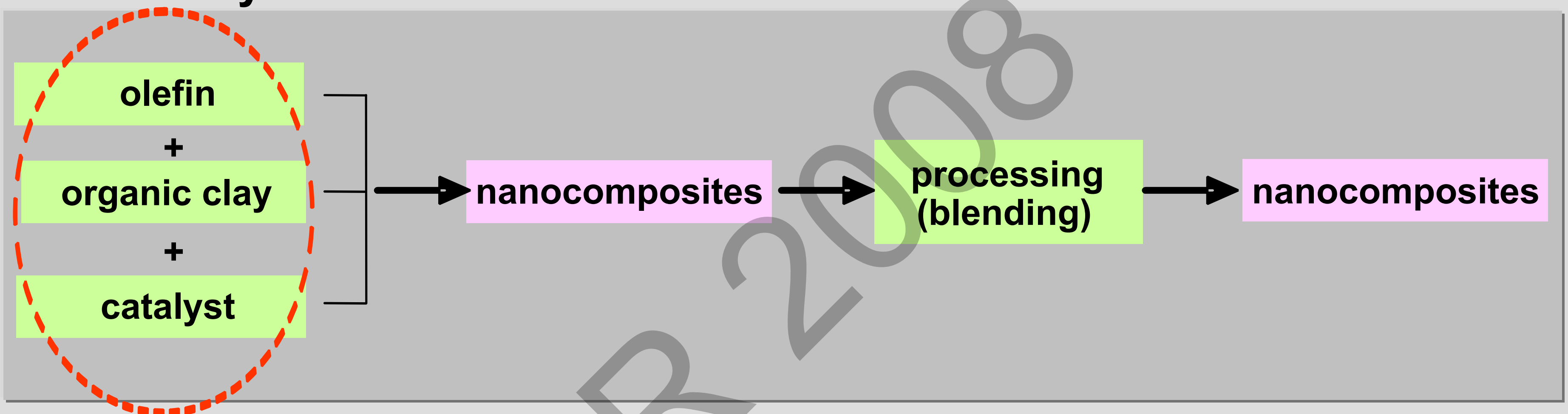
- **Nylon-clay nanocomposite bottles**

Morphology of Clays



In-Situ Polymerization of Ethylene and Clay

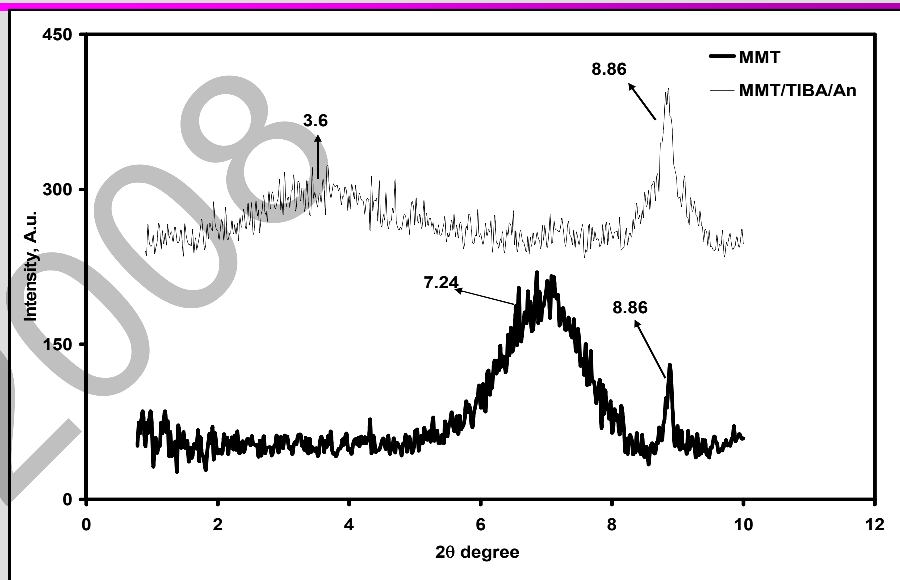
In-Situ Polymerization



Modification of Clay with Acrylonitrile

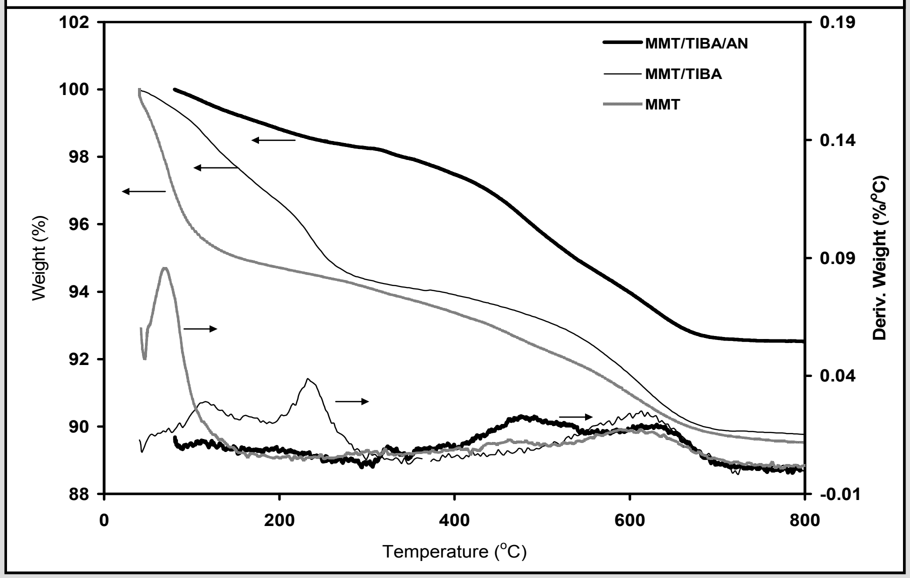
Small angle X-ray

diffraction patterns for MMT and MMT/TIBA/AN.



TGA and DTG

(derivative weight loss) curves of MMT, MMT/TIBA and MMT/TIBA/AN samples.



Functional Groups in PE, PE-MMT/TIBA/AN, Clay Residue

- **Clay Residue**

  (After Soxhlet extraction;

  PE-MMT/TIBA/AN)

- **PE-MMT/TIBA/AN**

  (sample 2)

- **Polyethylene**

  (sample 1)

