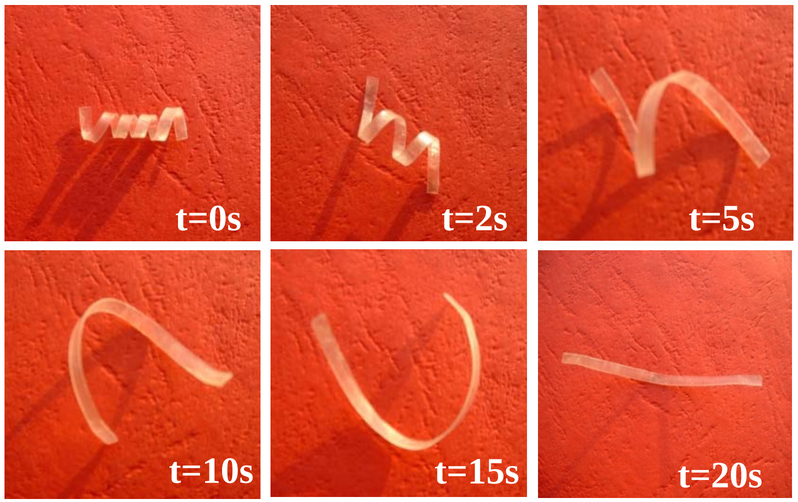
بسم الله الرحمن الرحيم

Effect of CNTs on Shape memory properties of PLLA/PCL blends

Maryam Amirian[1], Ali Nabipour Chakoli[2], Hossein Afarideh[3],



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[3]Sch. of Energy & Physics, Amirkabir Uni. of Tech.,Tehran, Iran,

Outline

- Background and Purpose
  - Biodegradable polymers
  - Shape memory polymers
- Materials and Experimental Procedures
- Crystallinity of composites
- Shape memory effect of composites
- Conclusions

Background

Biodegradable polymers

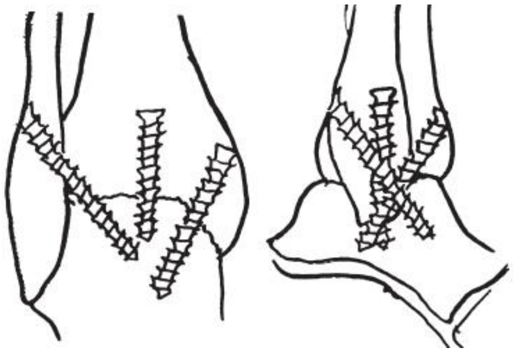
Polyesters:

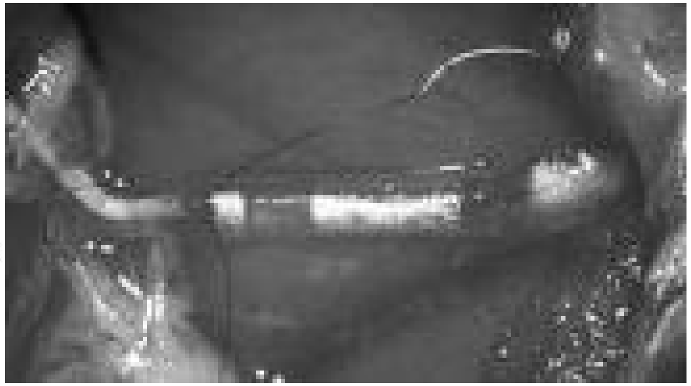
Poly L-lactide (PLLA),

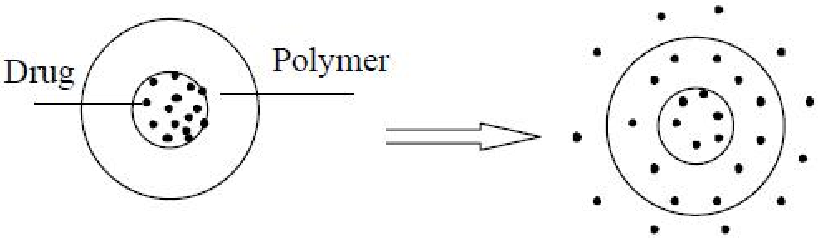
Poly glycolic acid,

Poly e-caprolactone (PCL) ,

Poly Ethyelene glycol

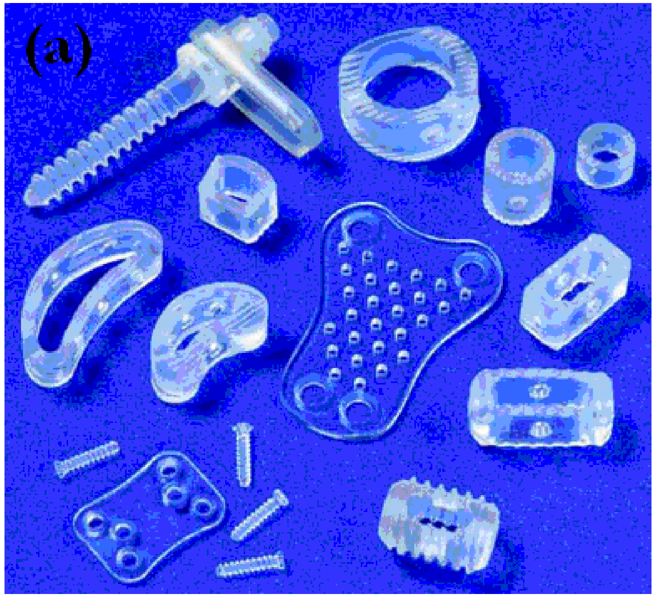


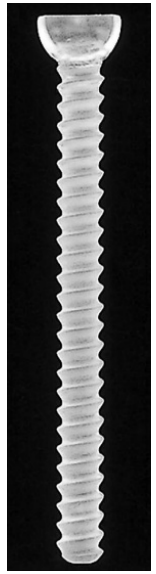




Application:

- An alternative to non-degradable polymers,
- Hard tissue engineering, bone fixing,
- Controlled drug delivery systems,
- Surface-eroding systems,



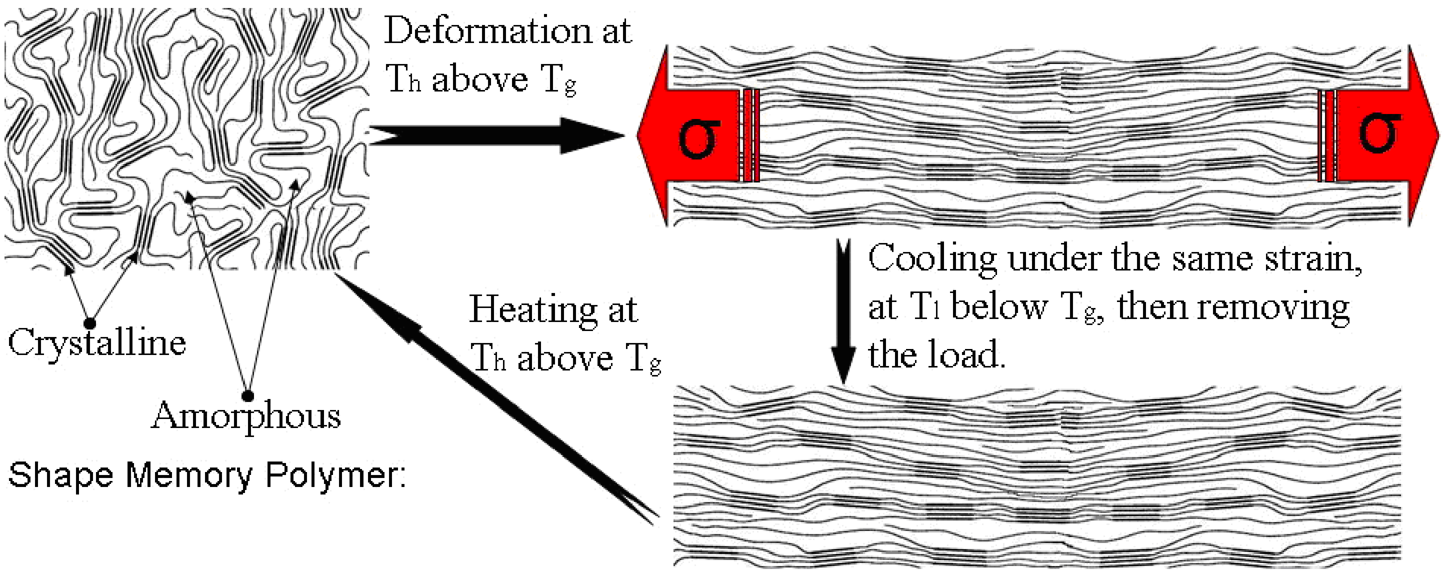


Background

shape memory polymers

Shape memory polymers (SMP)s can rapidly change their shapes from a temporary shape to their permanent shapes under appropriate stimulus such as:

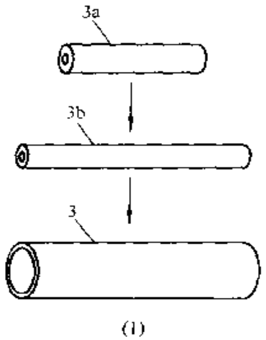
Temperature,
Light,
Electric field,
Magnetic filed,
pH,
Specific ions,
Enzyme,

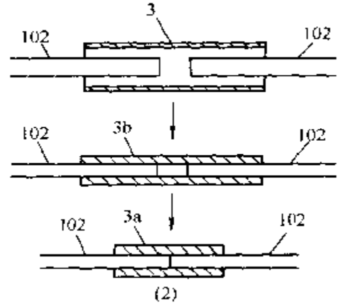


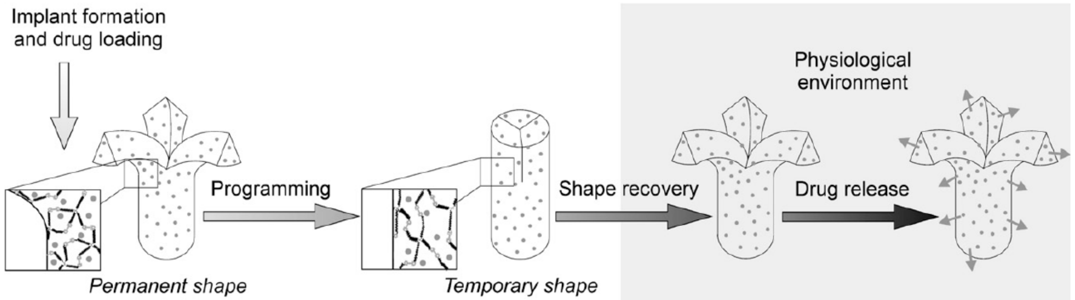
Background

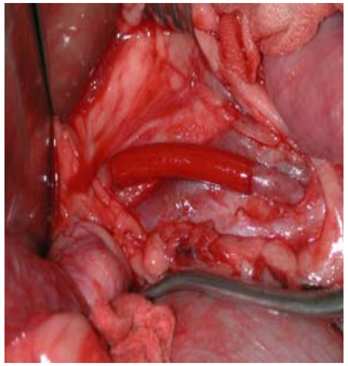
shape memory polymers

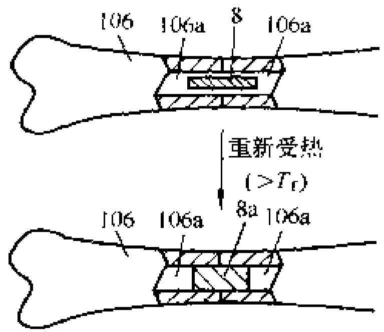
Application :
- ➢Surgical sutures and adhesives,
- ➢Tissue engineering,
- ➢Controlled drug delivery systems,
- ➢Surface-eroding polymers,

