Structure-Fracture properties under impact conditions: Characterization techniques.

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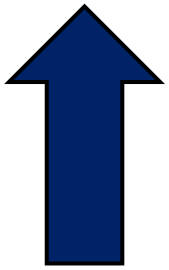
Introduction

Thermoplastic polymer materials + Nanofiller: Clays

Nanocomposites



Mechanical, thermal properties enhancement

¿?

What is the role of the clay in order to have an improvement in the composite?

Impact conditions

Introduction

- Degree of cristallinity.
- Spherulites size.
- Lammela thickness.
- Particle-matrix interface. Strength of interfacial interactions
- Morphology: intercalation or exfoliation.
- Microvoids coalescence.
- Dispersion of the nanofillers on the polymer matrix.
- Fracture surface.

Factors that influence mechanical behaviour Impact conditions

General objective

Characterize a polymer nanocomposite material focused on the structural factors that influence its fracture mechanical behavior under impact conditions.

Specific objectives

1. Analyze the morphology and distribution of nanoclays in the polymer matrix by the used of X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM).

2. Determine surface interaction between polymer chains and clay through an analysis of bonding/interface using Fourier Transform Infrared Radiation (FT-IR).

Specific objectives

3. Estimate degree of crystallinity and size of the spherulites of the nanocomposite by using Differential Scanning Calorimetry (DSC).

4. Analyze the fracture surface of the sample in order to identify fractured zones defined by crack propagation. This is achieved by using Scanning Electronic Microscopy (SEM).

5. Make a Dynamic Mechanical Analysis (DMA) to define the principal viscoelastic parameters in order to estimate fracture properties by applying fracture mechanics approaches.

X-Ray Diffraction→Morphology

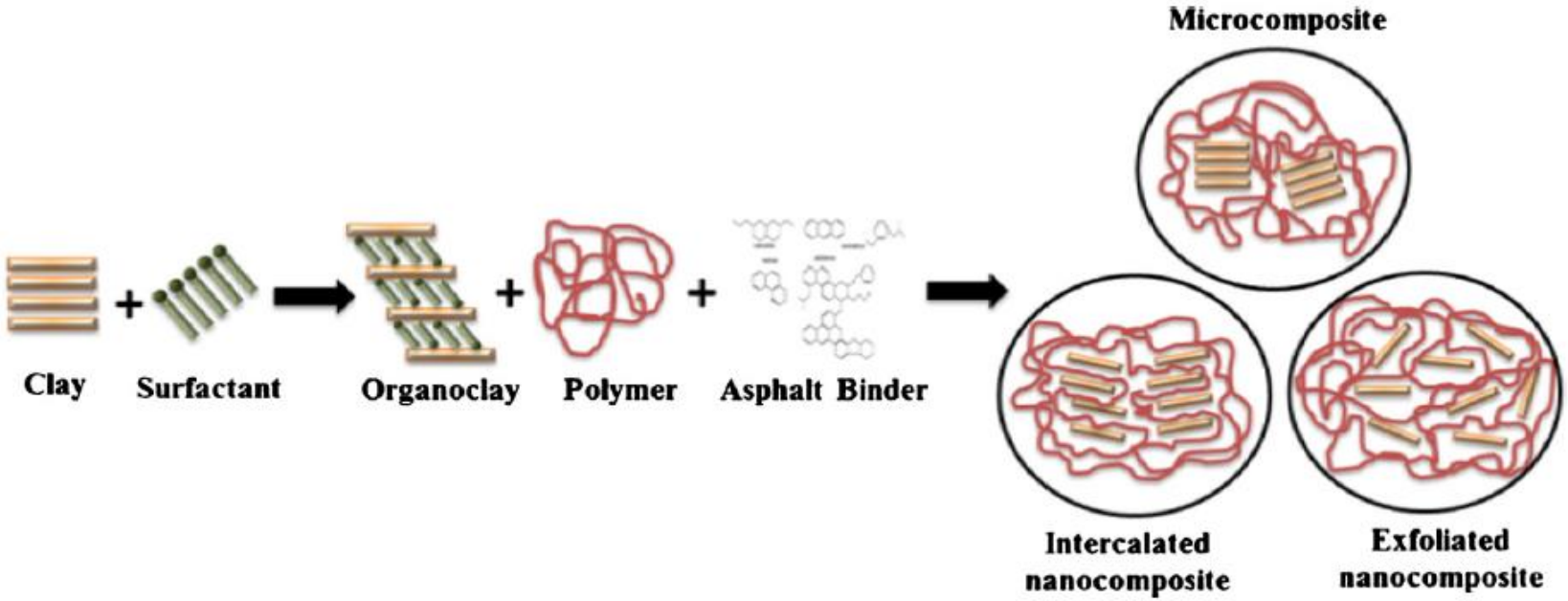


Figure 1. Schematically illustration of three different types of thermodynamically achievable polymer/layered silicate nanocomposites. Types of microstructures of polymer clay composites: a) microcomposites, b) intercalated nanocomposite, and c) exfoliated nanocomposite [].

X-Ray Diffraction → Morphology → Intercalated or exfoliated

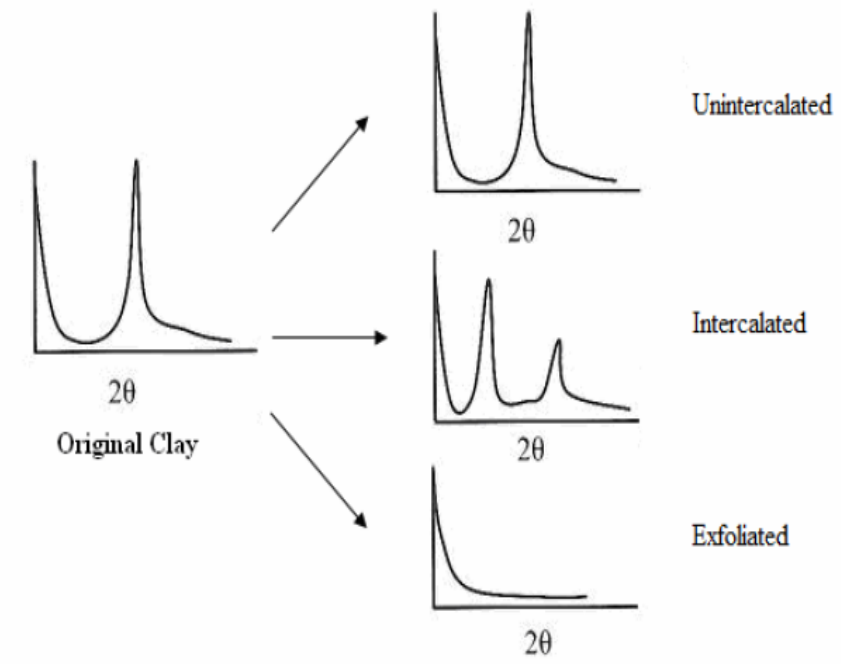


Figure 2. Schematic XRD patterns for different types of nanocoposites strctures [1].

