Today's Plan

From polymers structure to the properties

Glass transition

I. Some examples

Semi-crystalline polymers

- I. Crystallisation / Crystalline morphology
- Influence of processing on crystalline morphology **_**
- III. Mechanical properties

I- Some examples illustrating the key role of

the glass transition

- 1) Water based paint formulations
- 2) Rice milling
- 3) Reinforcement in nanocomposites

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From tin of paint ...



« environmental

friendly »

solvent emission i.e. without







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suspension of latex particles

film forming process

latex colloid

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2) Rice milling

paddy rice









Rice milling is removal of husk and bran to obtain the edible portion for consumption. During that process, some grains break.

The temperature and relative humidity conditions of the rice milling process, have a strong influence on the Head Rice.



Optimizing the rice milling process



[Yang et al., Vol 85, Biosystems Engineering, 2003]

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3) Nanocomposites



The volume of particules being constant :

interfacial area **Л** r ⁻¹

d_s distance between particle's surfaces ▲

Polymeric matrix: giration radius (2-20 nm) $\sim d_{\rm s}$

Increasing the stiffness by decreasing Tg

• Tg decreases in small thickness samples



In the vicinity of the particle, the polymer matrix glass transition changes

This induces a strong effect on the reinforcement in nanocomposites.

Semi-crystalline polymers

I. Crystallisation / Crystalline morphology

Semi crystalline polymers Structural conditions to crystallize



Crystallisation process



Temperature / Time

Chain folding process

Crystallisation at T_{C} if mobility (T > T_{g})

Entanglements/branching limit chain folding



Multi-scale representation of the microstructural morphology of semi-crystalline polymers







The properties of the amorphous regions is controlled by the chains traversing the layers, and the entanglement of loops.

Spherulites

The crystalline lamellae arrange themselves in larger structures called spherulites, which nucleate during the solidification process, and coalesce into a polyhedral structure akin to that of a metal polycrystal.



(a) Stages in the formation of a spherulite from a stack of lamellae

>multiscale morphology





Spherulite struture Polypropylene



Other semi-crystalline polymers in nature

A mixture of ice crystals and an amorphous matrix is a two phase frozen system



Potato starch at high magnification in polarised light



Other semi-crystalline polymers in nature



Collagen is the main protein of connective tissue



X_c: crystallinity rate

• From density measurements



- ρ : polymer density
- $\rho_{\rm C}$: crystalline phase density
- ρ_{a} : amorphous phase density

 From enthalpic measurements (DSC)



H_{fo}: melting enthalpy of a crystal



Others techniques: X Rays, Infrared Spectroscopy ...

Semi-crystalline polymers

II. Influence of processing on crystalline morphology

Influence of cooling rate on lamellar structure

Cooling rate increasing



fully adjacent re-entry model

C Inla

"Real polymer"

random switchboard

model



Structure of injected sample Profil of crystallinity





Semi-crystalline polymers

III. Mechanical properties

Mechanisms of deformation Pertinent scales



E : Young modulus σ_y : Yield stress



Mechanisms of deformation: microscopic plasticity



Tensile test





Tensile testing of polyethylene

[http://www.doitpoms.ac.uk/]

Mechanisms of deformation iPP



Conditions leading to ductile behaviour

Time temperature conditions:
$$T_g < T < T_f$$
 $T_g (PP) \sim -10^{\circ}C$ $T_m \sim 165^{\circ}C$ Interlamellar connectivity: $M_w > M'_c$ $M'_c (PP) \sim 200 \text{ kg/mol}$ Spherulite size: $F_s < F_{sc}$ Spherulite size: $F_s < F_{sc}$

ic properties	hous polymer	e modulus depends on :	allinity degree	structural parameters thickness, ous layer thickness, entanglement	ration, of tie molecules)		
fect of crystallinity rate on elast	Crystals act as reinforcing fillers in amorph	Tensile	- crysta	-micros (crystal i amorpho	• • • • • • • • • • • • • • • • • • •	Crystallinity Degree [%]	odulus vs. crystallinity of high density polyethylene llized at elevated pressure and temperature. in uniaxial compression with initial compression ⁻¹ at room temperature [96].
ш		1000	eqM]su	Elastic Modul	400		Fig. 8. Elastic r samples cryst Measurements rate of 0.0011

Effect of crystallinity rate

Crystals act as reinforcing fillers in amorphous polymer



[A. Ershad Langoudri, PhD, 2000]

Temperature dependence



Tensile testing of 38% semi- crystalline PET at different temperatures

 $Tg \approx 80^\circ C$

Semi-crystalline polymers: Summary

- Macromolecular (MM) chains fold to produce crystalline lamellae. The crystalline and amorphous regions are interconnected, through tie molecules or loops.
- When lamellae are nucleated from a small area, round agglomerates known as spherulites are formed.
- Polymer crystallisation and spherulite formation have been discussed. Processing conditions affect crystallisation process.
- under a uniaxial tensile stress above its glass transition temperature have Mechanisms of deformation by which a semicrystalline polymer deforms been presented (necking, cold drawing, hardening...)
 - Conditions leading to a ductile behaviour have been discussed.
- Crystalline ratio and temperature have a large effect on mechanical behaviour.

Thank you for your attention

Lecture# 6 will be given on Friday May 29th