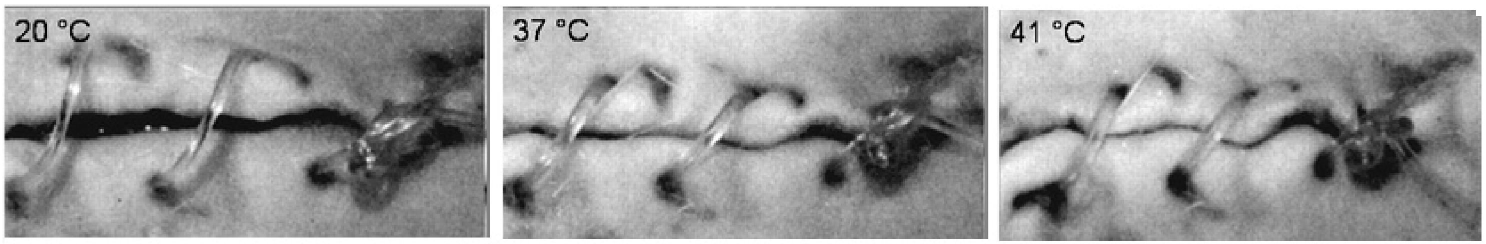










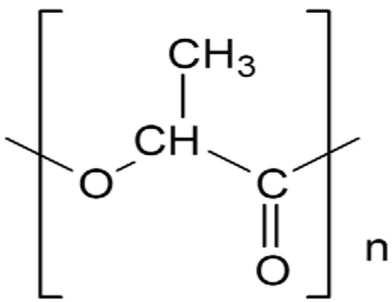


Background

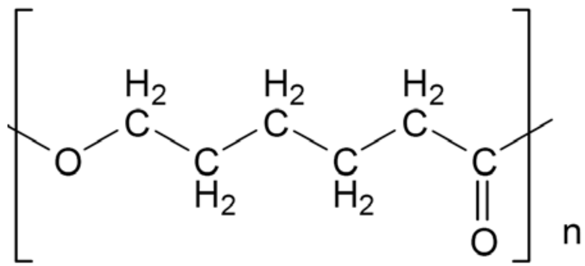
Poly L-lactide (PLLA), Poly ε-caprolactone (PCL)

PLLA and PCL are linear aliphatic thermoplastic polyesters, which has good mechanical properties, thermal plasticity, and shape memory effect.

PCL is flexible, soft, tough and has a lower melting point (60 ℃), while PLLA is rigid, hard, brittle and has a higher melting temperature(178~182 ℃).
The blend of these polymers possessed properties partly like that of PLLA and partly like that of PCL.



Poly(L-lactide)
PLA

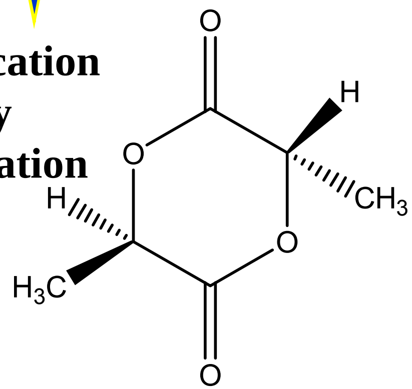


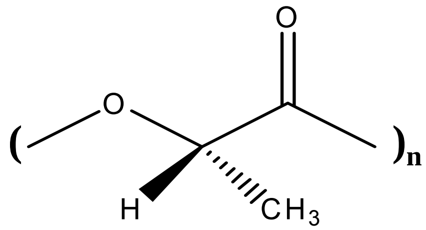
Poly(ε- caprolactone)
PCL

Background

Poly L-lactide (PLLA cycle)

Purification by distillation



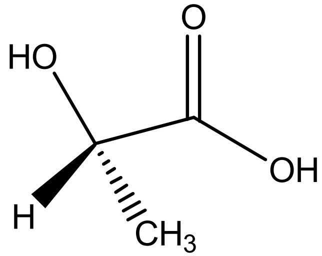


Condensation process

Products Packaging, Textiles, Medicine

Reduction to monomer

Lactic acid from Dextrose



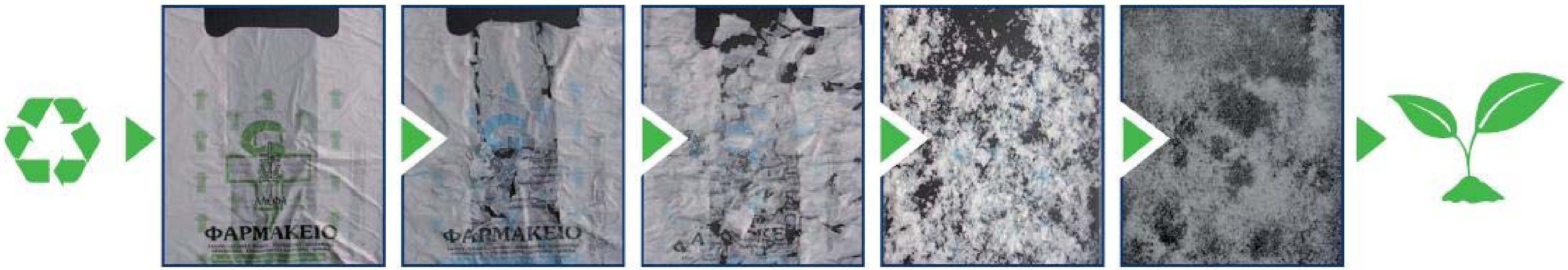
Reduce Global Green House Effect

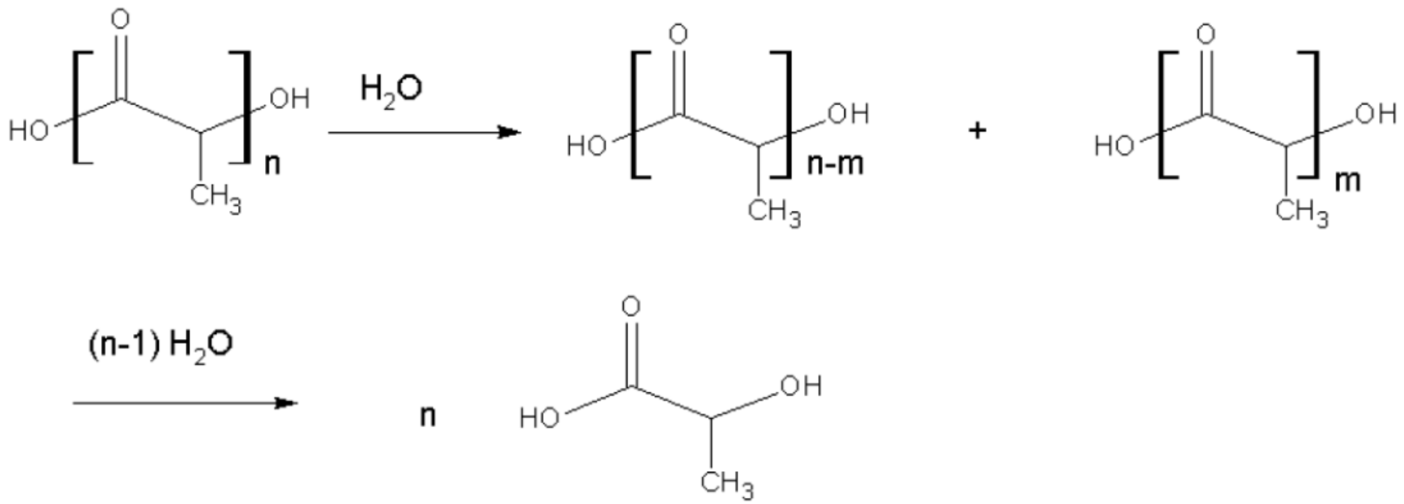
Reduction of annually renewable resources

Biomass, corn

Background

PLLA degradation





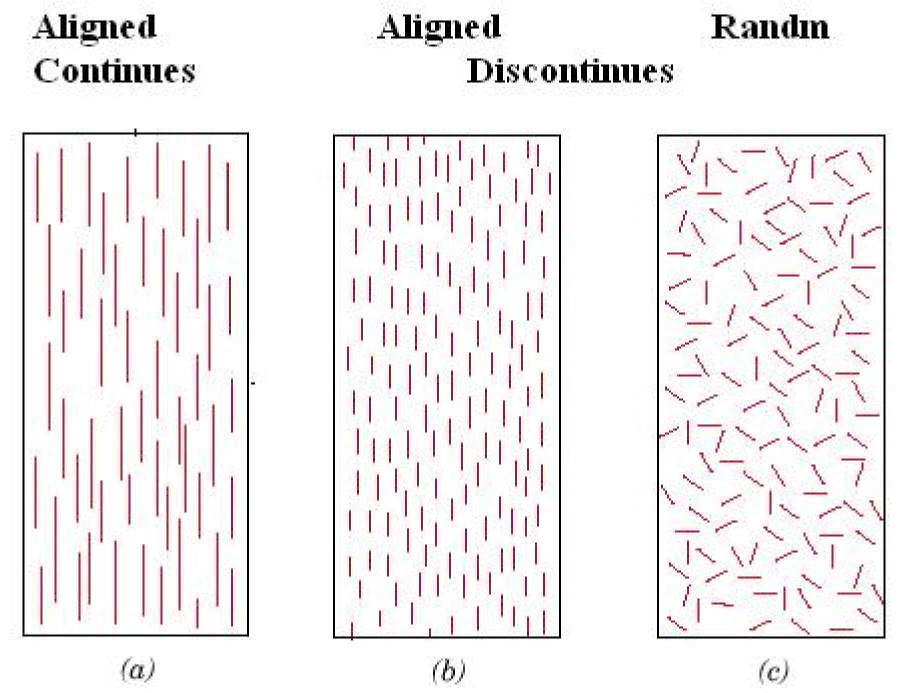
- **Degradation time for Biodegradable polymers: 6 months to 2 years**
- **Degradation time for Conventional plastics**: **500 – 1000 years**

Purpose

To improve the mechanical properties of PLLA, fabrication of PLLA composites was considered.

Four main system requirements
for effective reinforcement.
1- Large aspect ratio,
2- Good dispersion,
3- Alignment,
4- Interfacial stress transfer

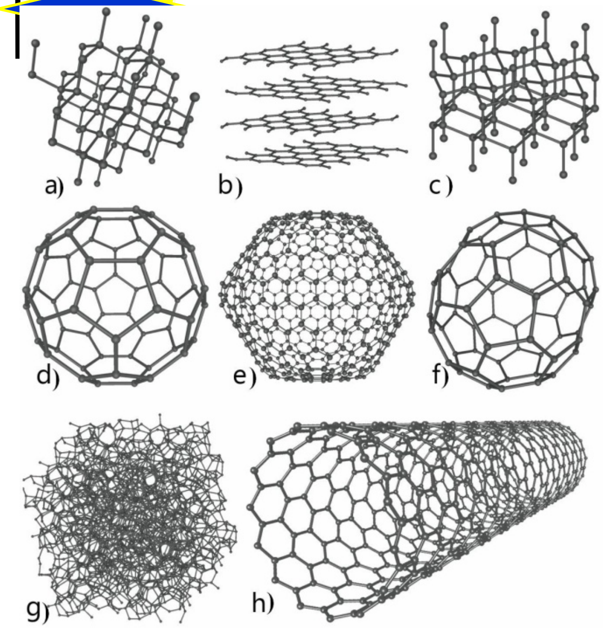
Reinforcement Materials:
Alumina, Glass, Glass fiber, Boron, Silicon carbide, Clay, Carbon, Carbon fiber, Carbon Nanotubes,

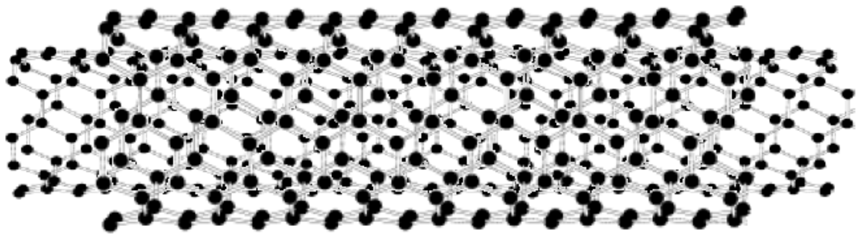


Because of their unique mechanical properties, CNTs are considered to be ideal candidates for PLLA reinforcement.