X-Ray Diffraction []

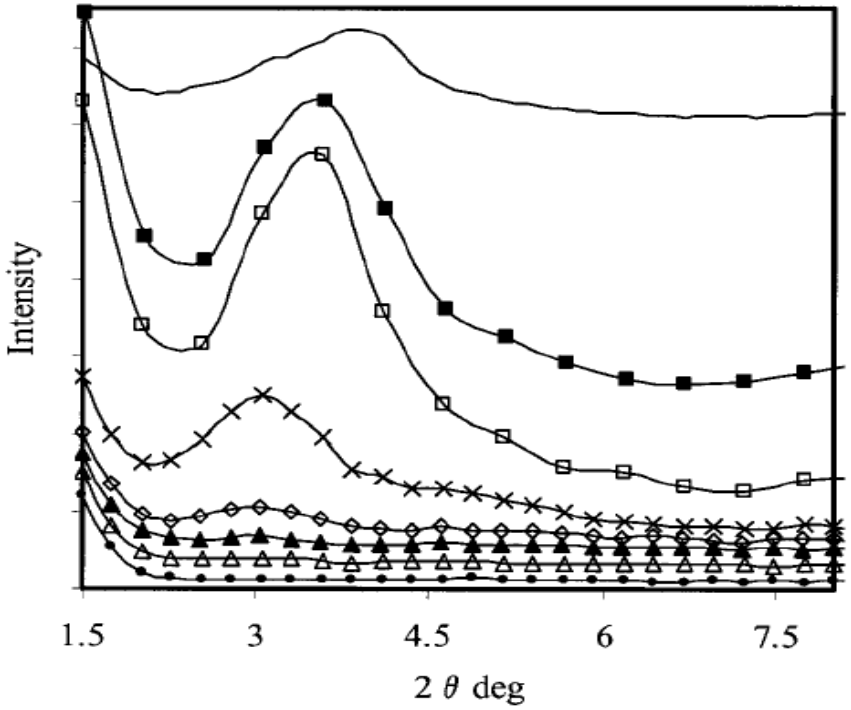


Figure 1 XRD data of the extrudates of nanoclay-filled PP containing (●) 0 wt %, (△) 5 wt %, (▲) 10 wt %, (◇) 20 wt %, (×) 30 wt %, (□) 40 wt %, (■) 50 wt %, and (—) 100 wt % clay.

Bragg's law

$$2d_{001} \sin\theta = n\gamma$$

where, d_{001}: spacing between the planes in the atomic lattice, θ: angle between the X-ray and the scattering planes, n: is an integer, and λ: the wavelength of X-ray wave.

How the sample is prepared?

Samples could be prepared by mounting and pressing the clays into an aluminum holder (50x45x2mm) with a glass back support. Then sample could be hold in a diffractometer equipment.

TEM → Distributtion of clay plateles → Uniform disttribution []

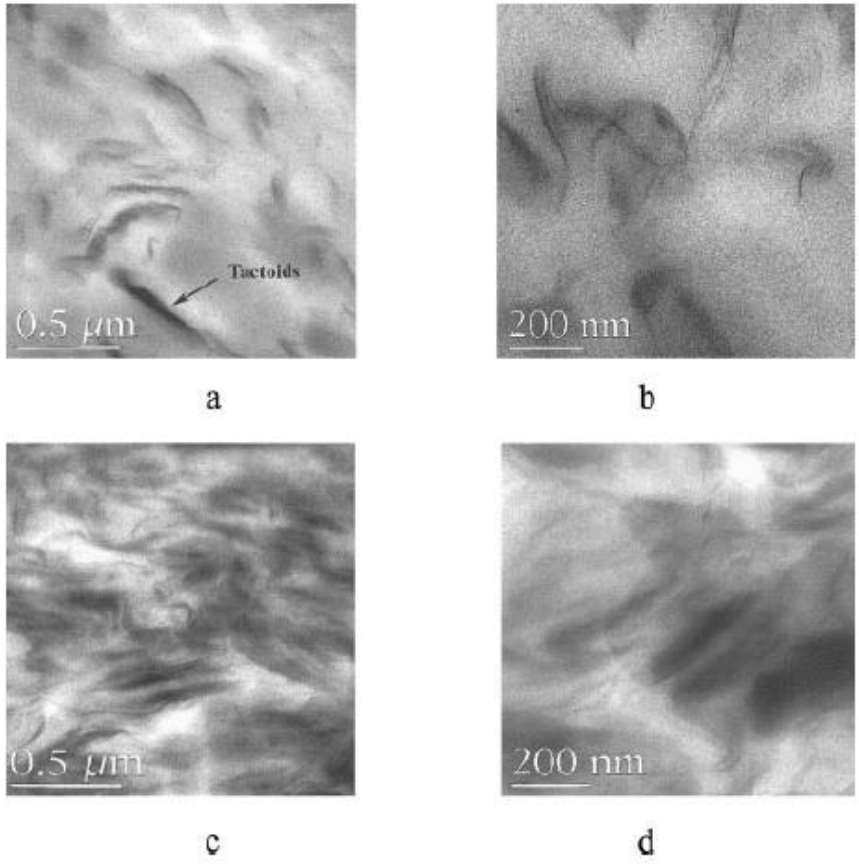


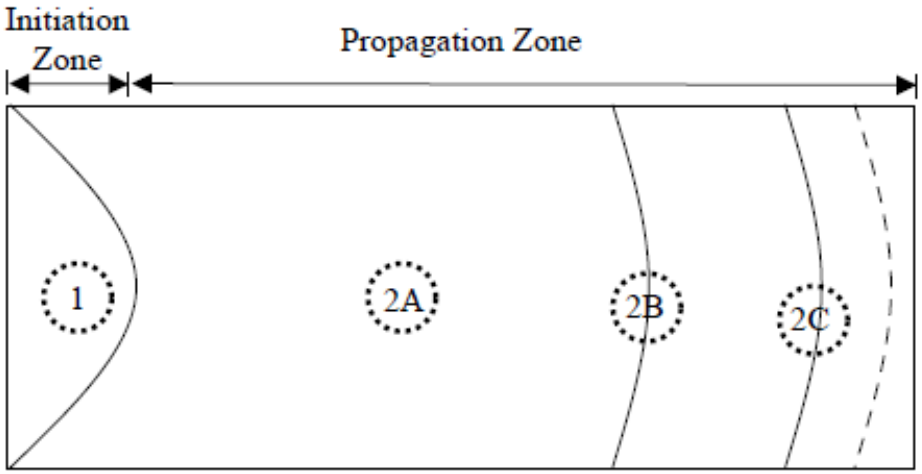
Figure 3 TEM photomicrographs of clay-filled PP containing (a) 10 wt % clay (low mag), (b) 10 wt % clay (high mag), (c) 50 wt % clay (low mag), and (d) 50 wt % clay (high mag).

How the sample is prepared?

For nanomaterials in the form of particles (or aggregates even of micrometer size) preparation is simple: disperse the material in a volatile solvent, place a few drops over a TEM grid, dry, and should be ready.

