Polymer processing influence on the double electrical percolation threshold in PLA/PCL/GNP nanocomposites

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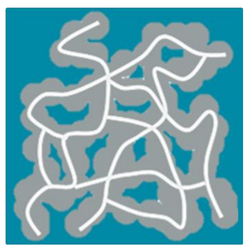
Introduction

Context/ interest:

- Percolation theory: Explains the transition from an insulating material to a conductive one in conductive filled polymer composites.
- Electrical percolation threshold: Minimal filler concentration required to acquire a conductive network within the polymer matrix
- How to reduce the electrical percolation threshold? By creating a **double electrical percolation threshold** resulting from adding the conductive filler to an immiscible polymer blend matrix
  Required conditions for the **double electrical percolation threshold** [1], [2]:
  1) Co-continuous polymer blend
  2) Selective localization of the conductive filler in a single polymer phase

1  2 

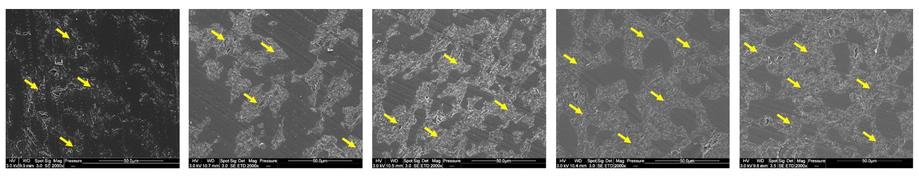
Objectives:

- Obtaining the **double electrical percolation threshold** in poly(lactic acid) (PLA)/ polycaprolactone (PCL)/ Graphene nanoplatelets (GNP) nanocomposites
- Studying the influence of different manufacturing processes on the co-continuous microstructure and the electrical conductivity of PLA/PCL/GNP nanocomposites
  The used processes are:

✓ **Compression molding**
✓ **3D printing** (Fused Filament Fabrication or FFF) preceded by **single-screw extrusion**
In our previous work, a comparison between 3D printing and injection molding influence on the microstructure and therefore the electrical conductivity of PLA/PCL/GNP composites took place [3].

Compression molded samples

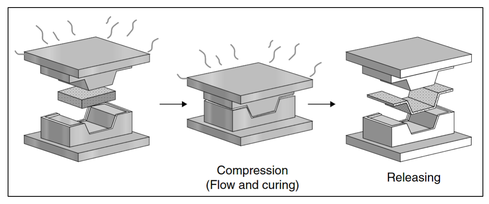
Selective localization of graphene in the PCL phase


PLA65/PCL35/10 wt.% GNP PLA60/PCL40/10 wt.% GNP PLA50/PCL50/10 wt.% GNP PLA40/PCL60/10 wt.% GNP PLA30/PCL70/10 wt.% GNP

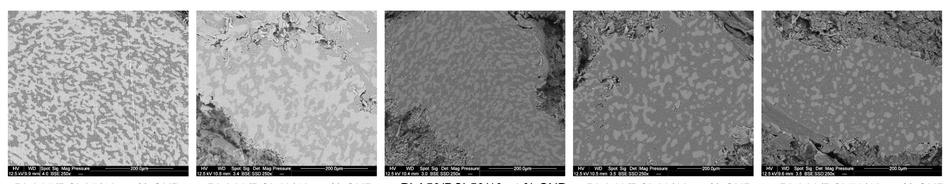
- PLA/PCL/GNP compression molded composites: Permanent selective localization of GNP in the PCL phase **(The graphene + PCL zones are indicated by yellow arrows.)**
- Good dispersion of graphene particles in the PCL phase

Processing steps:

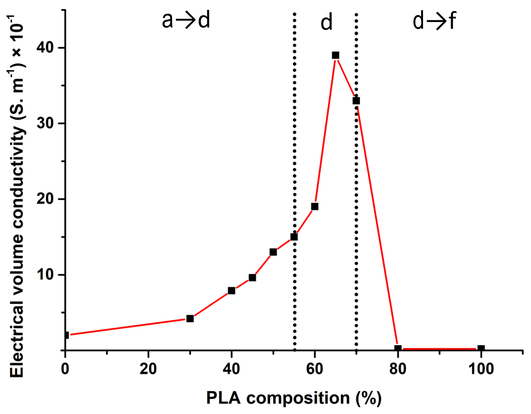
- Twin-screw extrusion to blend PLA, PCL, and GNP together
- Compression molding to prepare samples for analysis
- PLAx/PCLy/10 wt.% GNP were produced **(x varies between 0 wt.% and 100 wt.% in the polymer total weight percentage).**