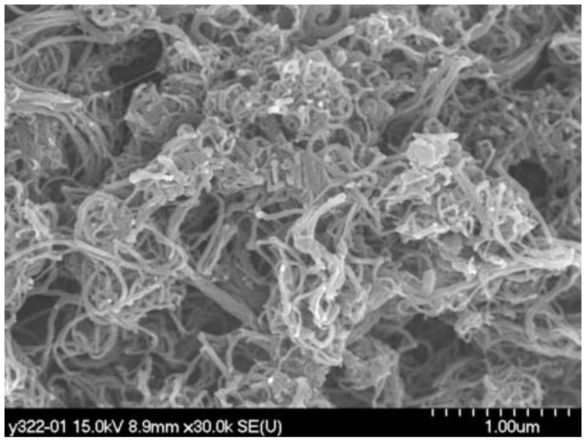
Background

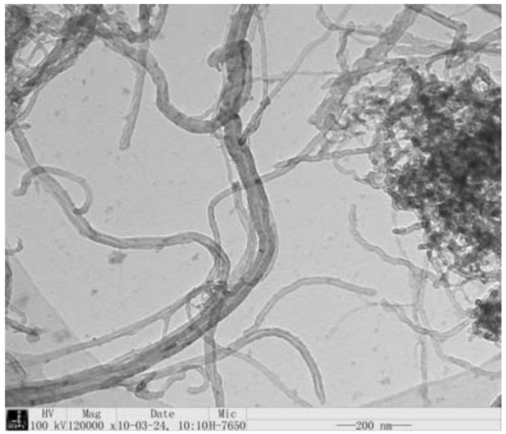
CNTs





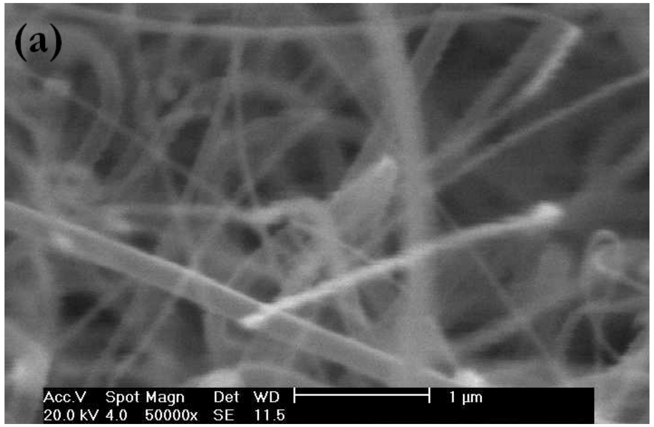
Carbon Allotrops

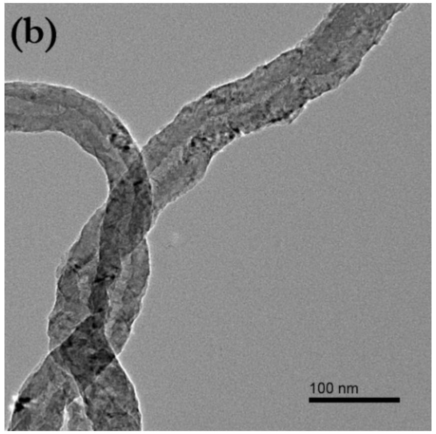




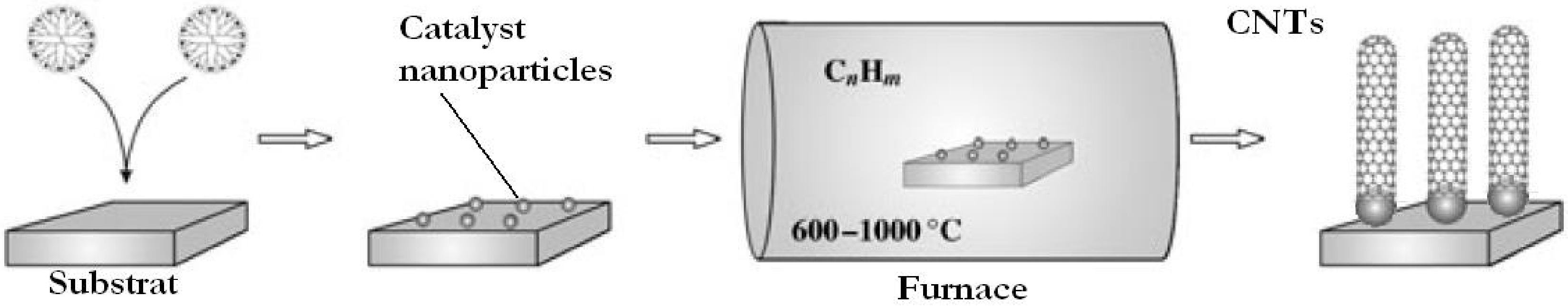
Background
CNTs

Modulus: 270 GPa to 1 TPa, Strength: 11–200 GPa,

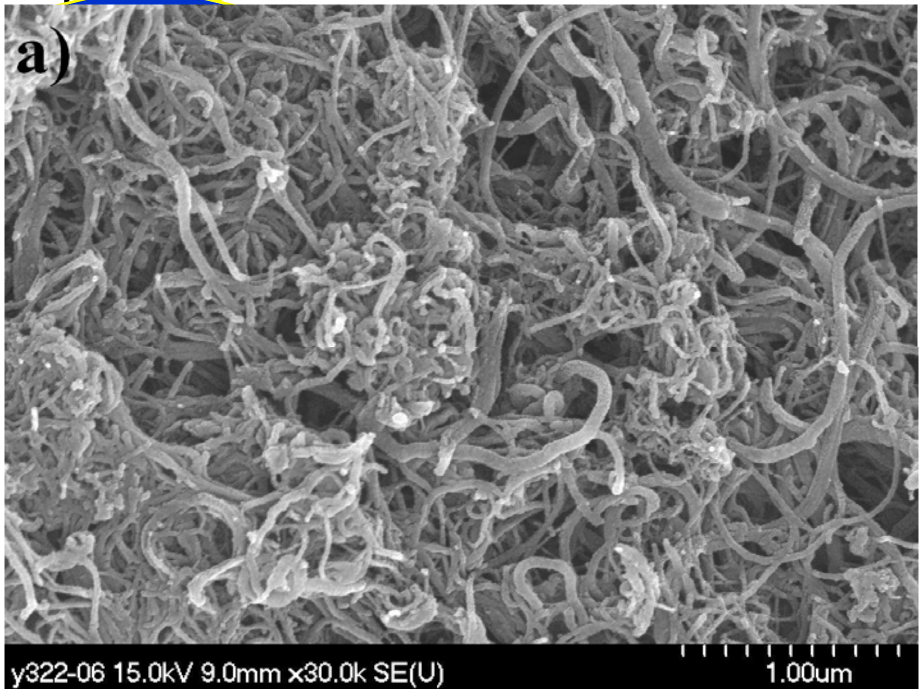


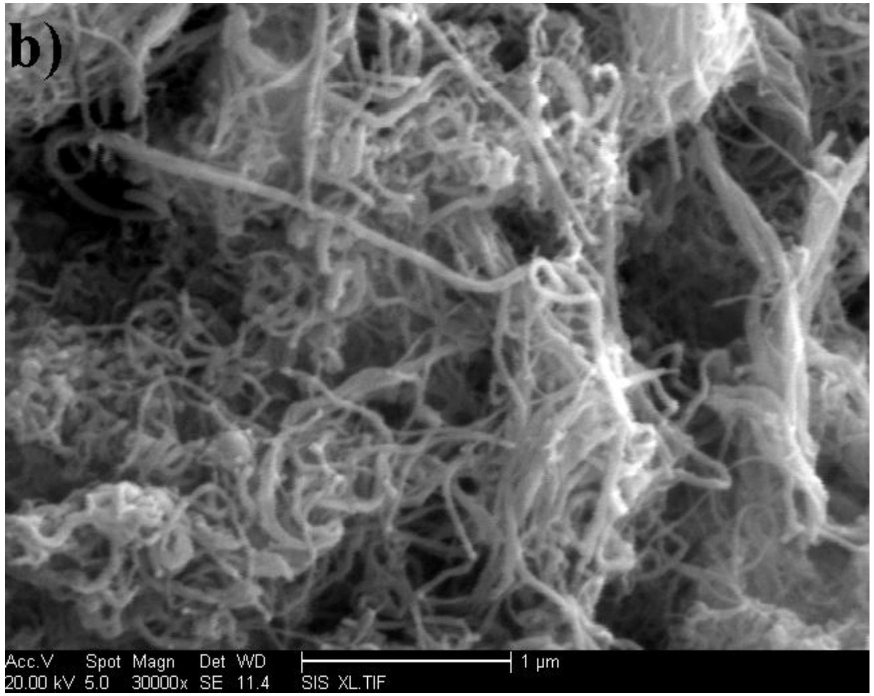


Synthesis methods:
Electric arc-discharge, Laser ablation, Catalytic decomposition of gaseous hydrocarbons



Morphology, SEM



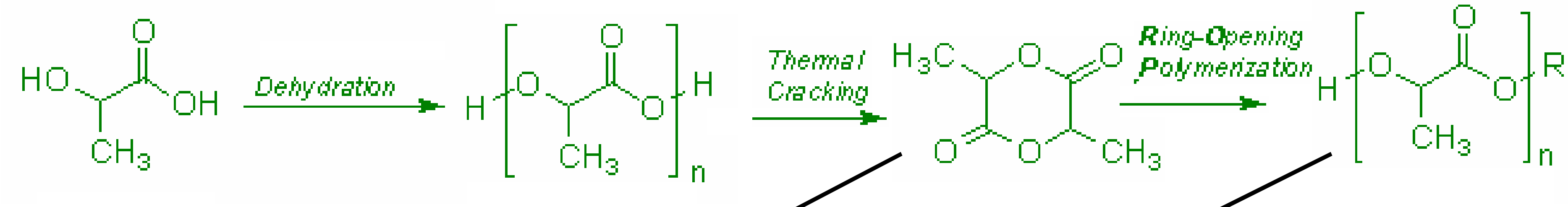


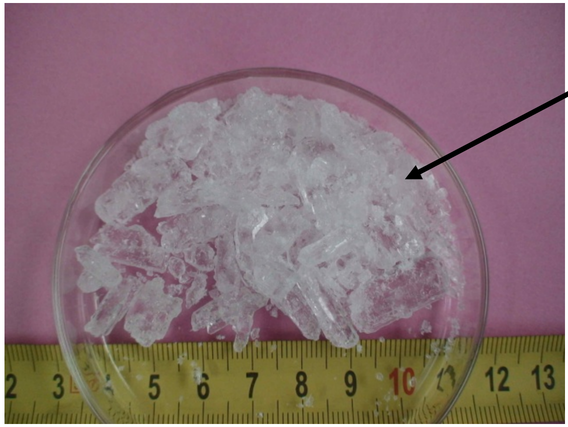
neat pMWCNTs (a), purified pMWCNTs (b)

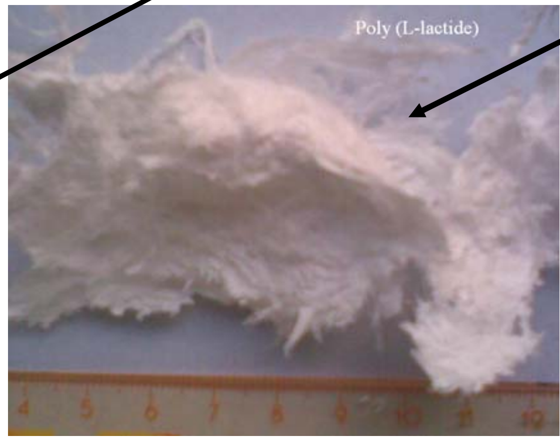
pristine MWCNTs have some agglomerated MWCNTs and bundled MWCNTs

After purification, Most of agglomerated MWCNTs, bundled MWCNTs, carbon nanofibers, amorphous carbon and metallic catalysis nanoparticles are removed