Sample preparation is specially important in TEM to ensure that "thin enough" samples can be observed. Thin enough is usually ≤100 nm, but for large atomic number elements a thinner sample may be preferable, and for lighter elements thicker samples may be used

SEM → Fracture surface analysis → Fracture zones and mechanisms



Zone	Fracture
1	Initiation zone
2 A	Brittle-like
2 B	Less brittle-like
2 C	Stick-slip
2 D	Slow shear zone
2 E	Rapid shear zone

SEM

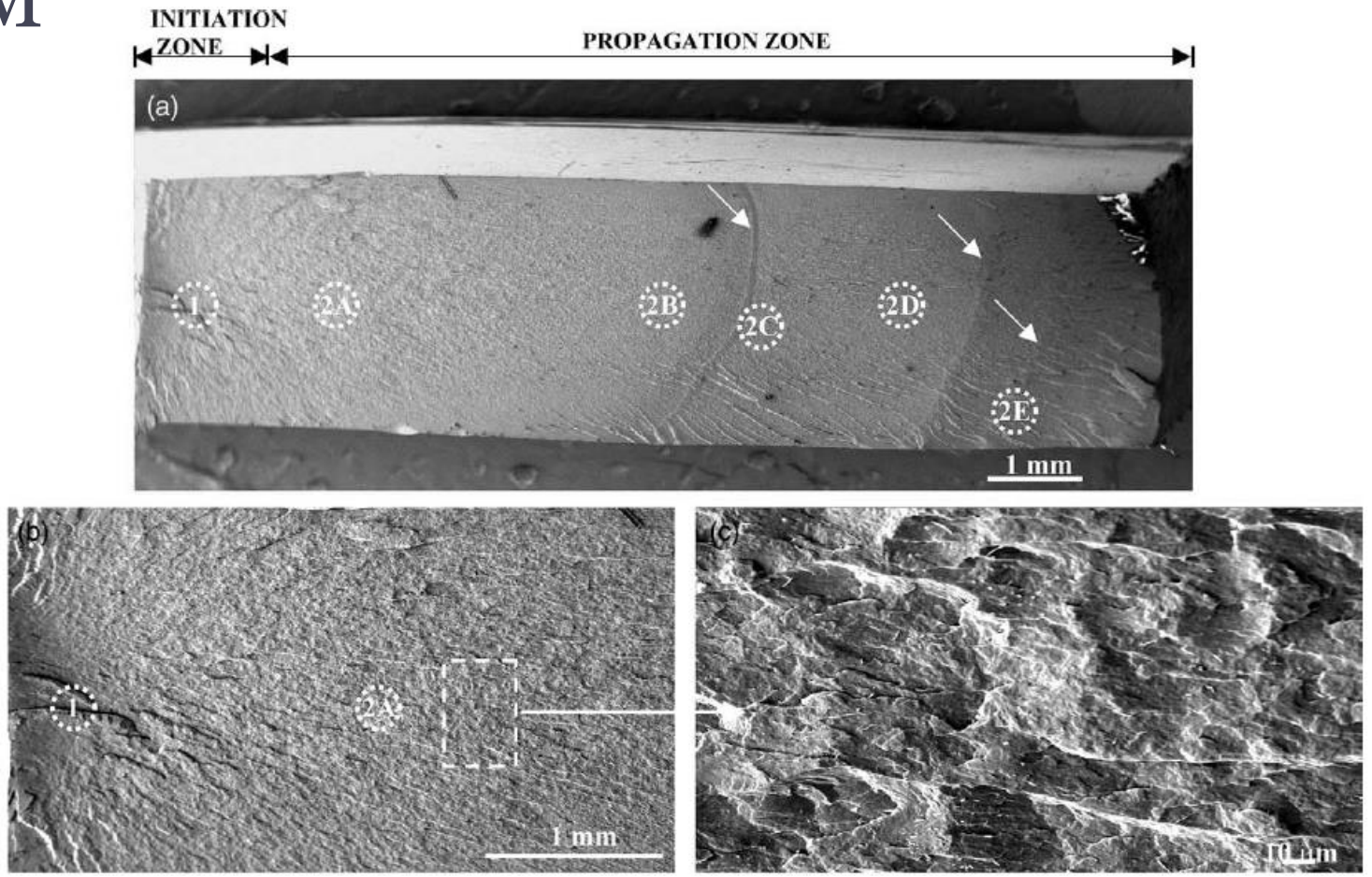


Figure. SEM of the fracture surface of neat PP impacted tested at 20 °C showing initiation differentvpropagation zones (zone 2A: brittle-like; 2B: less brittle-like zone with small vein-type features; zone 2C: stick-slip; zone 2D: slow shear zone and zone 2E:vrapid shear zone) at different magnifications.

SEM

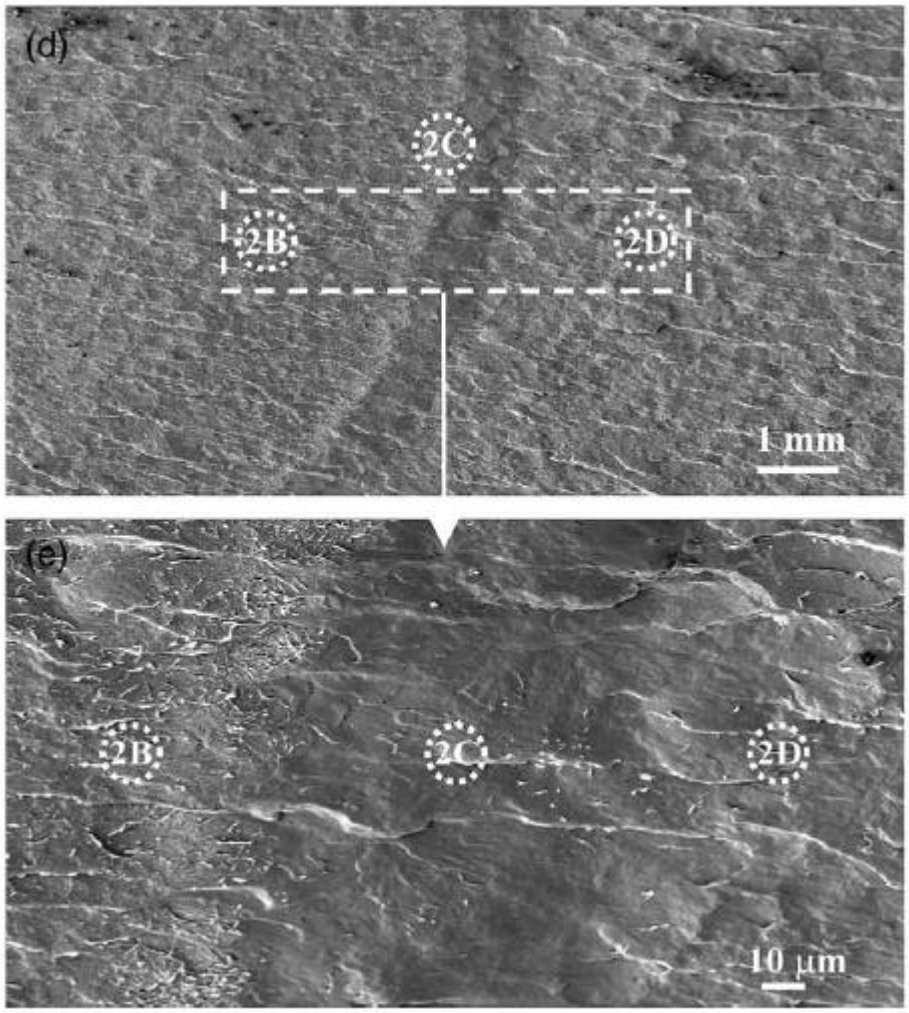
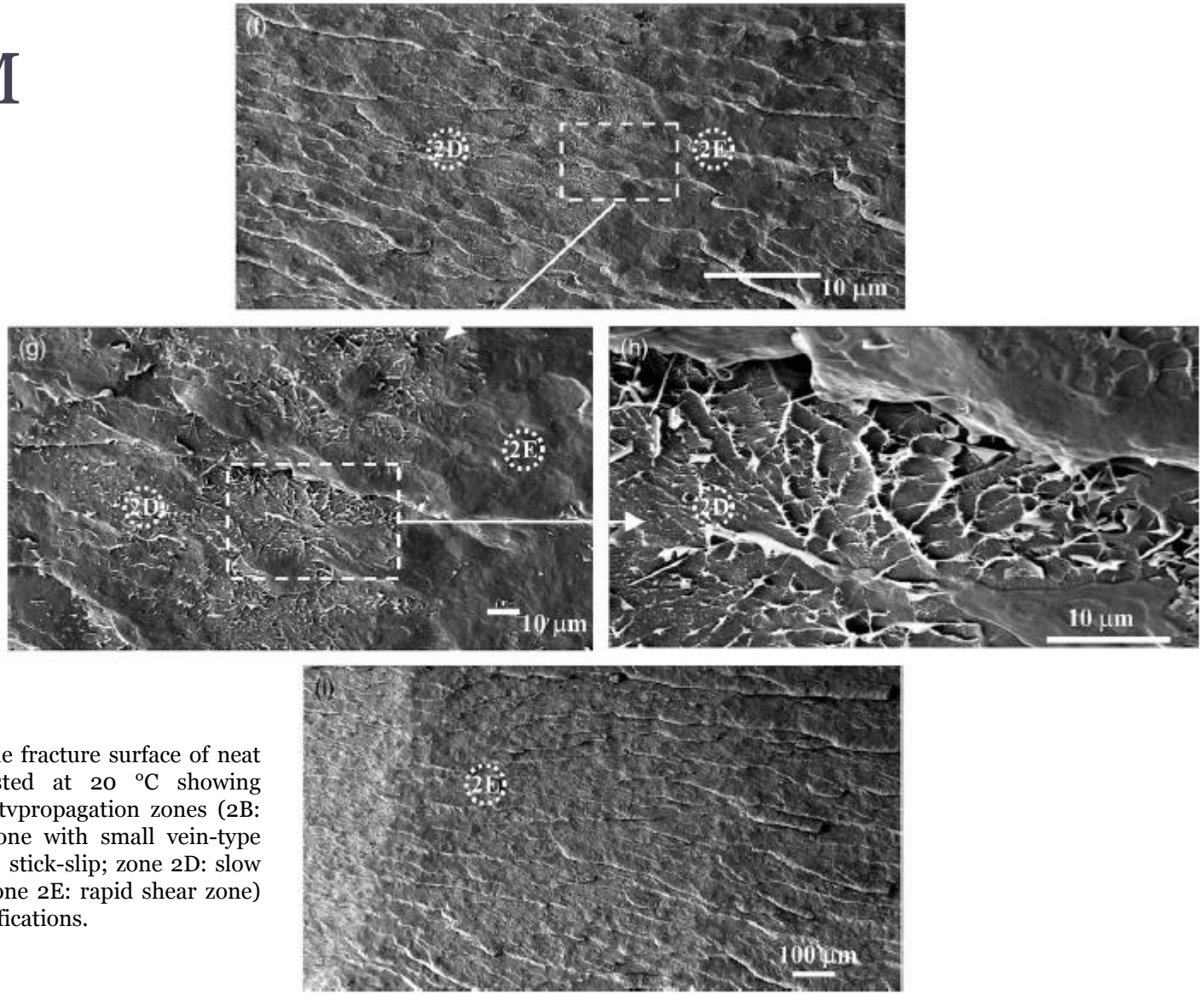