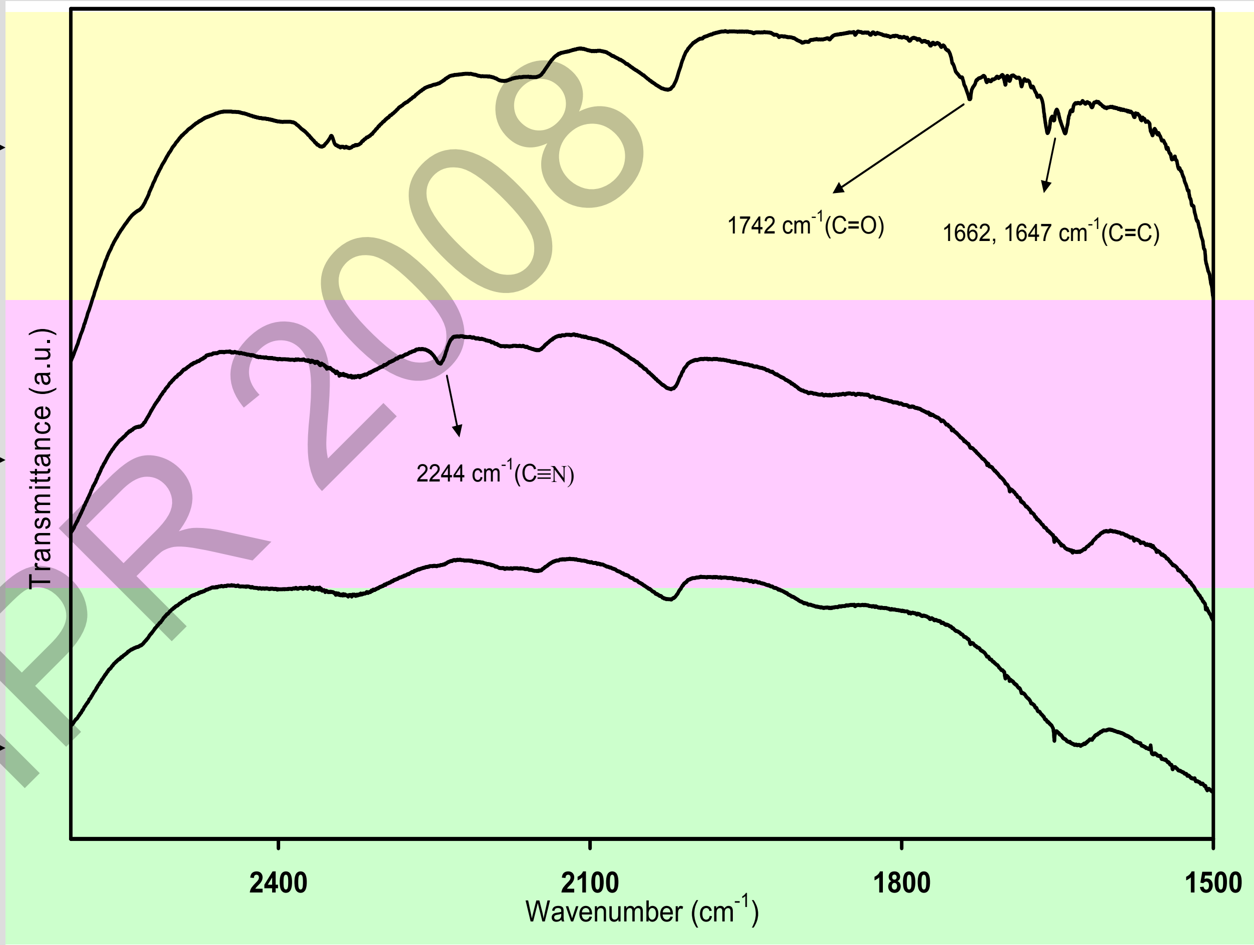