Synthesis of PLLA



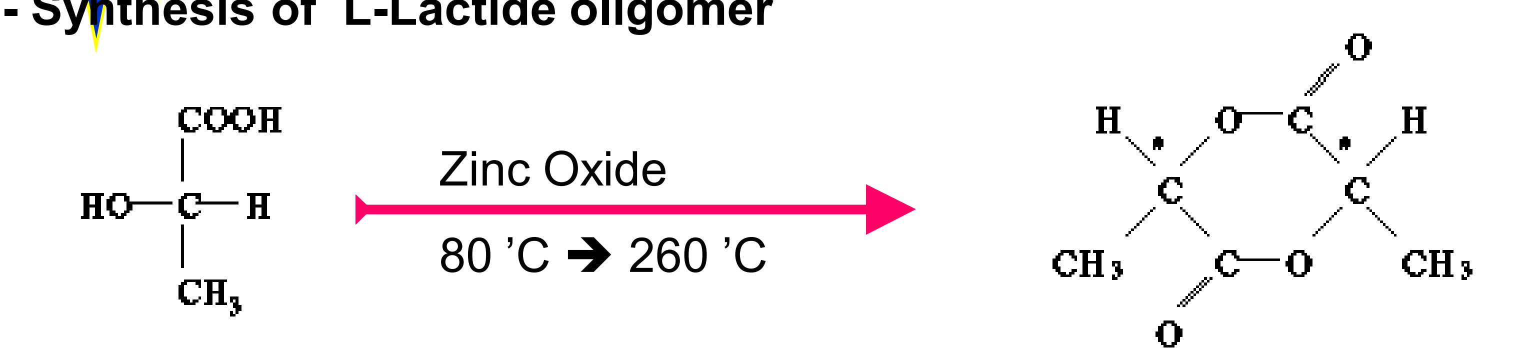




L-lactide Oligomer **PLLA** **PCL**

Experimental:
LA and PLLA synthesis

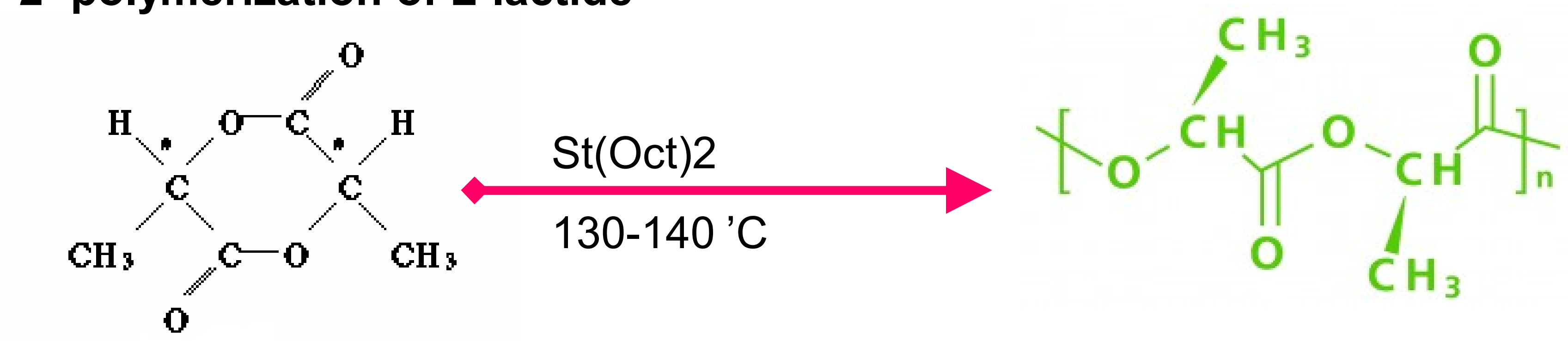
1- Synthesis of L-Lactide oligomer



L-lactic acid

L-lactide

2- polymerization of L-lactide

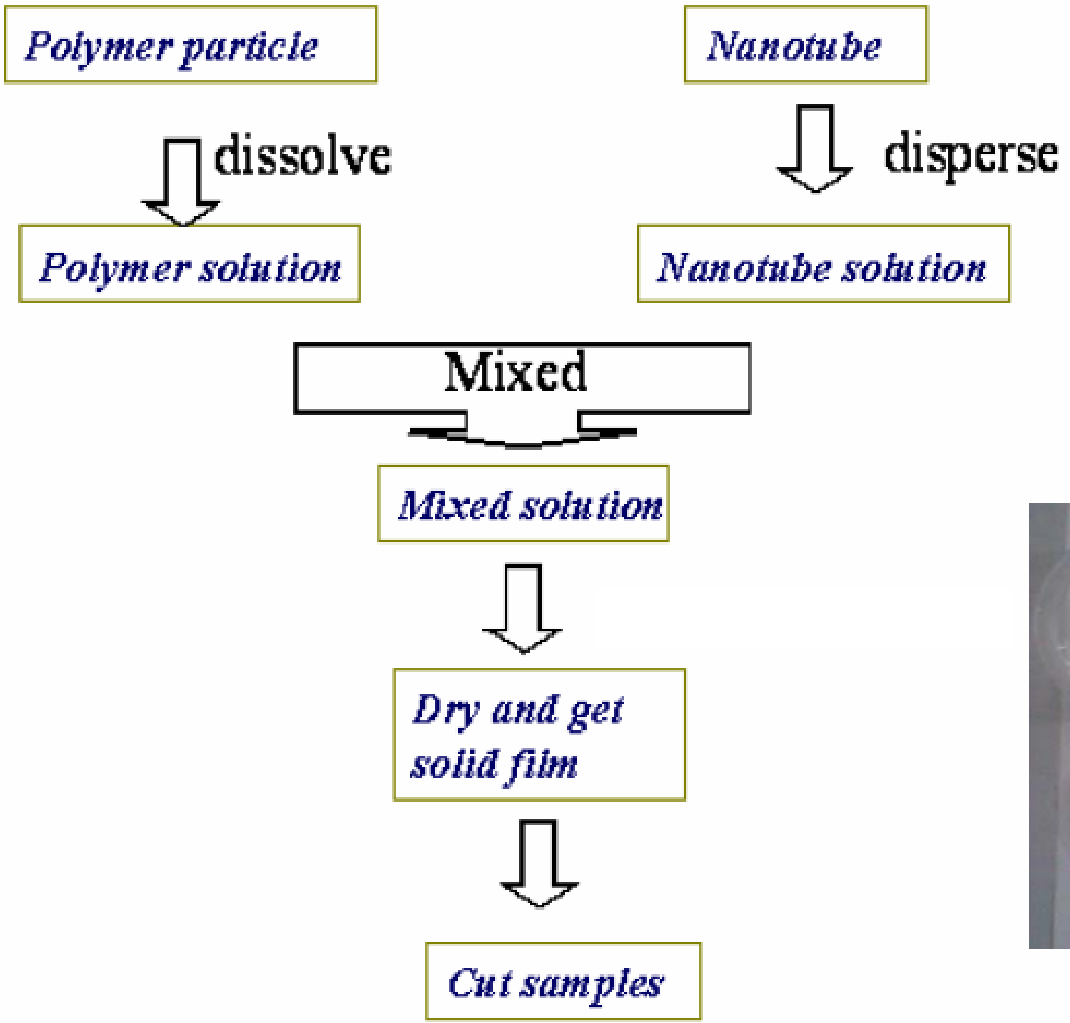


L-lactide

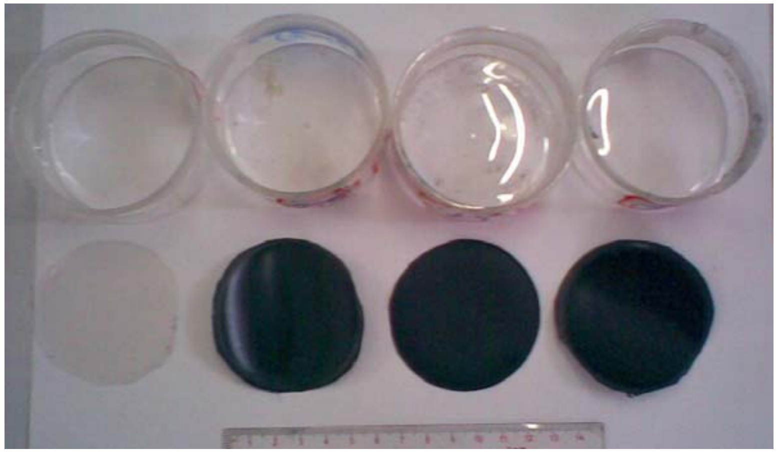
Poly (L-lactide)

Experimental:

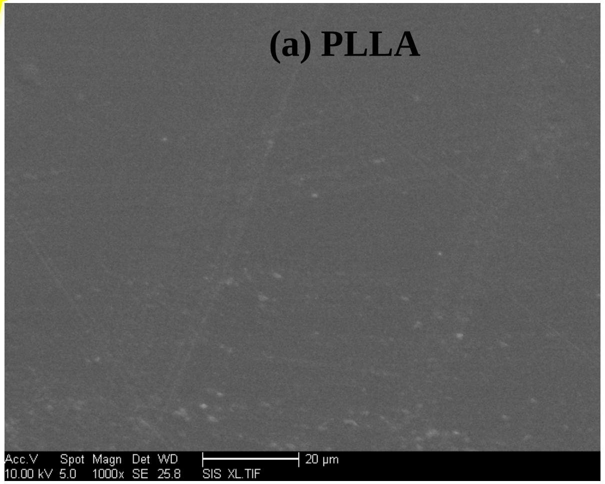
Solution casting of composites

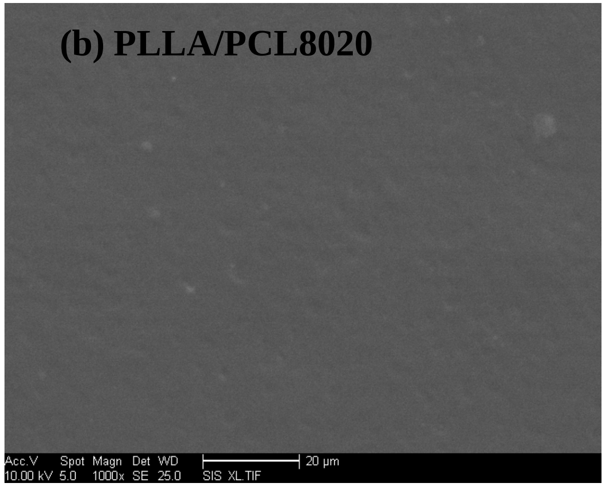


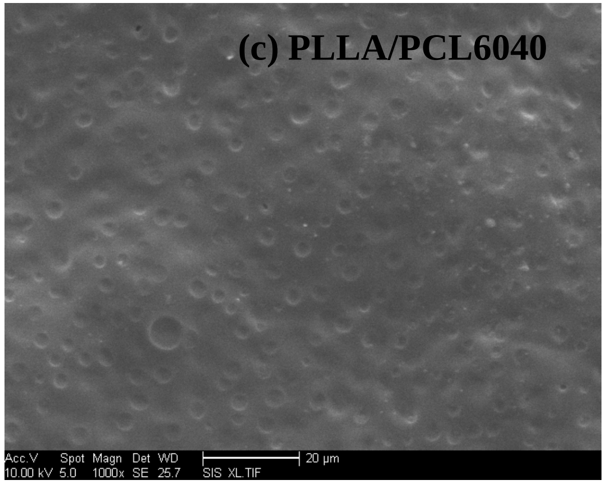
Solution casting using chloroform as solvent