Figure. SEM of the fracture surface of neat PP impacted tested at 20 °C showing initiation differentvpropagation zones (2B: less brittle-like zone with small vein-type features; zone 2C: stick-slip; zone 2D: slow shear zone and zone 2E: rapid shear zone) at different magnifications.

SEM



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SEM

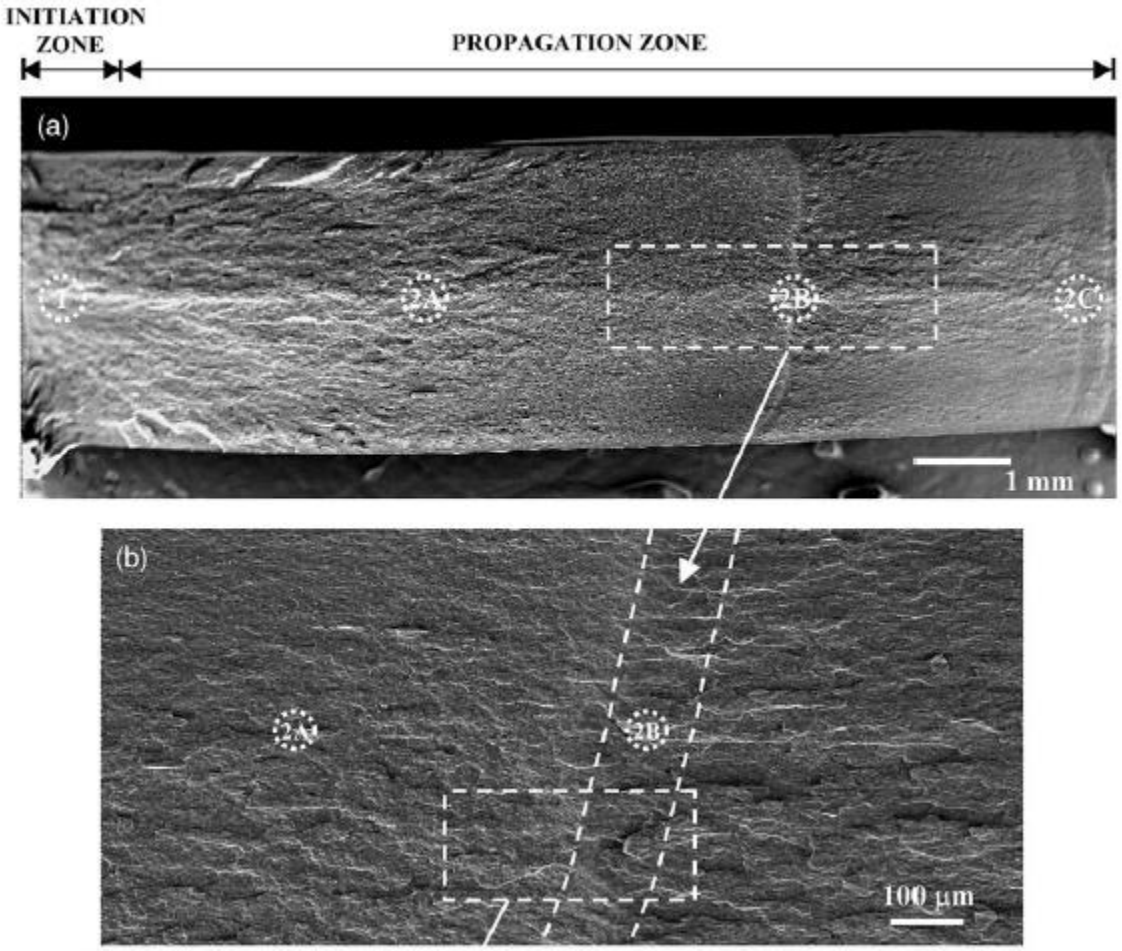
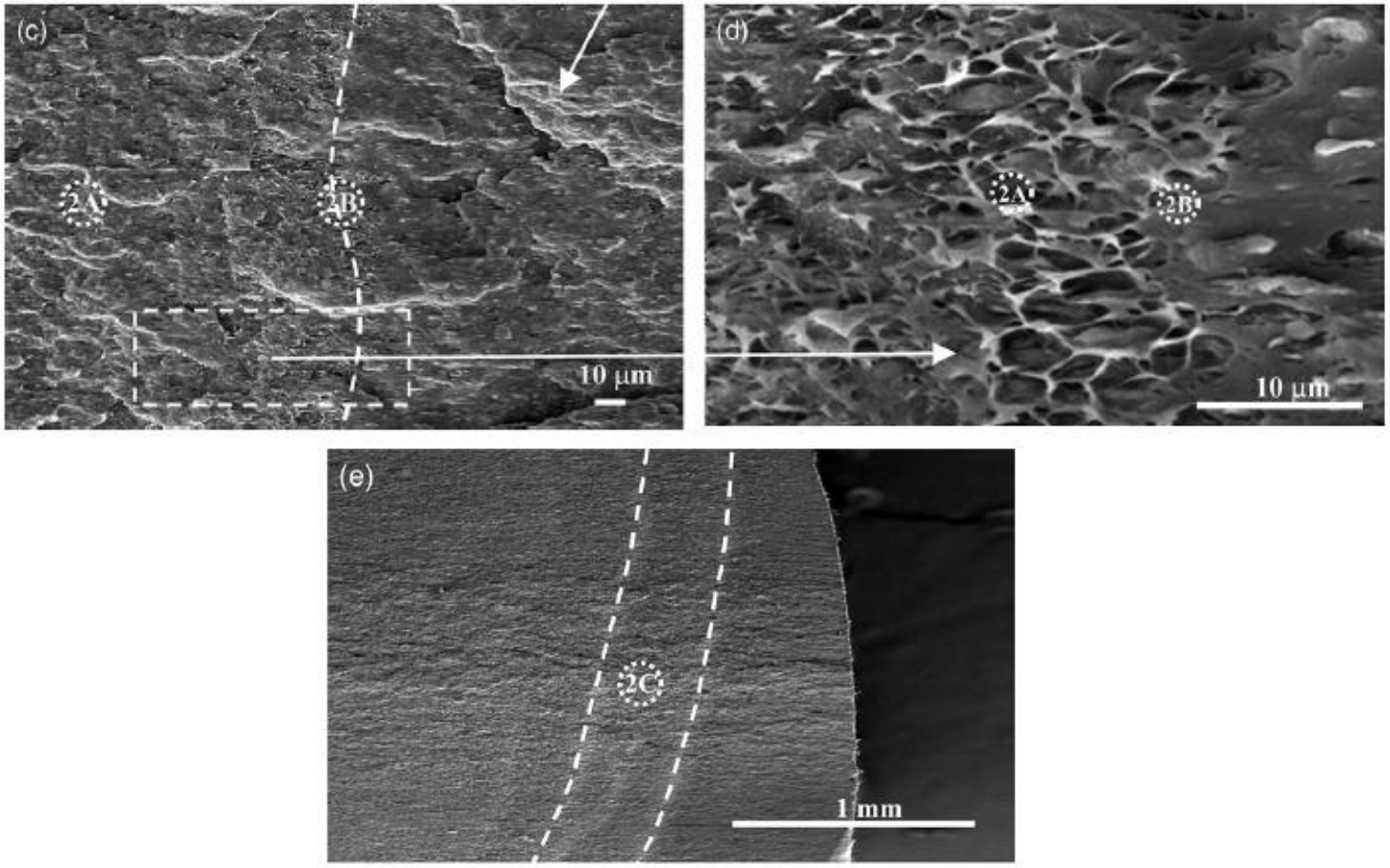