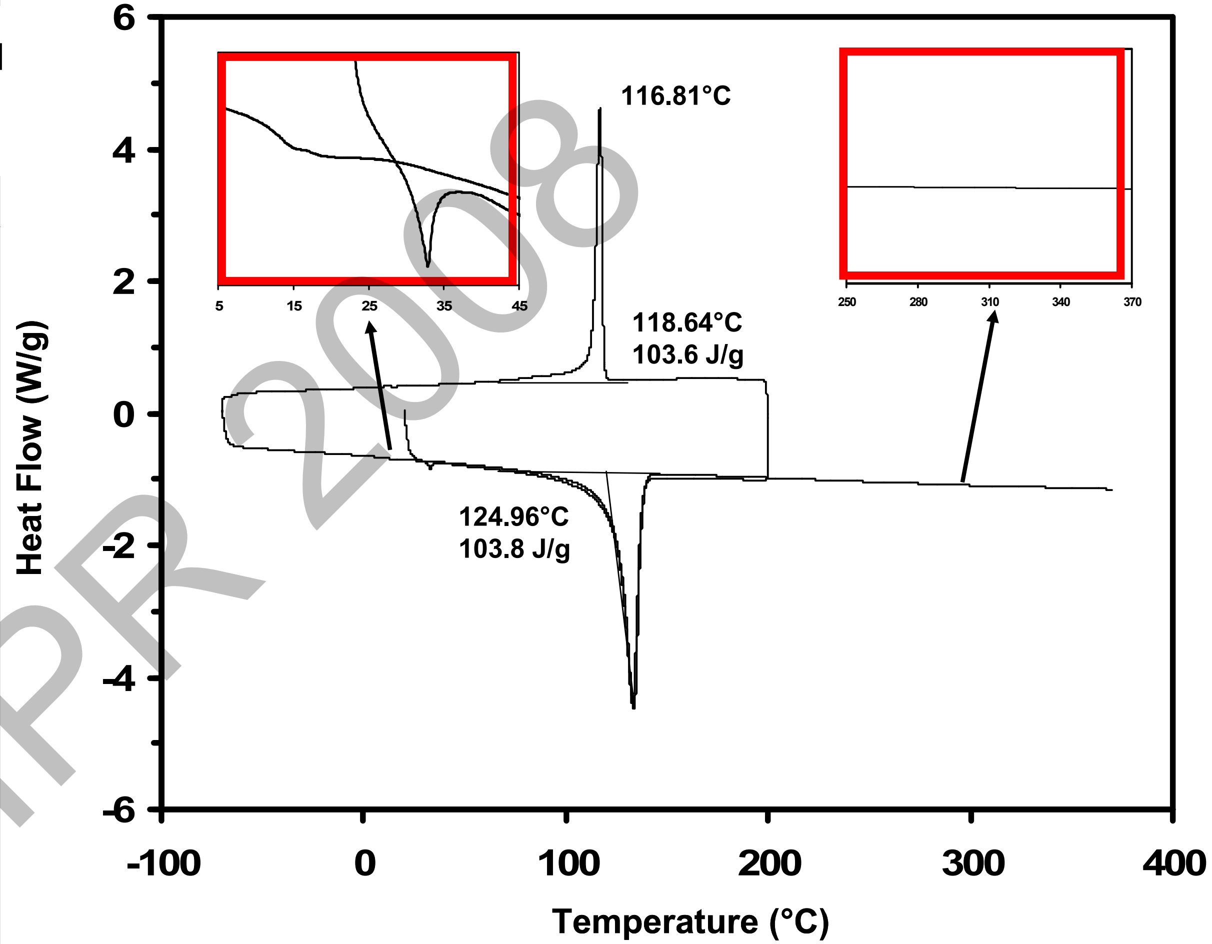