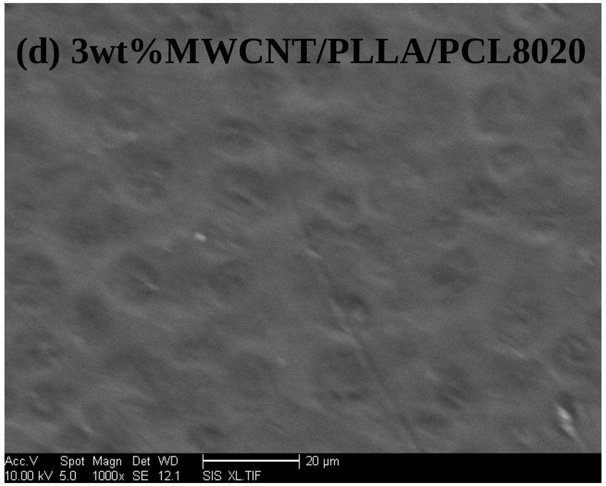


Morphology, SEM



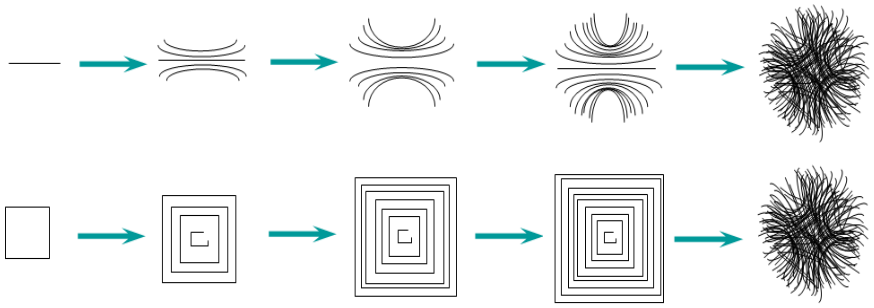


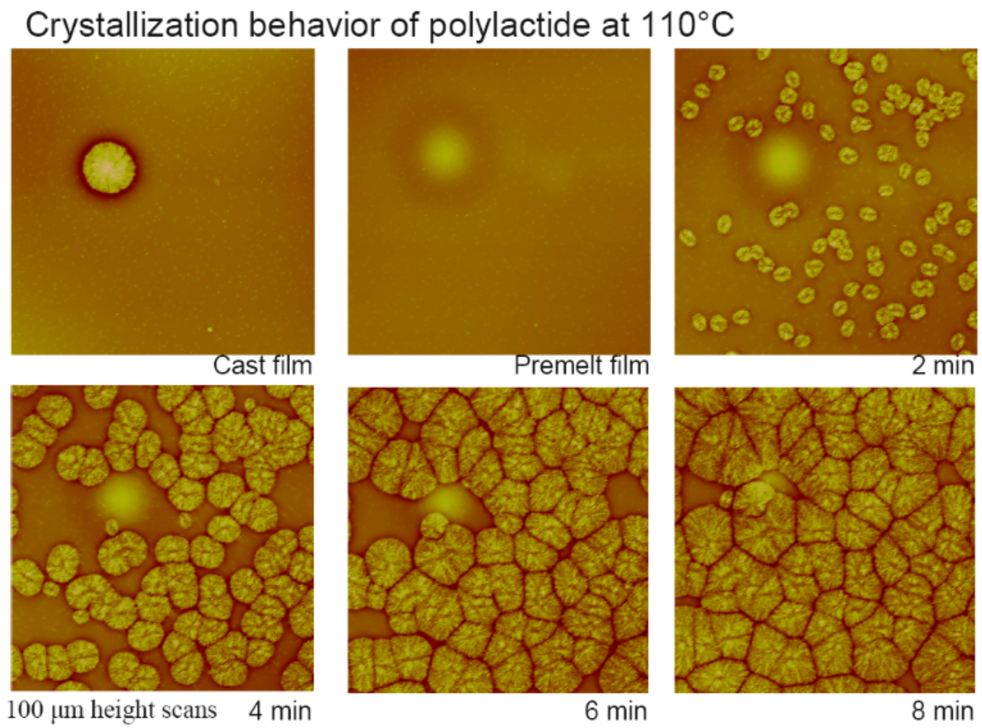




Crystallization

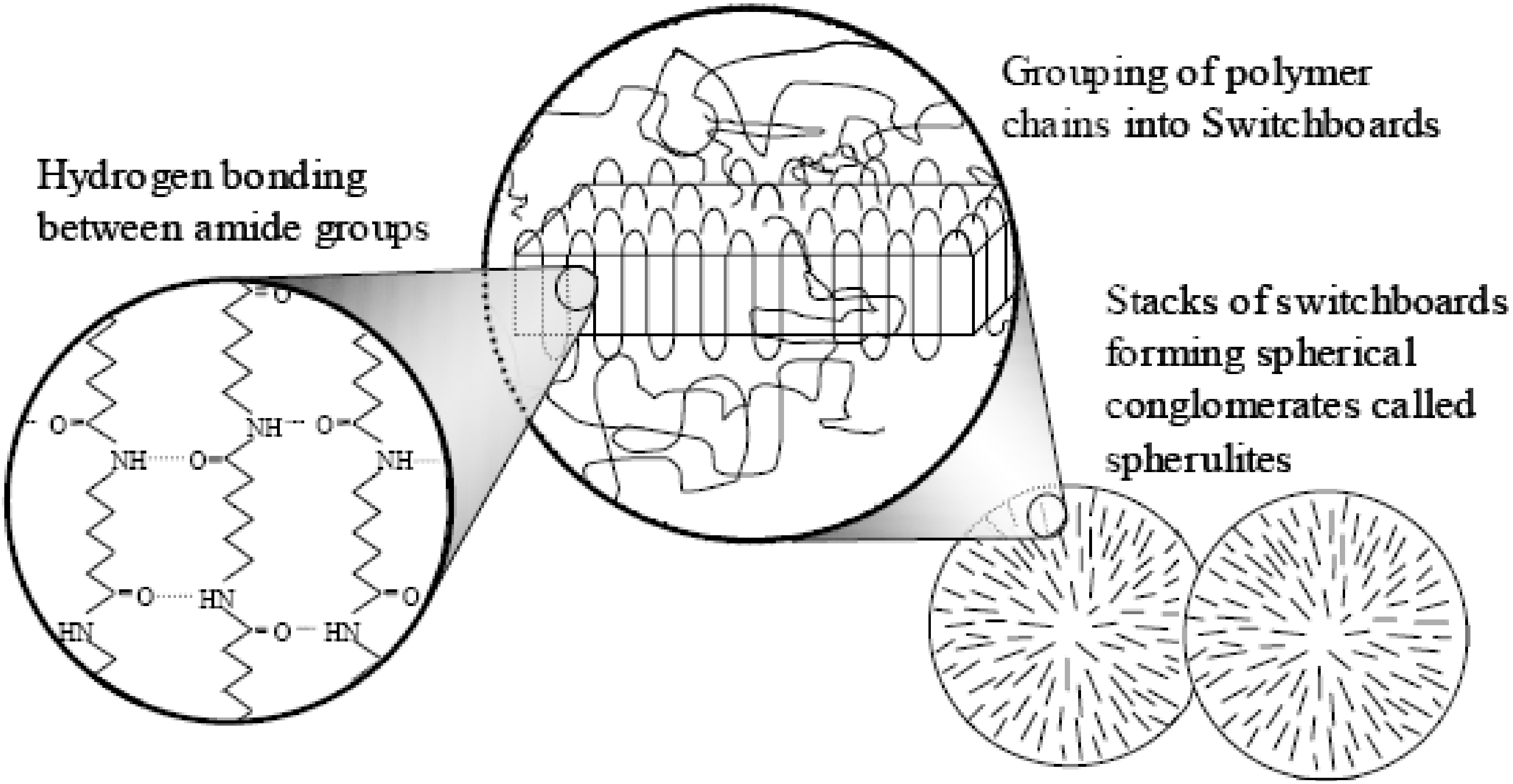
Schematic representation for growth of spherulites in polymer thin films.





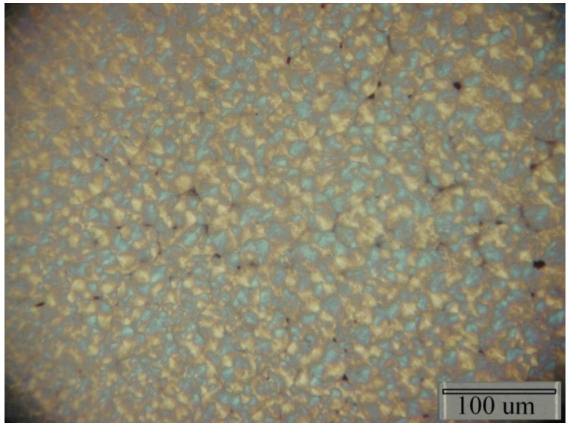
The series images refer to crystallization behavior of PLLA at 110 ° C.

Crystallization



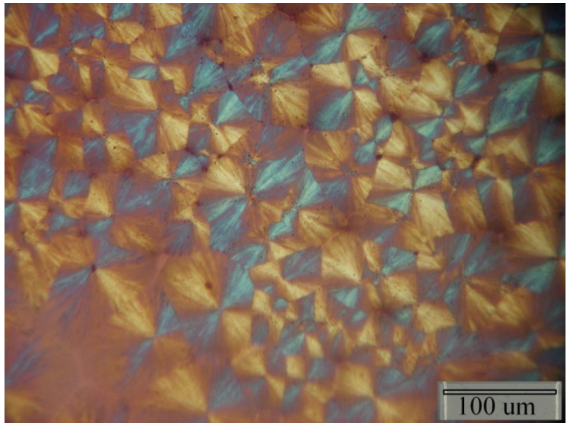
schematic representation of arrangement of polymer chains for creation of lamellaes and spherulites.

Structure, POM

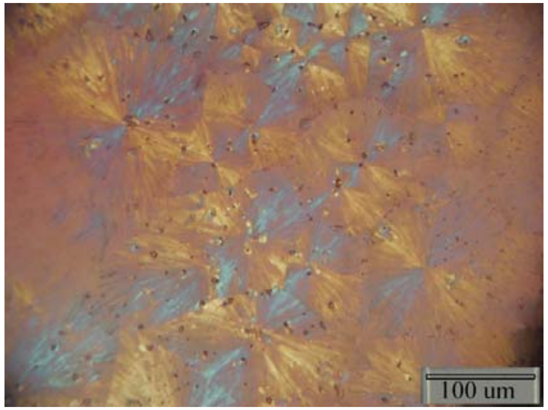


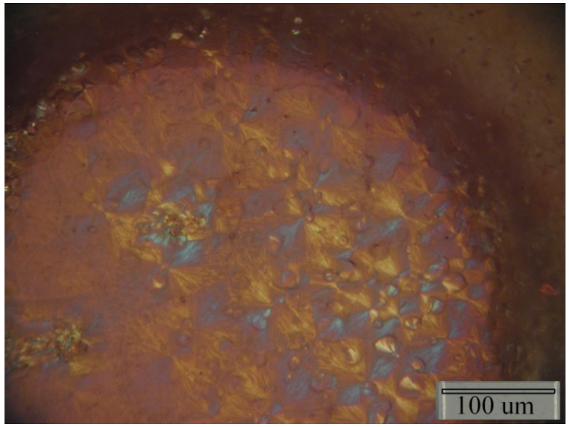
PLLA

PLLA/PCL9010



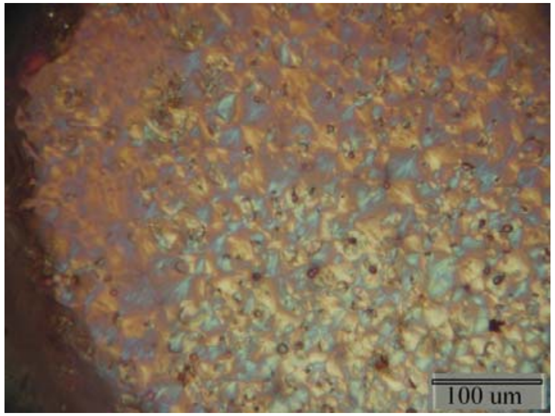
PLLA/PCL8020



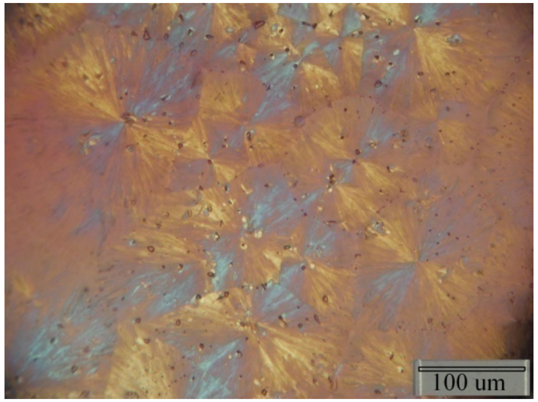


PLLA/PCL7030

PLLA/PCL6040

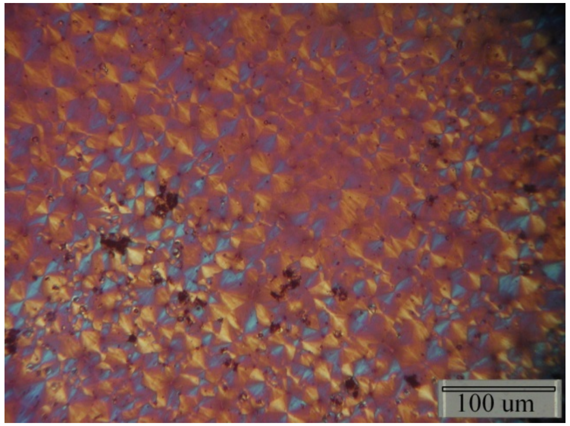


Structure (POM)

