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

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Outline

- Background and Purpose
  - Biodegradable polymers
  - Shape memory polymers

- Materials and Experimental Procedures
  - Crystallinity of composites
  - Shape memory effect of composites

- Conclusions
Polyesters:
- Poly L-lactide (PLLA),
- Poly glycolic acid,
- Poly e-caprolactone (PCL),
- Poly Ethylene glycol

Application:
- An alternative to non-degradable polymers,
- Hard tissue engineering, bone fixing,
- Controlled drug delivery systems,
- Surface-eroding systems,
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 field, 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 °C), while PLLA is rigid, hard, brittle and has a higher melting temperature (178~182 °C).

The blend of these polymers possessed properties partly like that of PLLA and partly like that of PCL.

![Chemical structures of PLLA and PCL](image)
Background
Poly L-lactide (PLLA cycle)

Biomass, corn

Lactic acid from Dextrose

Condensation process

Purification by distillation

Lactic acid OH

O

H

HO

H

CH₃

Reduction to monomer

Reduce Global Green House Effect

Reduction of annually renewable resources

Products
Packaging, Textiles, Medicine
Degradation time for Biodegradable polymers: 6 months to 2 years
Degradation time for Conventional plastics: 500 – 1000 years
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

\[
\begin{align*}
\text{HO-} & \text{C-} \text{O-} \text{OH} \quad \text{Dehydration} \\
\text{CH}_3 & \quad \xrightarrow{H_2O} \quad \text{H-} \left[ \text{O-} \text{C-} \text{O-} \right]_n \text{H} \\
& \quad \xrightarrow{\text{Thermal Cracking}} \quad \text{H}_3\text{C-} \text{O-} \text{C-} \text{O-} \text{CH}_3 \\
& \quad \xrightarrow{\text{Ring-Opening Polymerization}} \quad \left[ \text{O-} \text{C-} \text{O-} \right]_n \text{R}
\end{align*}
\]

L-lactide Oligomer  PLLA  PCL
Experimental: LA and PLLA synthesis

1- Synthesis of L-Lactide oligomer

$$\text{L-lactic acid} \rightarrow \text{L-lactide}$$

$$\text{Zinc Oxide} \quad 80 \degree C \rightarrow 260 \degree C$$

2- Polymerization of L-lactide

$$\text{L-lactide} \rightarrow \text{Poly (L-lactide)}$$

$$\text{St(Oct)2} \quad 130-140 \degree C$$
Experimental:

Solution casting of composites

Polymer particle

\[\downarrow \text{dissolve}\]

Polymer solution

Nanotube

\[\downarrow \text{disperse}\]

Nanotube solution

Mixed

Mixed solution

\[\downarrow \text{Dry and get solid film}\]

Cut samples

Solution casting using chloroform as solvent
Morphology, SEM

(a) PLLA

(b) PLLA/PCL8020

(c) PLLA/PCL6040

(d) 3wt%MWCNT/PLLA/PCL8020
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)

- 0.5% MWCNTs
- PLLA/PCL8020
- 1% MWCNTs
- 2% MWCNTs
- 3% MWCNTs
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: two peaks at $\theta = 17^\circ$ and $19.3^\circ$

PCL: two peaks at $\theta = 21.3^\circ$ and $23.7^\circ$
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 ($\varepsilon_m$)  $\varepsilon_u$  $\varepsilon_p$

Strain fixity ($R_f$),

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

Strain recovery ($R_r$),

\[
R_r(\%) = \frac{\varepsilon_m - \varepsilon_p}{\varepsilon_m} \times 100
\]
Shape memory analysis

(a) Shape fixity (Rf) (%)

[Strain 50%, Recovery Temperature 70 °C]

(b) Shape recovery (Rr) (%)

[Strain 50%, Recovery Temperature 70 °C]

(a) Shape fixity (Rf) (%)

[Strain 100%, Recovery Temperature 70 °C]

(b) Shape recovery (Rr) (%)

[Strain 100%, Recovery Temperature 70 °C]
Shape memory analysis

(a) [Strain 50%, Recovery Temperature 70 °C]
- Shape fixity (Rf) (%)
- MWCNTs contents (wt%)

(b) [Strain 50%, Recovery Temperature 70 °C]
- Shape recovery (Rr) (%)
- MWCNTs contents (wt%)

(a) [Strain 100%, Recovery Temperature 70 °C]
- Shape fixity (Rf) (%)
- MWCNTs contents (wt%)

(b) [Strain 100%, Recovery Temperature 70 °C]
- Shape recovery (Rr) (%)
- MWCNTs contents (wt%)
Properties (Shape Memory by tensile test)

Trainability of composites under shape memory test

Shape recovery Temperature 70°C, Strain 100%

MWCNTs contents (wt%)
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.
Thank you