Figure 5-2. FT-IR spectra for the comparison of functional groups between 1500 cm^{-1} and 2700 cm^{-1}:

Thermal Behavior of PE-MMT/TIBA/AN

- **DSC Curves**; PE-MMT/TIBA/AN (sample 6); 2nd DSC thermogram



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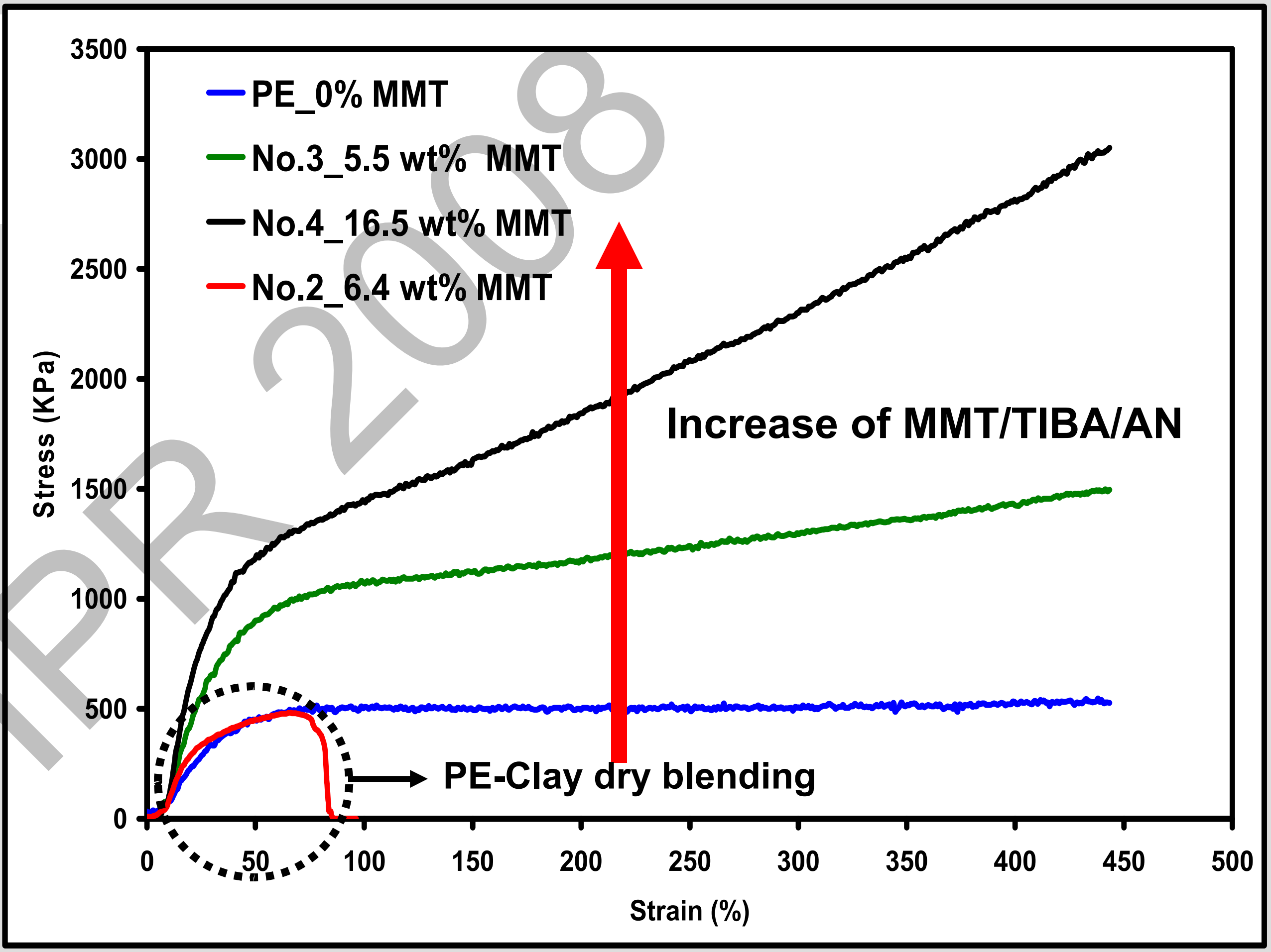
Tensile Properties of PE-MMT/TIBA/AN Composite

Stress-strain curves

• Tensile properties are increased as MMT content increase



Conclusions

- Excellent intercalation and exfoliation of clay particles with acrylonitrile monomer.
- Strong interfacial interaction between polyethylene matrices and clay surface.
- Developed a new synthetic method; in- situ copolymerization of ethylene and acrylonitrile.
- Enhanced mechanical properties in polyethylene-acrylonitrile clay composite.

Contributions

➢ Scientific

- Synthesized ethylene-acrylonitrile copolymer.
- Introduced interfacial interaction between polyethylene matrices and clay surface with acrylonitrile modification.

➢ Industry

- Developed a new synthetic method: in-situ copolymerization of ethylene and modified clay with bifunctional molecules.