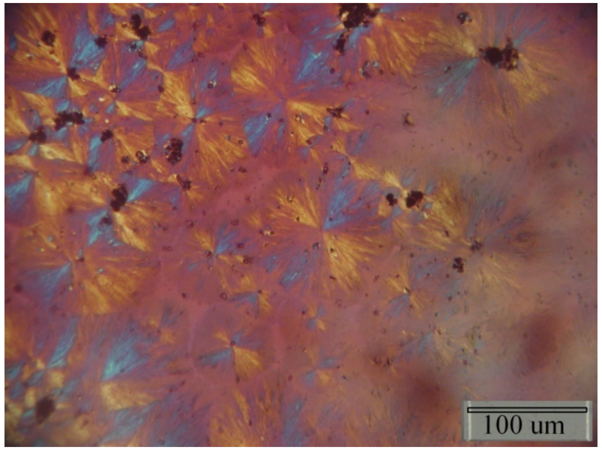


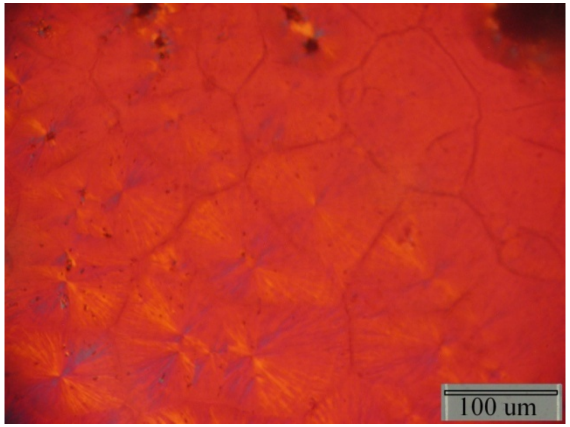
PLLA/PCL8020

0.5% MWCNTs



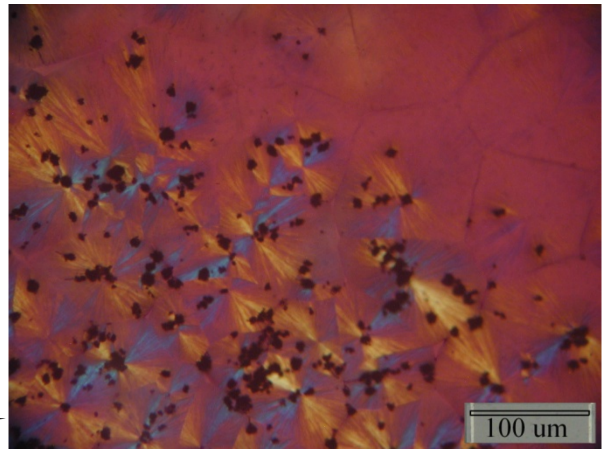
1% MWCNTs





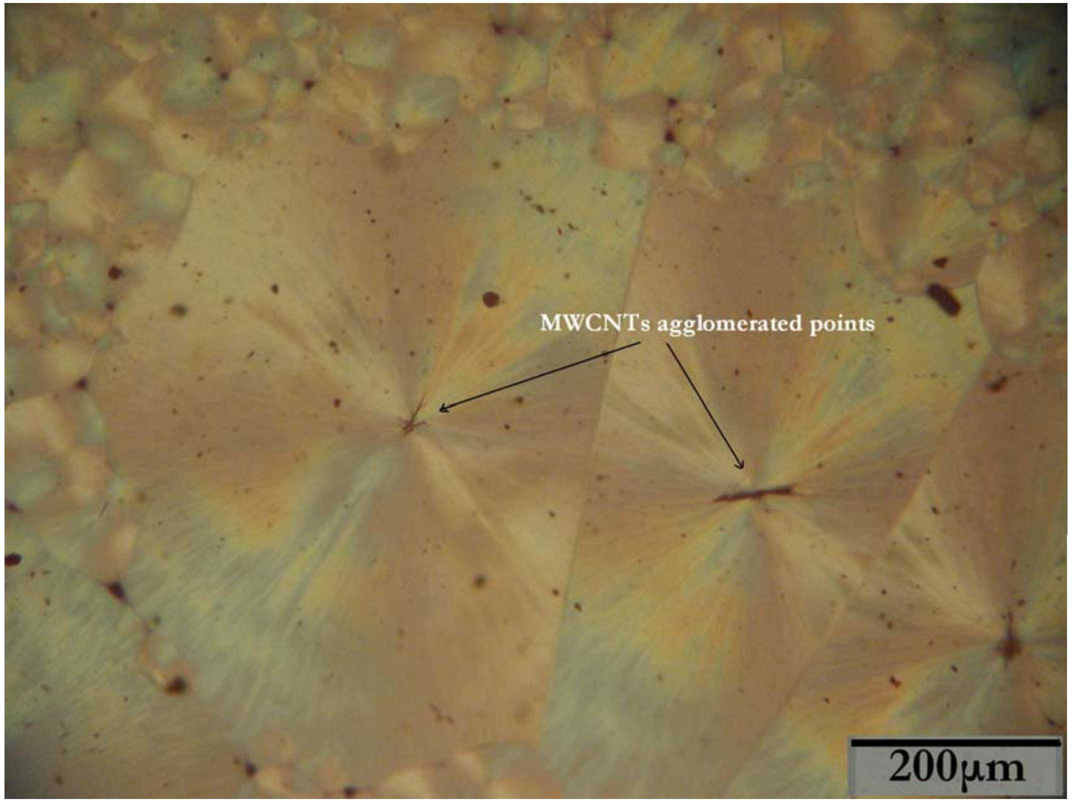
2% MWCNTs

3% MWCNTs

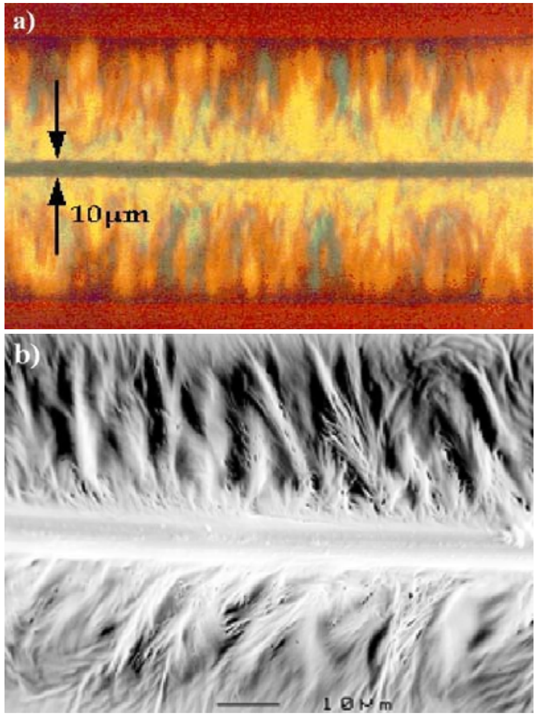


Crystallinity, POM

Ref: J. Macromol. Sci. B. Phy. 2003, B42(3 & 4): 479~488

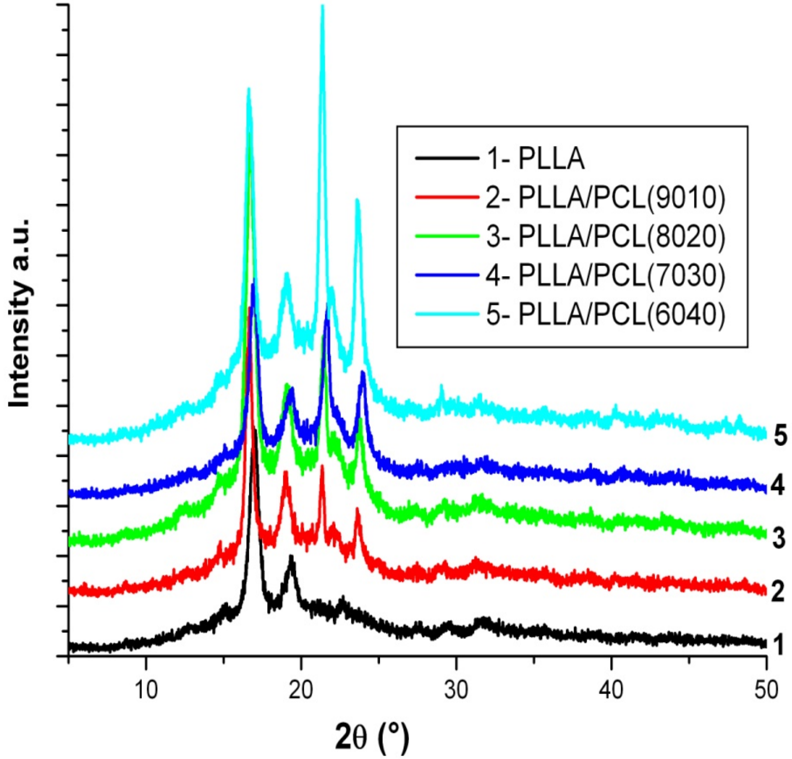


carbon fiber graft polymer

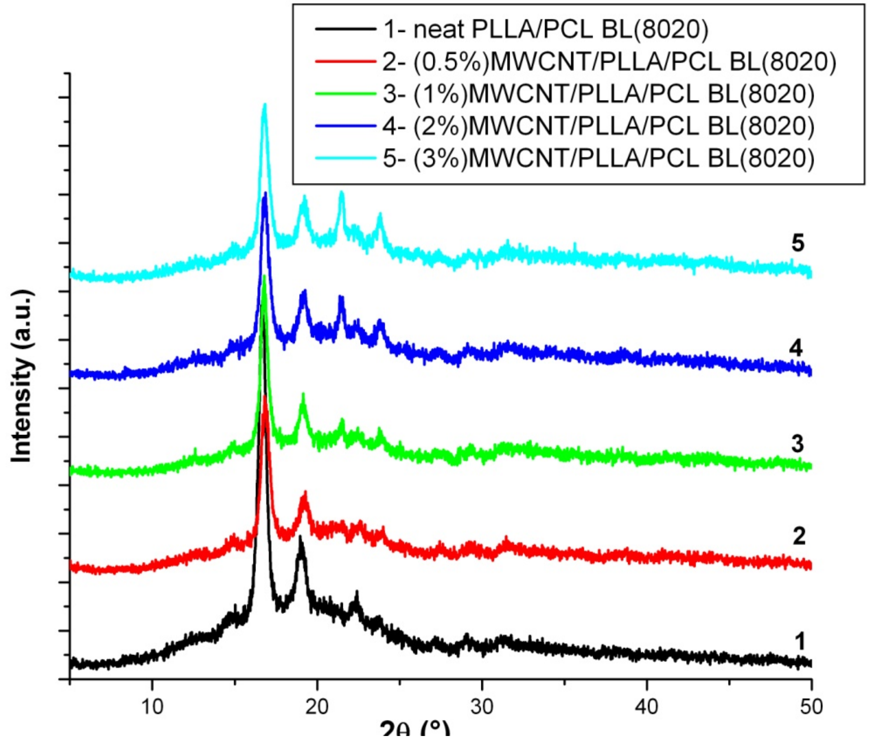


Nucleation point of large spherulites are entangled and aligned MWCNT-g-PLLAs. orientation of grafted PLLA chains on the sidewall of MWCNTs accelerate the crystallization of matrix PLLA chains