Co-continuous microstructure

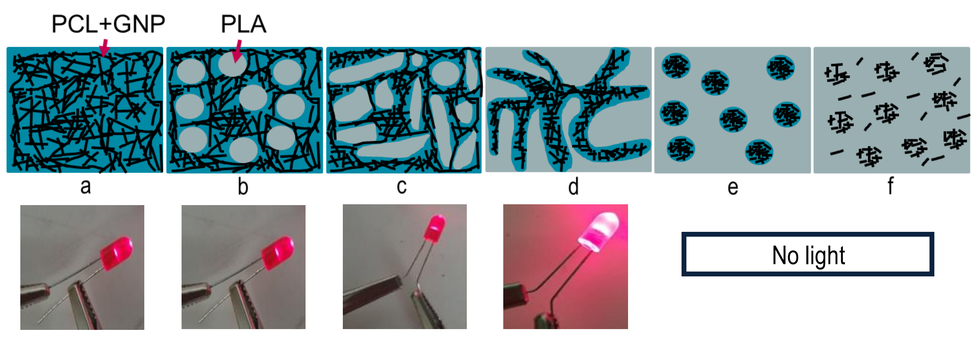

PLA65/PCL35/10 wt.% GNP PLA60/PCL40/10 wt.% GNP PLA50/PCL50/10 wt.% GNP PLA40/PCL60/10 wt.% GNP PLA30/PCL70/10 wt.% GNP

- Co-continuous microstructure is present in PLA65/PCL35/10 wt.% GNP and PLA60/PCL40/10 wt.% GNP formulations (The brighter phase is the PLA phase, and the darker phase is the PCL phase).
- The other samples possess a sea-island morphology where the PLA nodules are dispersed in the continuous PCL phase.



Evolution of the electrical conductivity as a function of the PLA content

Double electrical percolation threshold

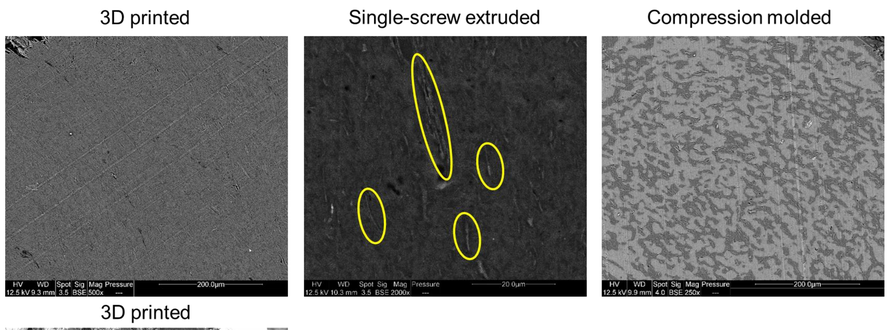


a→d: As the percentage of PLA increases from 0 wt.% to 55 wt.% in the composites, the electrical volume conductivity increases due to the greater confinement of the GNP dispersed in the PCL matrix.

d: Co-continuous morphologies are observed in the PLA55/PCL45-PLA70/PCL30 range with 10 wt.% GNP. The electrical conductivity is the highest in this zone with the best results for PLA65/PCL35/10 wt.% GNP.
A double electrical percolation threshold can be highlighted in this zone.

d→f: The electrical volume conductivity decreases again with the increase of the PLA percentage to reach its minimal value at PLA/10 wt.% GNP.

3D printed samples

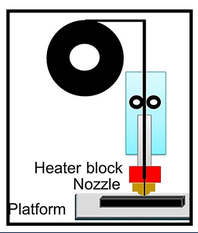


PLA65/PCL35/10% GNP

- 3D printed sample: Good adhesion between the layers
- 3D printed sample vs compression molded sample: Smaller co-continuous microstructure existing separately in each deposited layer

Processing steps:

- Twin-screw extrusion to blend PLA, PCL, and GNP together
- Single-screw extrusion to fabricate calibrated filaments
- Fused filament fabrication to manufacture the samples to be analyzed (compared with the compression molded samples)



Sample	Electrical volume conductivity (S. m^{-1})	Porosity (%)	LED (5 v)
PLA80/PCL20/10 wt.% GNP	< 10^{-5}	12	No light
PLA65/PCL35/10 wt.% GNP	0.1	16	
PLA50/PCL50/10 wt.% GNP	0.03	14	No light
PLA40/PCL60/10 wt.% GNP	0.019	14	No light
PLA30/PCL70/10 wt.% GNP	0.014	15	No light

References

[1]: Huang et al., Control of carbon nanotubes at the interface of a co-continuous immiscible polymer blend to fabricate conductive composites with ultralow percolation thresholds, Journal: Carbon, Vol 73, 2014, Pages 267-274

[2]: Chen et al., Balance the electrical properties and mechanical properties of carbon black filled immiscible polymer blends with a double percolation structure, Journal: Composites Science and Technology, Vol 140, 2017, Pages 99-105

[3]: Masarra et al., Fabrication of PLA/PCL/Graphene nanoplatelets (GNP) electrically conductive circuit using the fused filament fabrication (FFF) 3D printing technique, Journal: Materials, Vol 15, 2022

Conclusion

- This work succeeded for the first time to obtain the **double electrical percolation threshold** in PLA/PCL/GNP composite systems.
- The influence of several manufacturing processes on the co-continuity of PLA and PCL and consequently the electrical volume conductivity were addressed for the first time.
- Compression molded samples: Wide range of co-continuity that varies between PLA55/PCL45/10 wt.% GNP and PLA70/PCL30/10 wt.% GNP.
  Reason: Induced annealing effect
- 3D printed samples: PLA65/PCL35/10 wt.% GNP shows the highest electrical conductivity but still less than that of the compression molded sample
  Reason: Small co-continuous microstructure present in each deposited layer

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