➢ Society

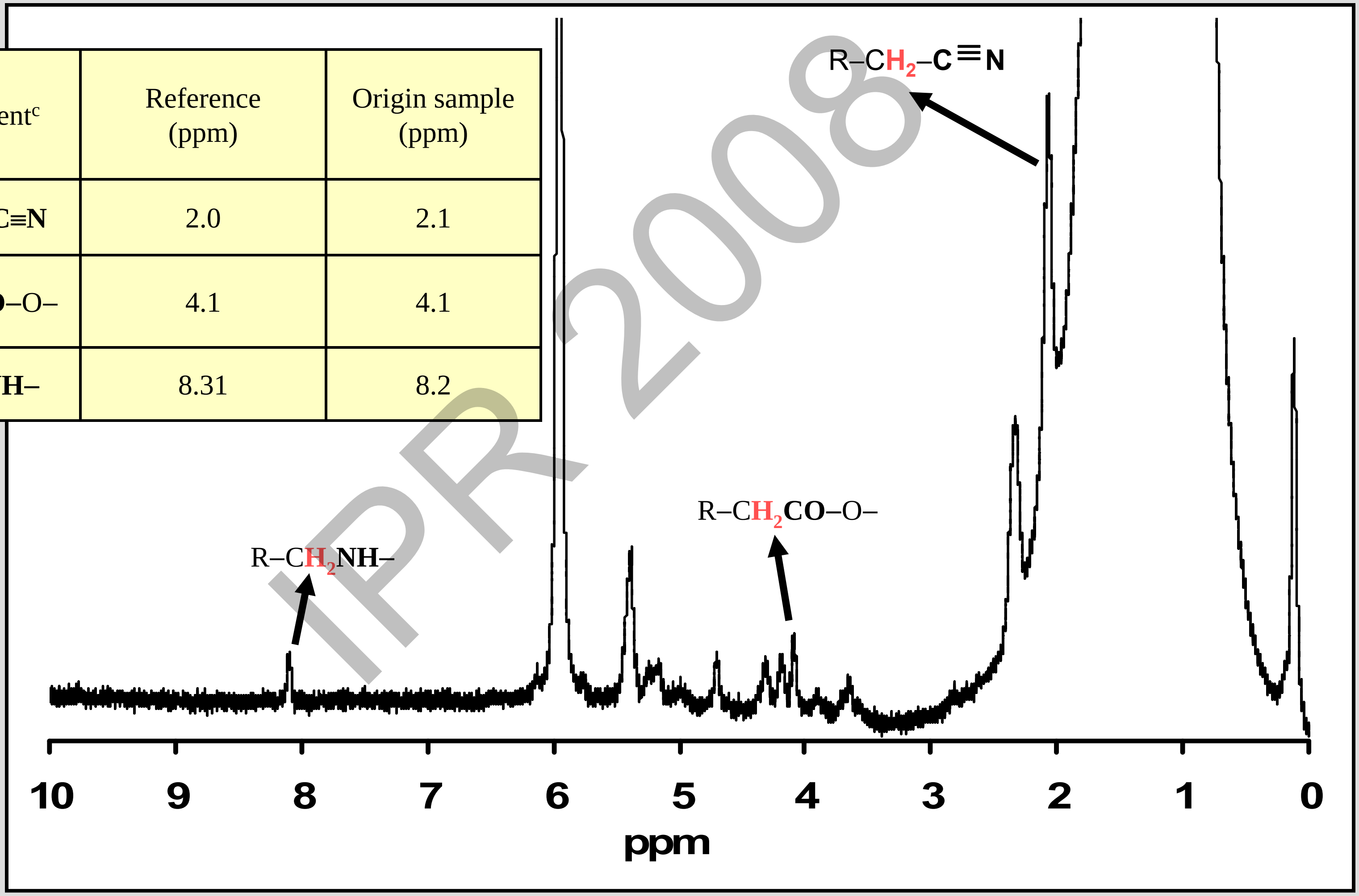
- Provided new knowledge for PE-Clay hybrid nanocomposites.