Crystallinity, XRD



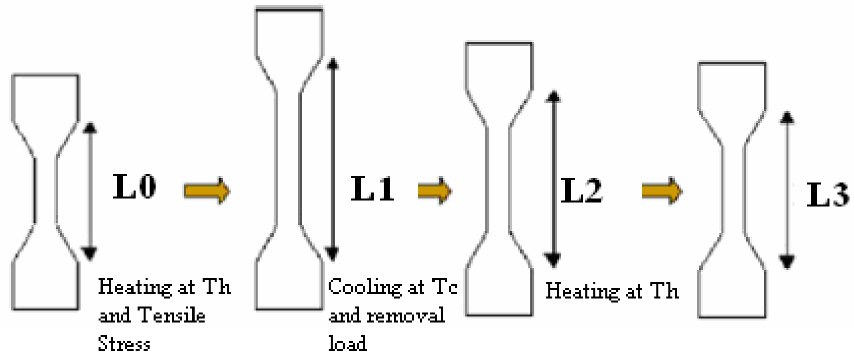
PLLA/PCL blends



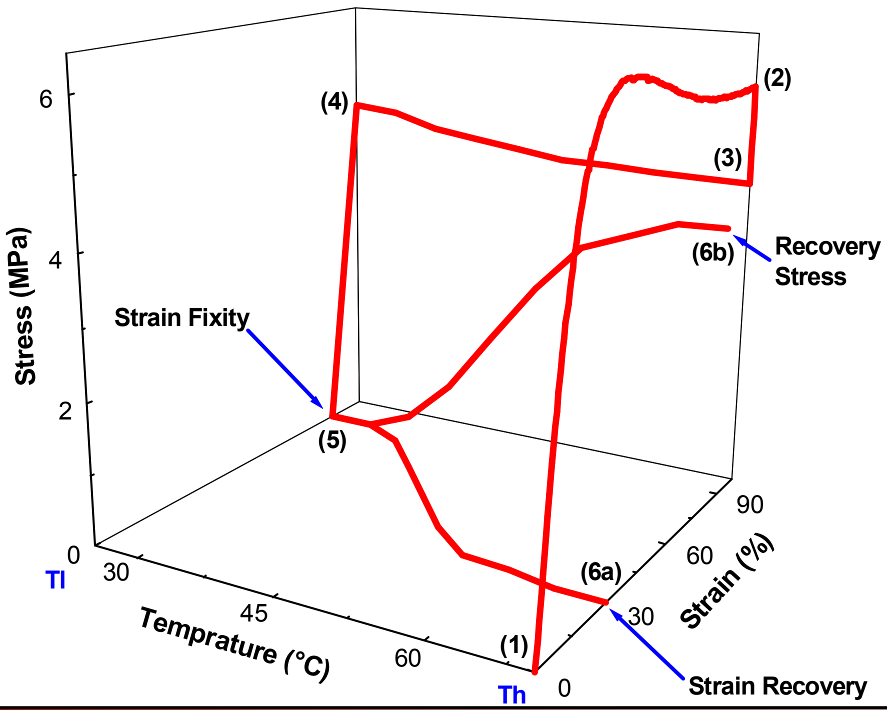
MWCNT/PLLA/PCL composites

PLLA: two peaks at 2θ=17° and 19.3°
PCL : two peaks at 2θ=21.3° and 23.7°

Shape memory analysis



Scheme of shape memory effect analysis under tensile test device.
L0: original length,
L1: strained at Th, L2: deformed length at Tl after load removal,
L3 = final length at Th

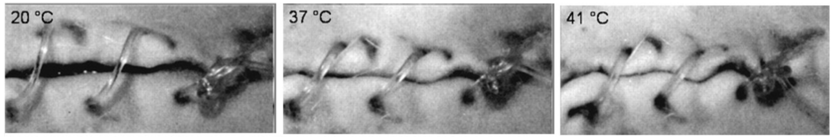


Scheme of typical SMP thermo mechanical cycles showing the shape memory effect and the recovery stress

Shape memory analysis

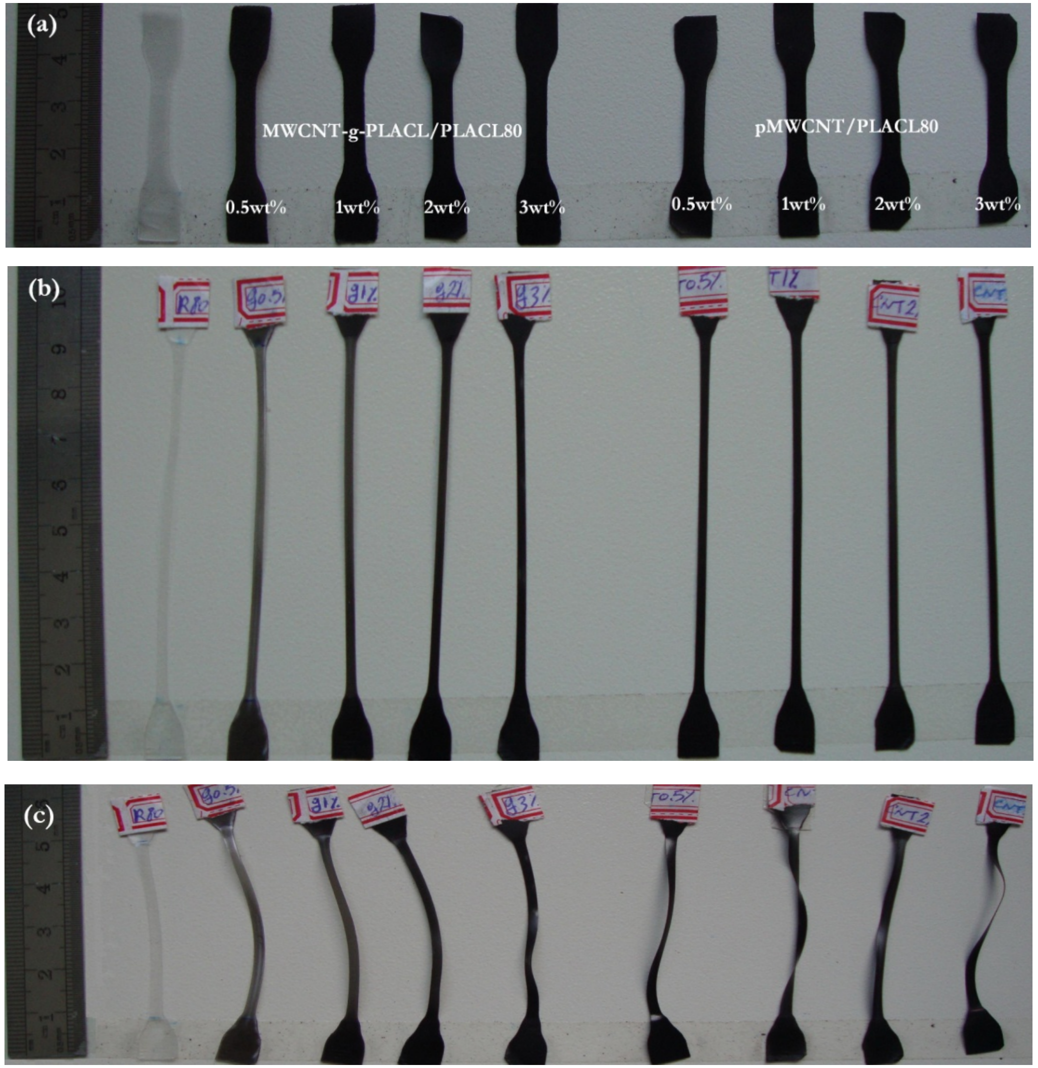
Strain fixity (Rf),

$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_m} \times 100$$

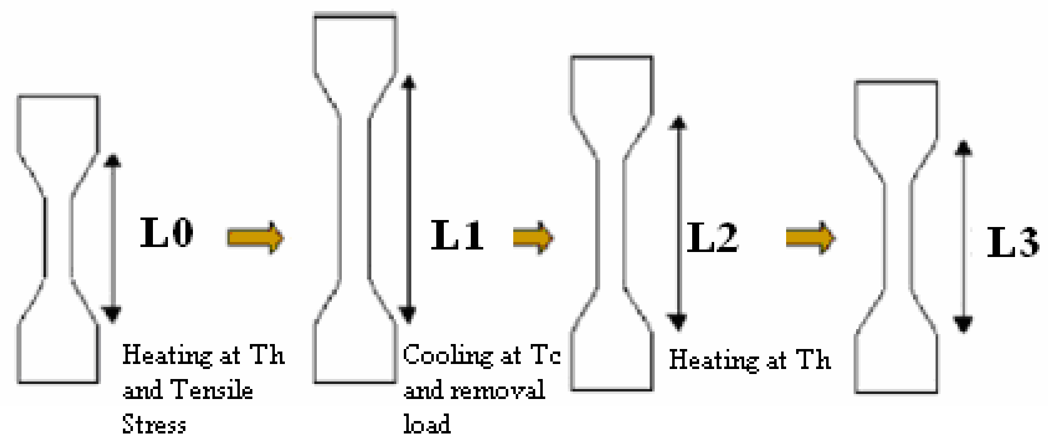


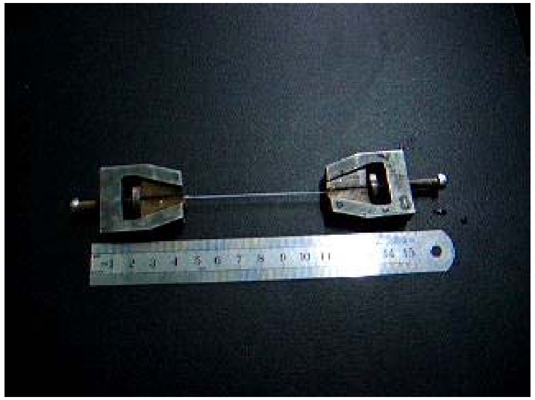
Strain recovery (Rr),

$$R_r(\%) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100$$



Shape memory analysis





strain (ε_m) ε_u ε_p

Strain fixity (Rf),

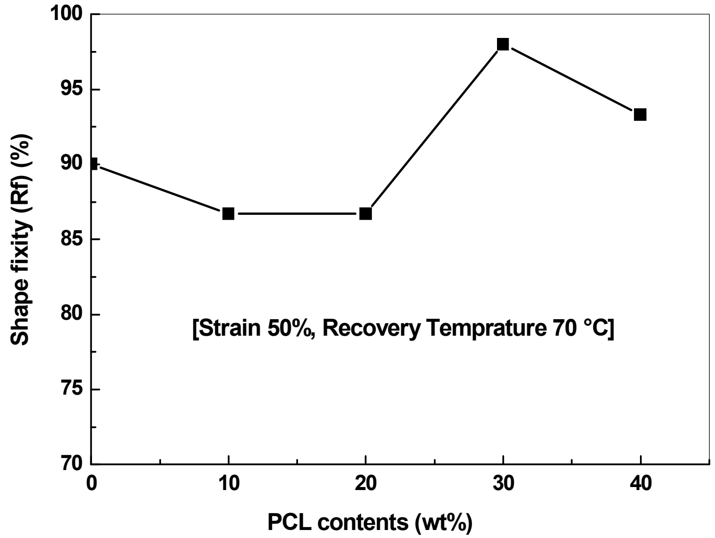
$$R_f(\%) = \frac{\varepsilon_u}{\varepsilon_m} \times 100$$