Figure. SEM of the fracture surface of PP-4 wt% clay nanocomposite impacted tested at 20°C showing initiation (zone 1) and propagation zone (zone 2). Similar behavior was observed at other temperatures.

SEM



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SEM

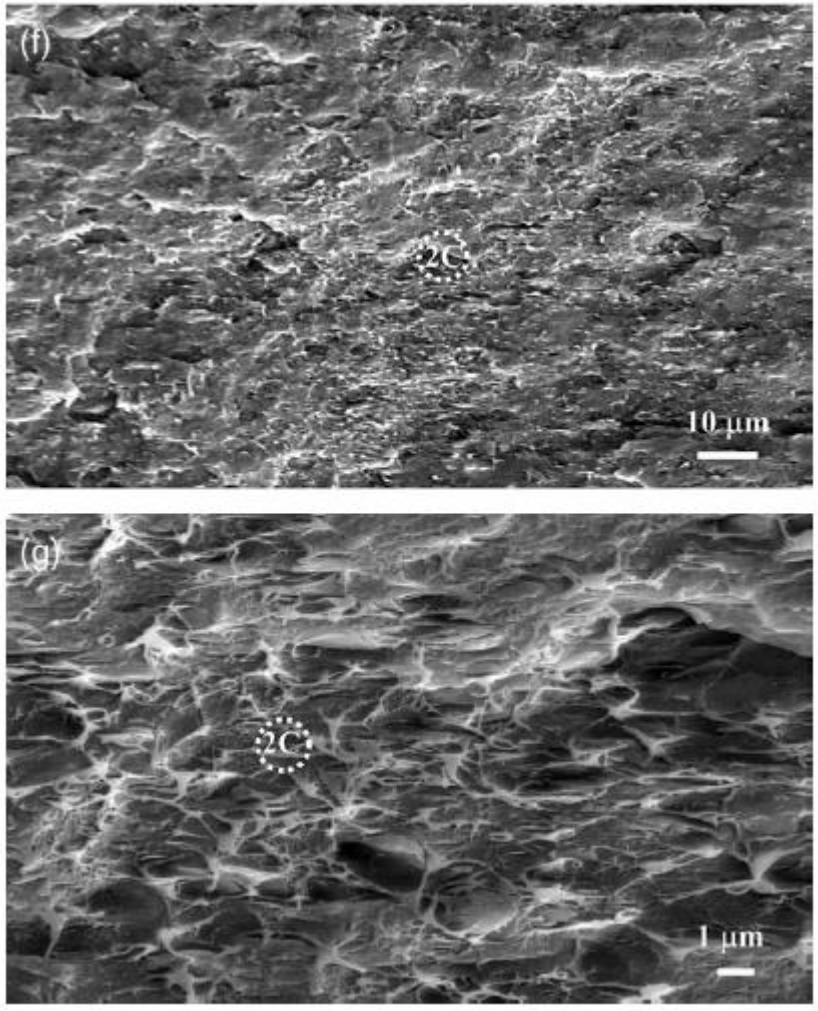


Figure. SEM of the fracture surface of PP-4 wt% clay nanocomposite impacted tested at 20°C showing initiation (zone 1) and propagation zone (zone 2). Similar behavior was observed at other temperatures.

How the sample is prepared?