Acknowledgements *Thank you!*

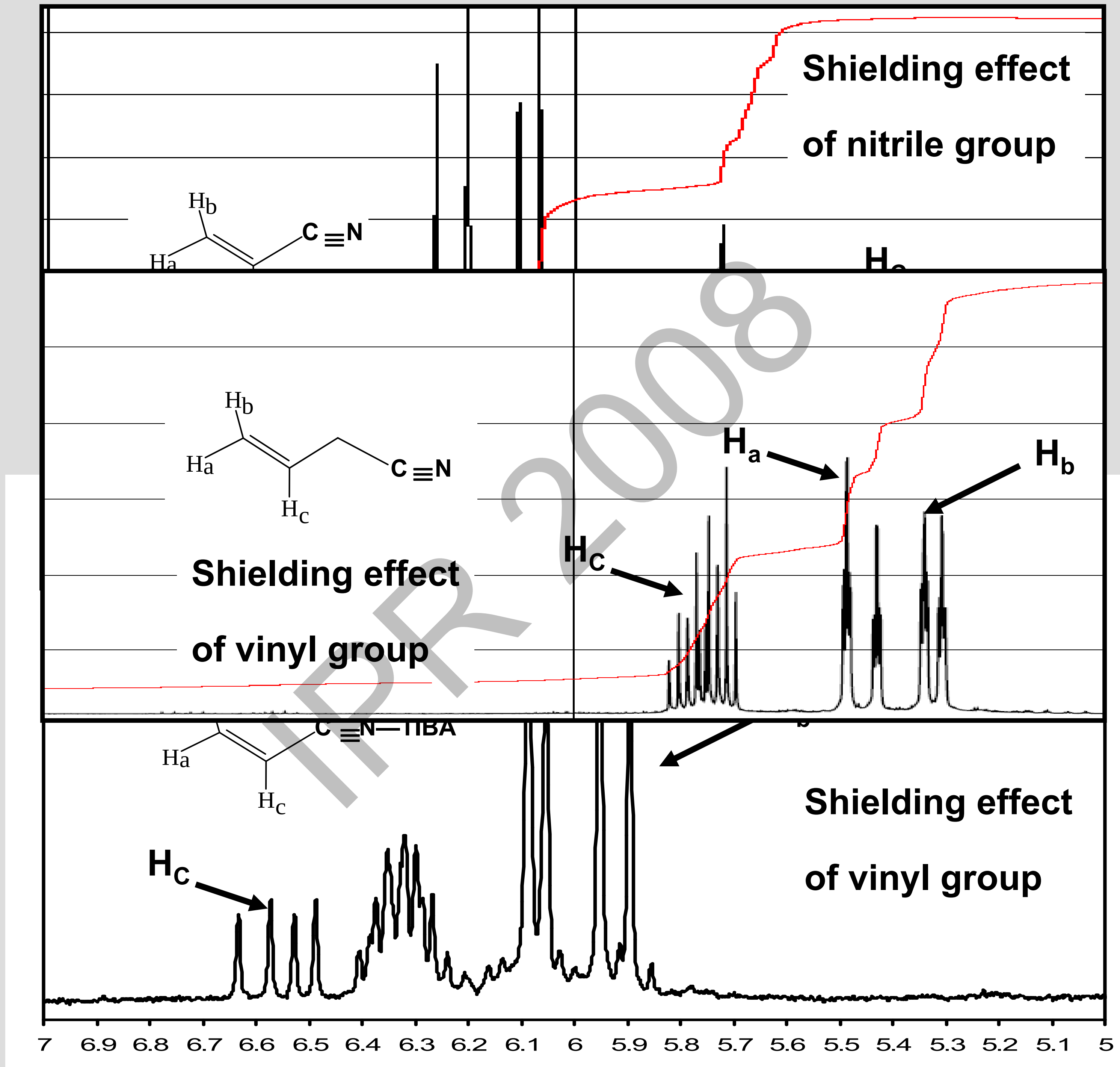
- **Prof. Joao Soares and Prof. Leonardo Simon**
- **Financial support from**
  - **NSERC**
- **Collaborators**
  - **Prof. Gunter Scholz (X-Ray and TEM)**