Strain recovery (Rr),

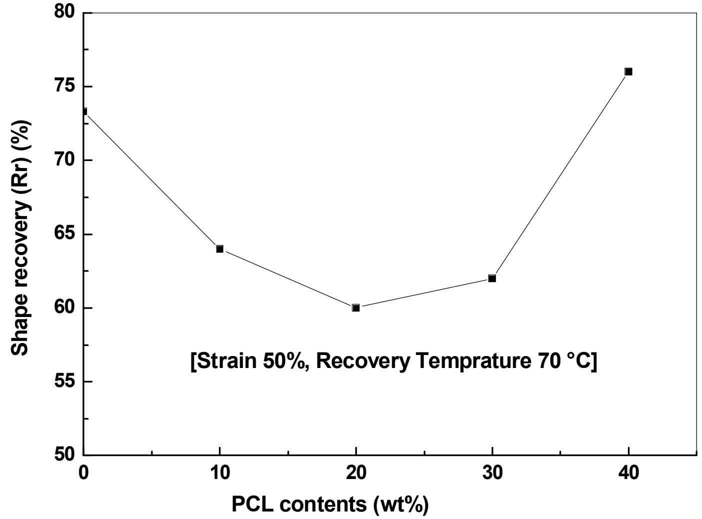
$$R_r(\%) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100$$

Shape memory analysis

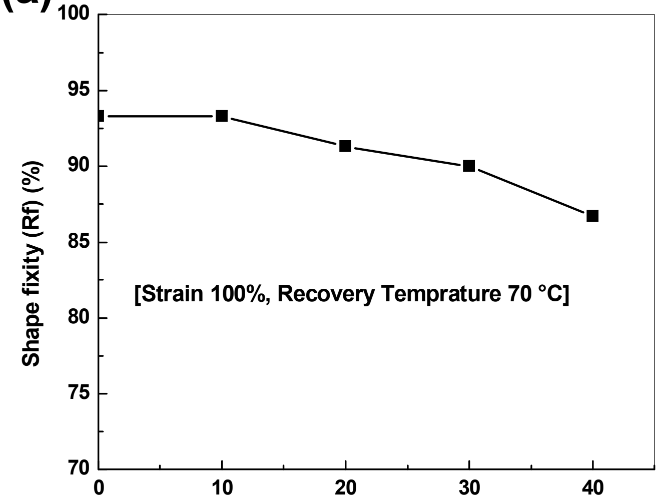
(a)



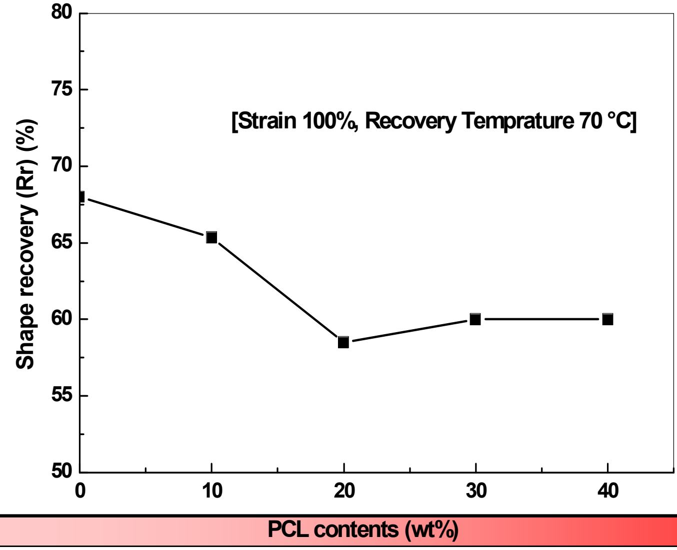
(b)



(a)

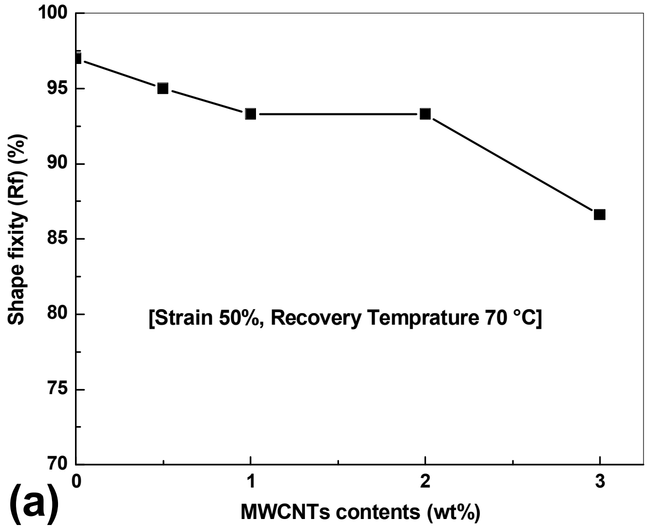


(b)

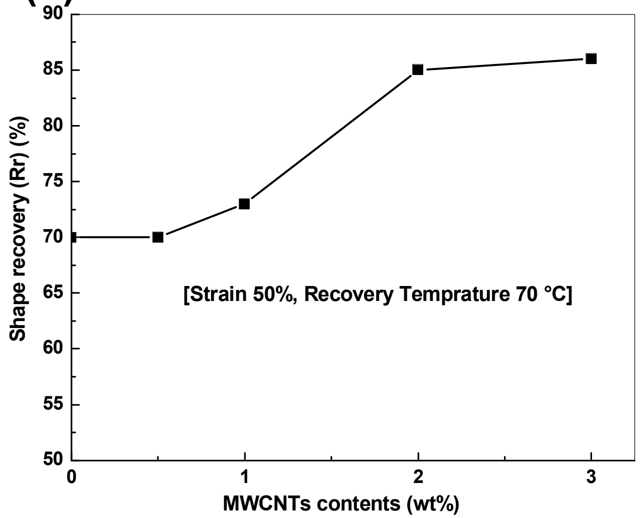


Shape memory analysis

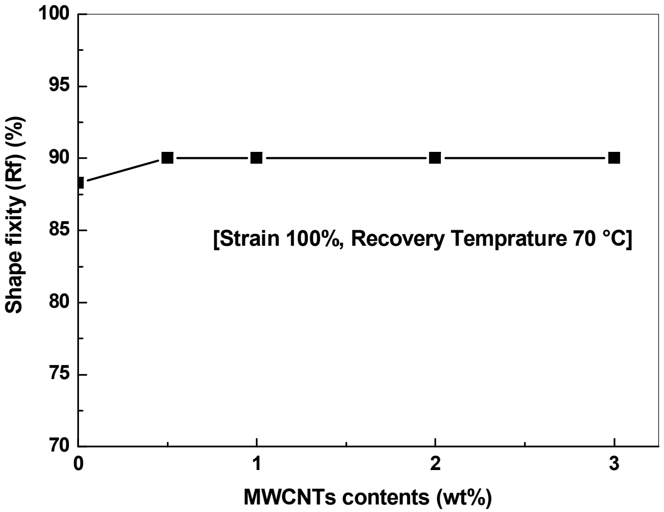
(a)



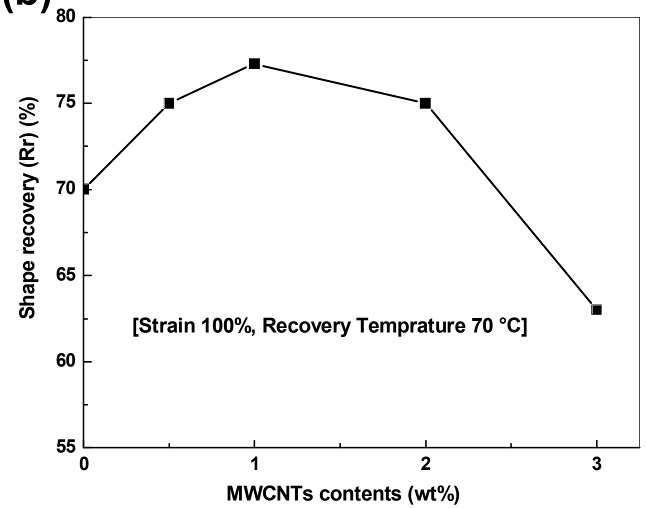
(b)



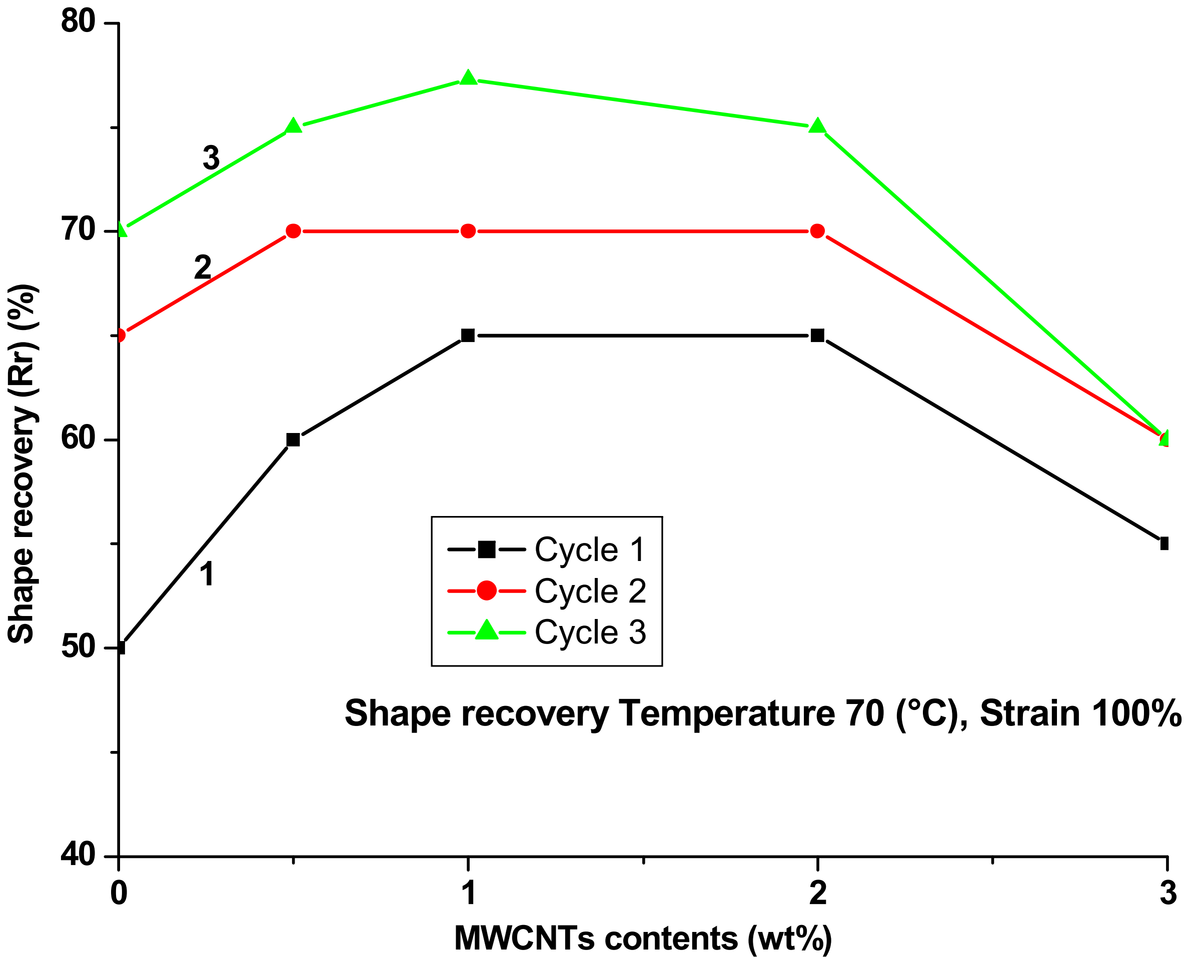
(a)



(b)



Properties (Shape Memory by tensile test)



Trainability of composites under shape memory test

Conclusions

1- PCL behaves as a polymeric plasticizer and enhances the flexibility of PLLA, while the MWCNTs enhance the mechanical strength of compounds.

2- Addition of MWCNTs to the blends increases the mechanical strength. The strain at break is effectively lower by the addition of MWCNTs to blend, and this is followed by increase in the strength at break.

3- MWCNTs in the composites increase the shape recovery ratio and decrease the shape fixity ratio.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United Nations Educational, Scientific and Cultural Organization
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Than you