Non-conducting samples may require thin conducting coating to prevent charging during observation. Gold coating may increase emission of SE and thus increase resolution for some features.
Samples must be firmly mounted and affixed to sample holder

DSC → Crystallinity → Glass transition temperature

The value of heat of fusion, measured by DSC method, is commonly used to calculate the degree of crystallinity

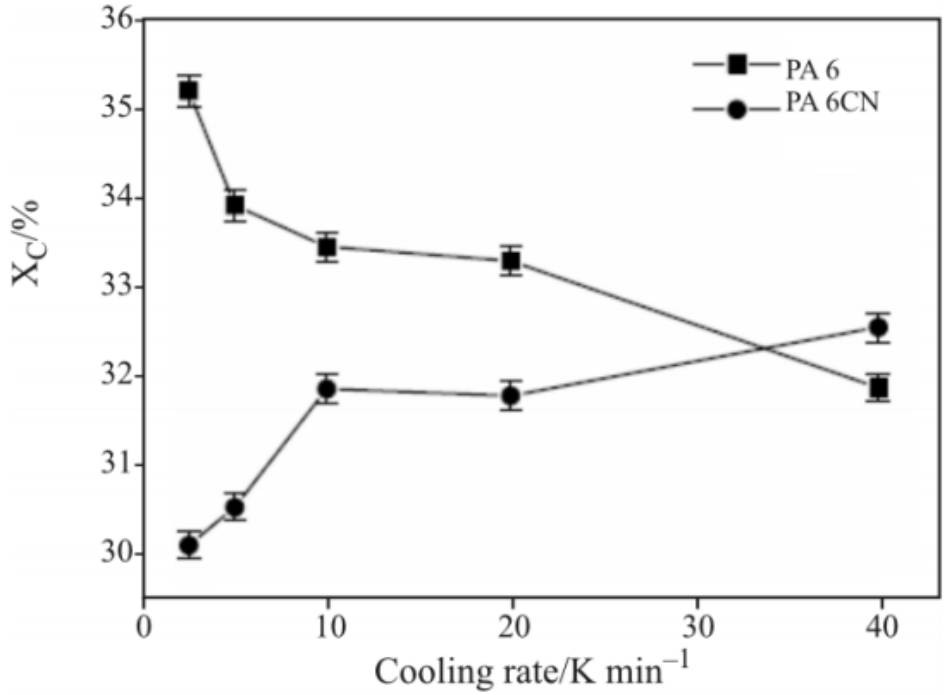


Fig. 2 Crystallinity degree of PA6 and PA6/CN at various cooling rates [7]

DSC → Crystallinity → Glass transition temperature

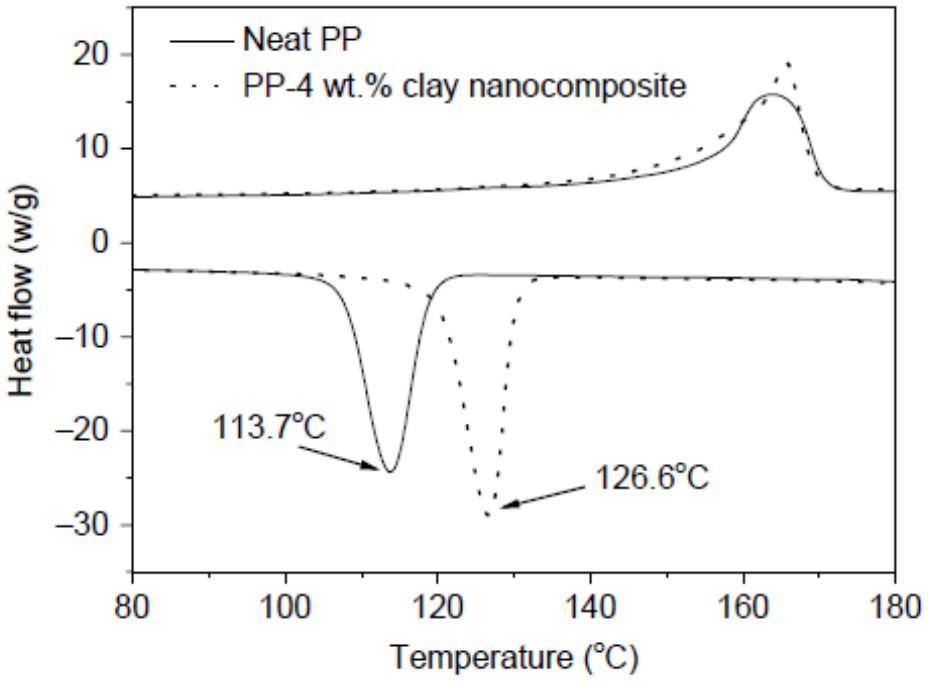


Fig. 2. Differential scanning calorimetry plots for neat PP and 4 wt% clay–reinforced PP nanocomposite.

Table 1
Physical and mechanical properties of neat PP and PP-4 wt% clay nanocomposites

Material	Neat-PP	PP-4 wt% clay
Heat of fusion (J/g)[a]	95	97
%Crystallinity (DSC)[a]	45	46
Crystallization temperature (°C)	114	127
Melting temperature (°C)	164	166
Lamellar thickness (nm)	5.32	5.82
Average spherulite size (μm)	210	14
Storage modulus at 25 °C (GPa)	2.2	3.3
T_g (°C)	9.2	10.0
Young's modulus (GPa)	0.54	0.83
Yield stress (MPa)[b]	33	38

[a] For 100% polymer.
[b] Engineering stress related to initial sample cross-section.

DSC

$$l = \frac{2\gamma T_m^0}{\Delta H_0 \rho (T_m^0 - T_m)}$$

Thompson-Gibbs equation.

where T_m^0 is the equilibrium melting temperature, T_m is the detected melting temperature by DSC, γ the surface free energy, ΔH_0 the heat of fusion for 100% crystalline PP, and ρ the density.