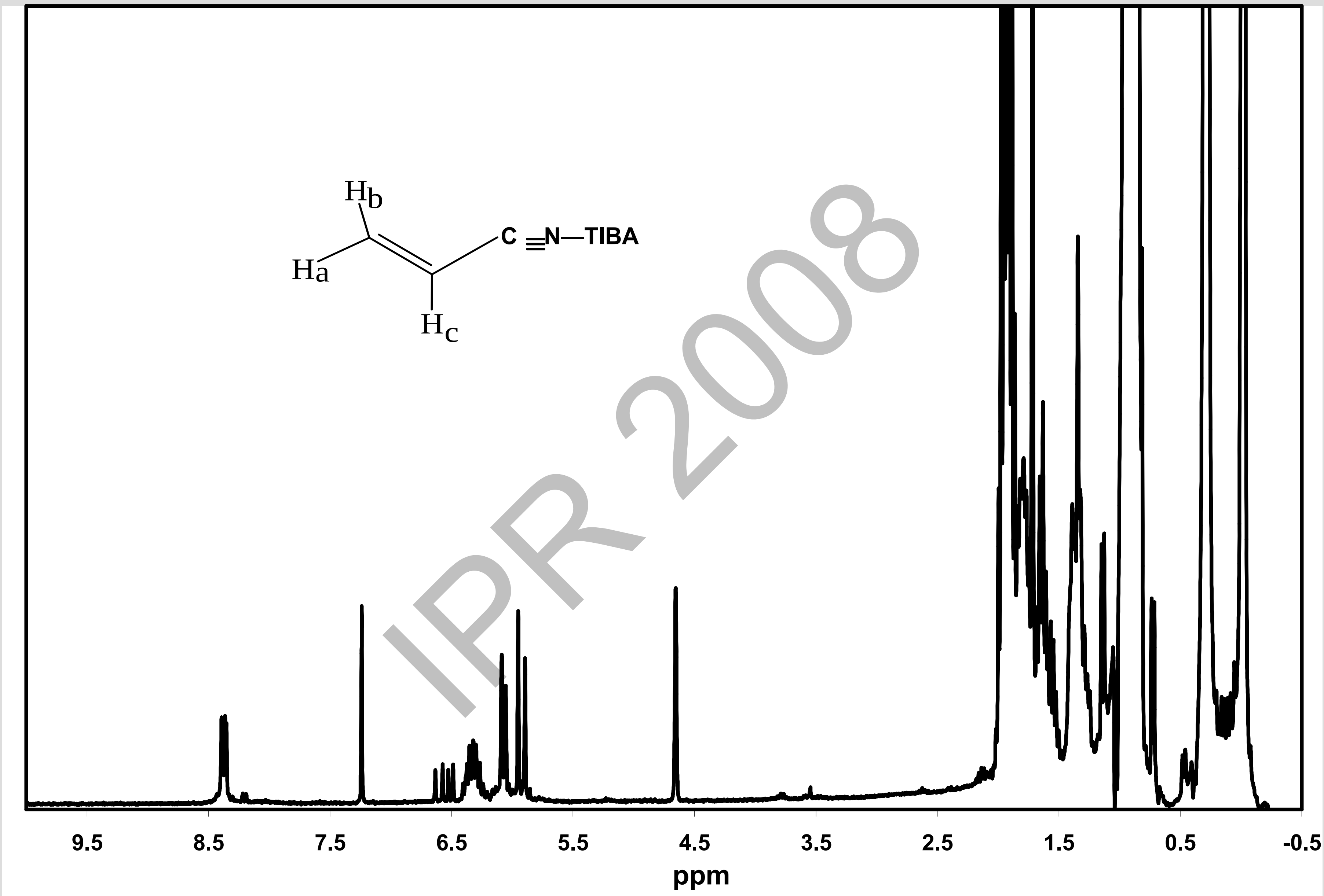
Functional Groups in Ethylene/acrylonitrile Copolymer

No.	Assignment[c]	Reference (ppm)	Origin sample (ppm)
1	R–CH_2–C≡N	2.0	2.1
2	R–CH_2CO–O–	4.1	4.1
3	R–CH_2NH–	8.31	8.2



^{1}H NMR spectrum of ethylene/acrylonitrile copolymer (No. 6 in Table 1.)


Shielding effect
of nitrile group
Hb
Ha
C≡N
Hb
Ha
Hc
C≡N
Shielding effect
of vinyl group
Ha
Hb
Hc
Ha
Hc
C≡N—TIBA
Hc
Shielding effect
of vinyl group
7 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5.2 5.1 5



Hb
Ha
Hc
C ≡N—TIBA
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
ppm