DSC

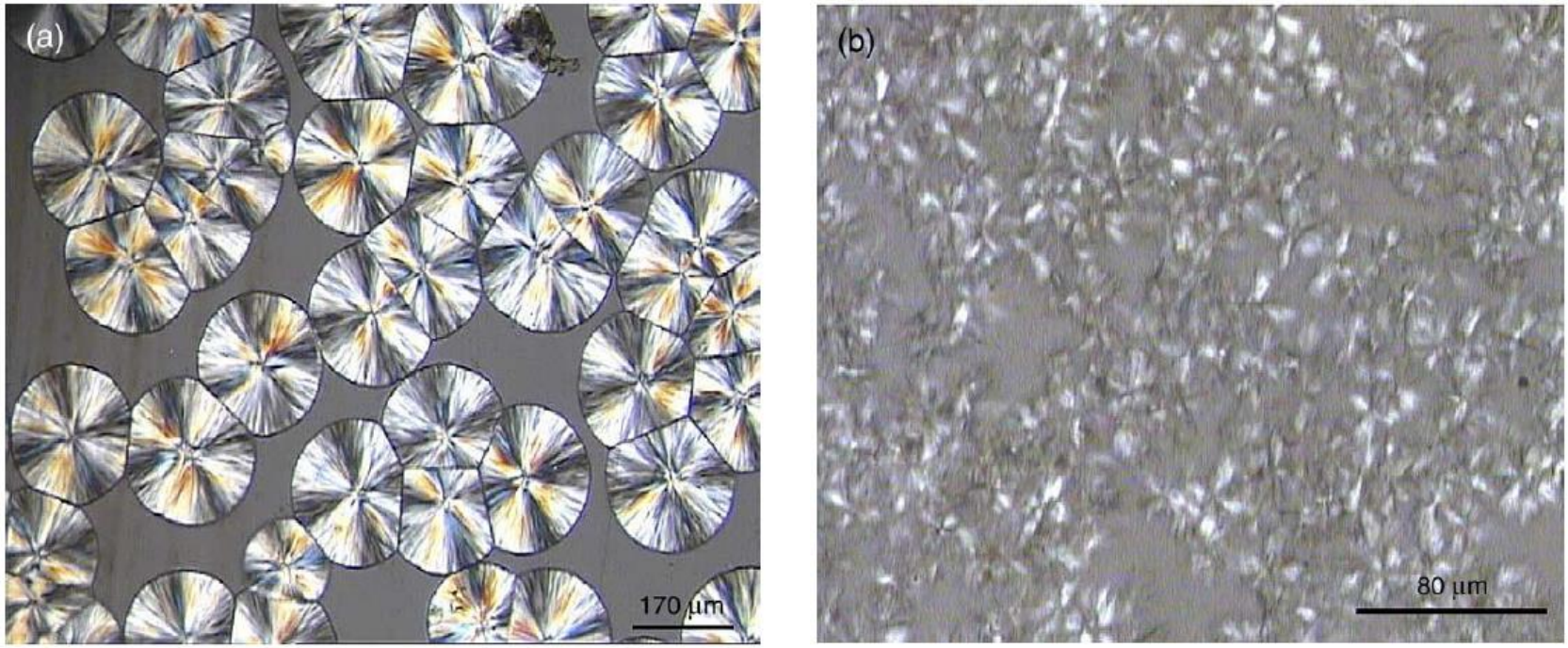
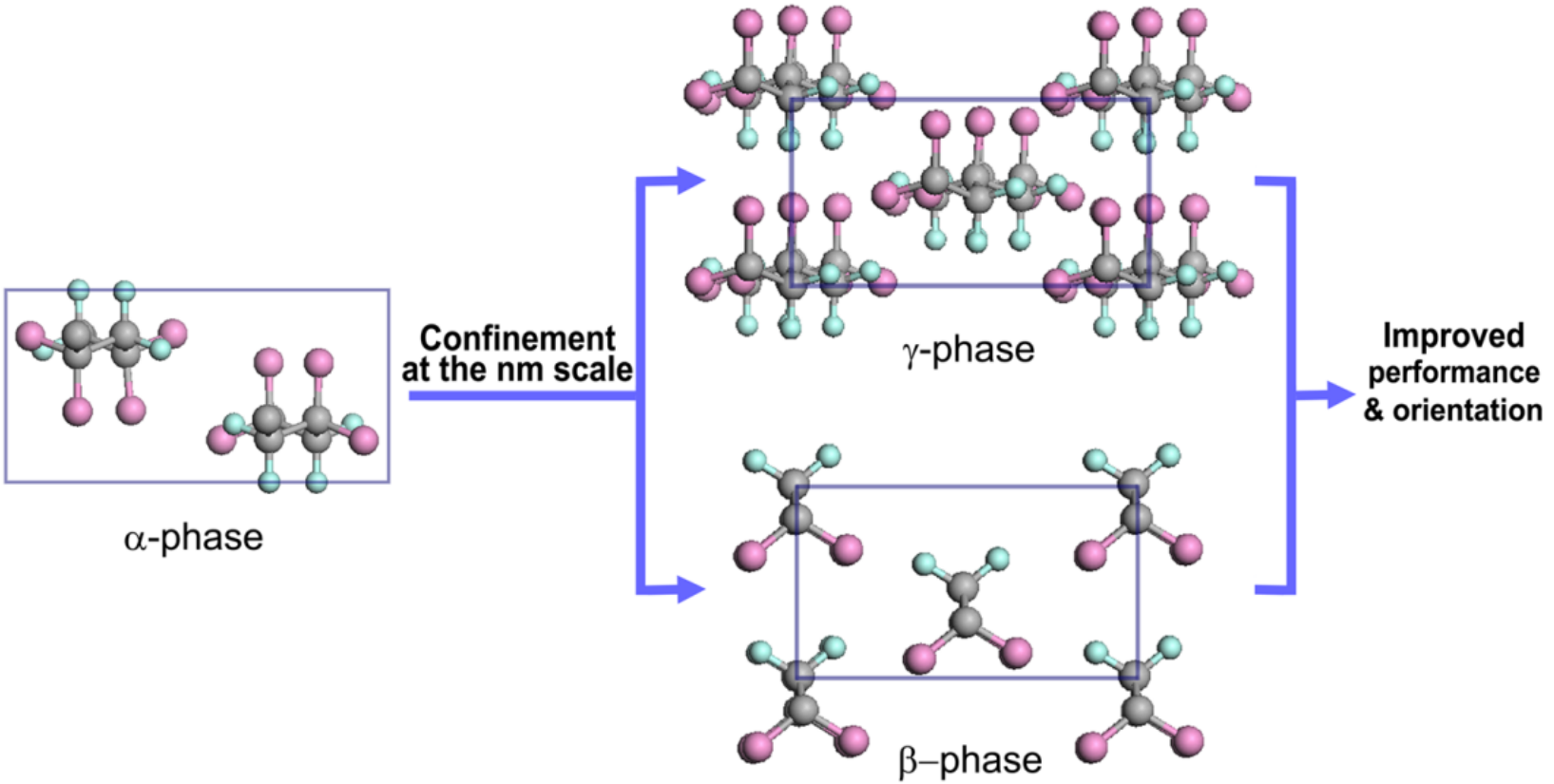


Fig. 3. Polarizing light micrographs of neat PP and 4 wt% clay–reinforced PP nanocomposite crystallized at 150 °C. (a) Neat PP and (b) 4 wt% clay reinforced PP nanocomposite.

How the sample is prepared?

Scans are carried out by taking the samples of about 3 to 6mg sealed in hermetic aluminum pans. Isothermal and dynamics modes can be used

FTIR


α-phase
Confinement at the nm scale
γ-phase
β–phase
Improved performance & orientation

FTIR → Polymer-particle interface: Phases, side groups and bonding.

An important factor that assists filler dispersion and determines the level of matrix reinforcement, is the interfacial bonding between the two phases.

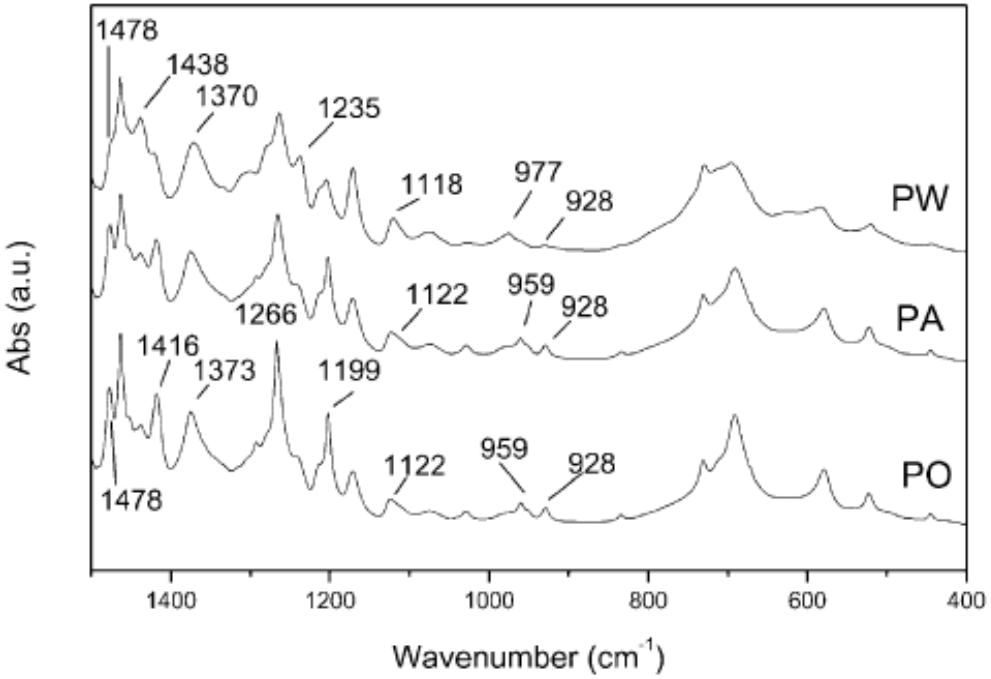


Fig. 1. FT-IR spectra of PA6 under various cooling conditions; PW: removed from the 250 °C oil bath and quenched in a water bath at 20 °C; PA: removed from the 250 °C oil bath and cooled in 20 °C air; PO: cooled down in oil bath from 250 to 20 °C by natural convection; the curves were stacked vertically for clarity.

FTIR

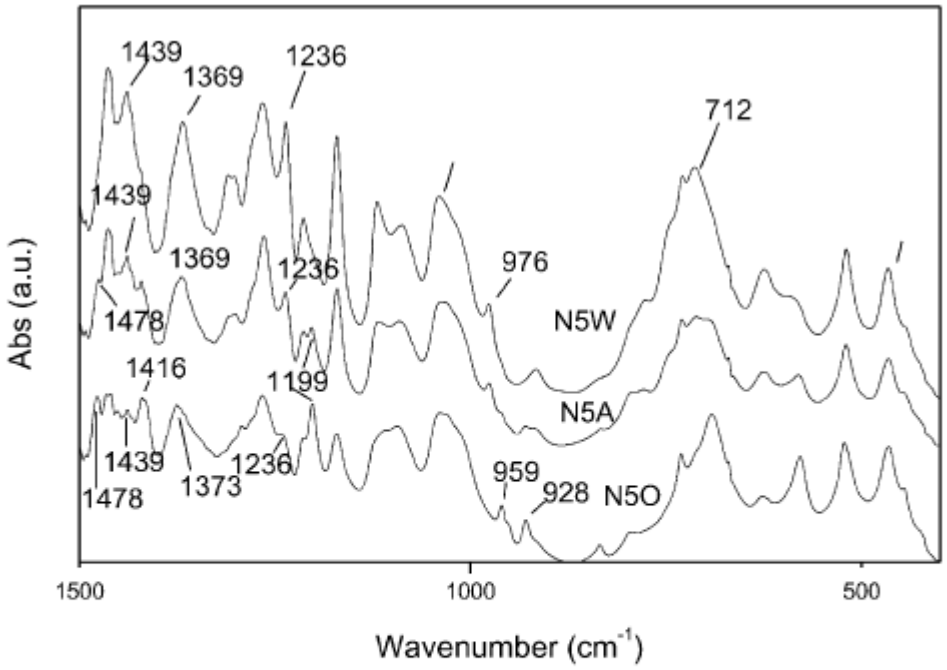
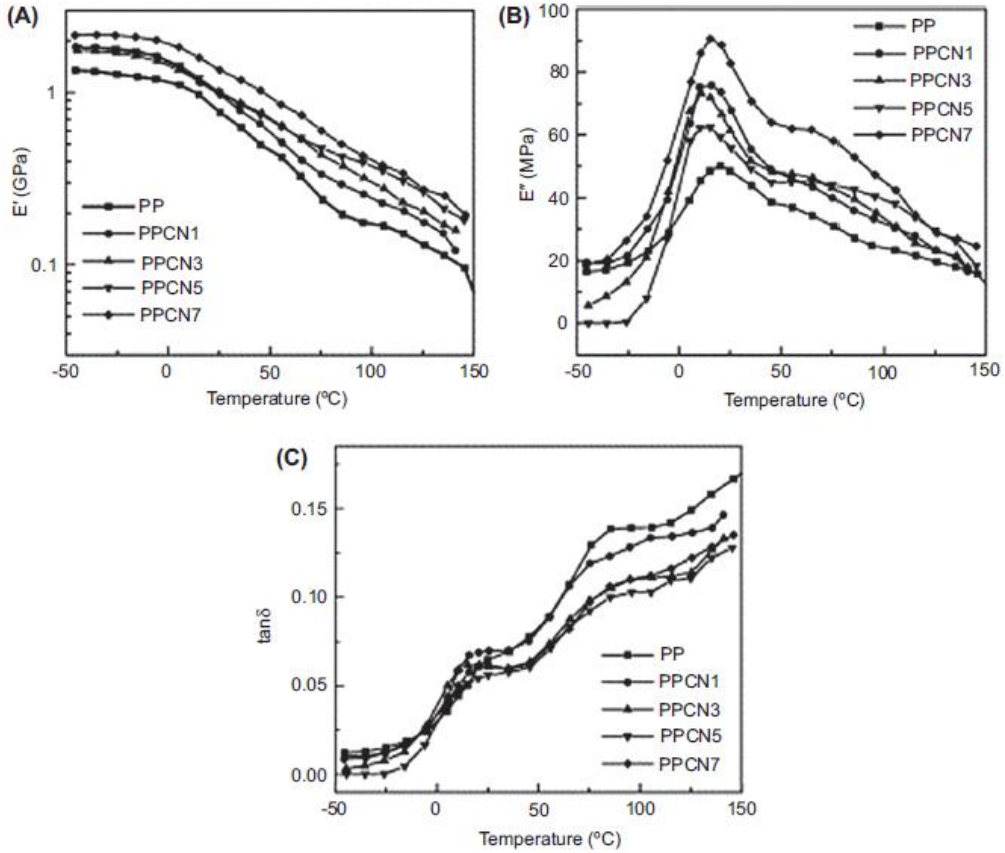


Fig. 2. FT-IR spectra of PA6/clay nanocomposite under various cooling conditions; N5W: removed from the 250 °C oil bath and quenched in a water bath at 20 °C; N5A: removed from the 250 °C oil bath and cooled in 20 °C air; N5O: cooled down in oil bath from 250 to 20 °C by natural convection; the curves were stacked vertically for clarity.

How the sample is prepared?

*For FTIR, solid samples were milled with potassium bromide (KBr) to form fine powder. This powder is compressed into a thin pellet which can be analyzed by infrared. KBr pellets were first compressed and then fixed on a sample holder by magnetic force [*Interfacial bonding characteristic of nanoclay/polymer composites*].*

DMA → viscoelastic properties → fracture mechanics approaches



■ **FIGURE 12.4** Dynamic mechanical spectra [(A) storage modulus E', (B) loss modulus E'', and (C) loss factor tan δ)] as a function of temperature for polypropylene (PP) and polypropylene—clay nanocomposites (PPCN). *Reproduced with permission from X. Liu, Q. Wu, PP/clay nanocomposites prepared by grafting-melt intercalation, Polymers 42 (2001) 10013—10019.*

How the sample is prepared?

A piece of the polymer nanocomposite can be used as a sample. The only limitation is to have the adaquate geometry ir order to fix to the chamber space and clamps.

How this info will help to my thesis project?

- Understand fracture mechanisms associated with crack propagation.
- Effect of nanoclay concentration (%wt) to mechanical properties under impact conditions.
- How the processing of nanocomposite affects its chemical structure and the the mechanical properties.
- Analyze structure/fracture properties relationships.
- Obtain mechanical parameters in order to estimate fracture resistance against crack propagation by using fracture mechanics approaches.
- Conclude the best parameters that make a better improvement on the fracture property of interest.