



Functionalization of polycaprolactone using glycidyl methacrylate in supercritical carbon dioxide for polycaprolactone-starch blend

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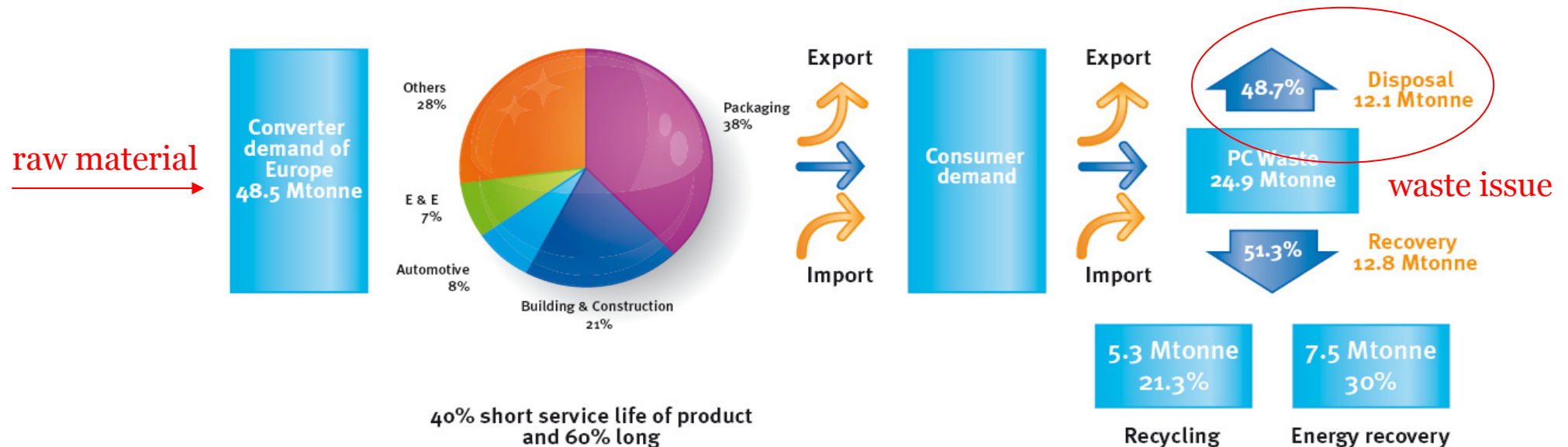
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Outline

- Introduction
- Research strategy
- Results and discussions
- Conclusions

Introduction

Plastic supply chain and waste management



Plastics from cradle to cradle in Europe (2008)

- The use of plastic is ‘irreplaceable’
- High demand of plastics requires high amount raw material
- High amount of plastic waste generated every year and most of the waste end up in the disposal

Bioplastic



- The focus here is on their functionality '*compostability*'.

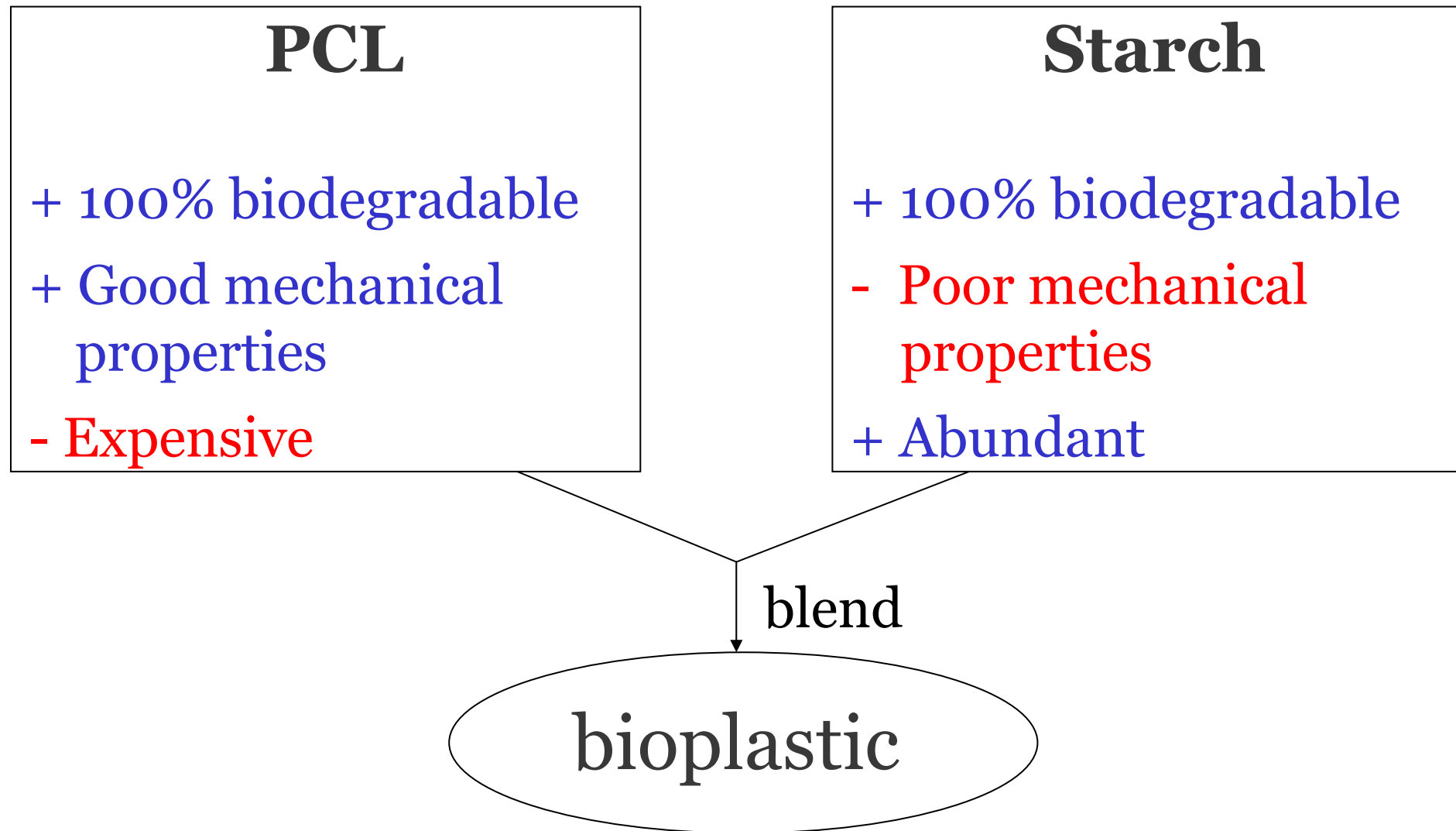
Compostable plastics certified according to EN13432 and based on renewable (biobased) and/or non-renewable (fossil) resources

- The focus here is their *raw materials basis*.

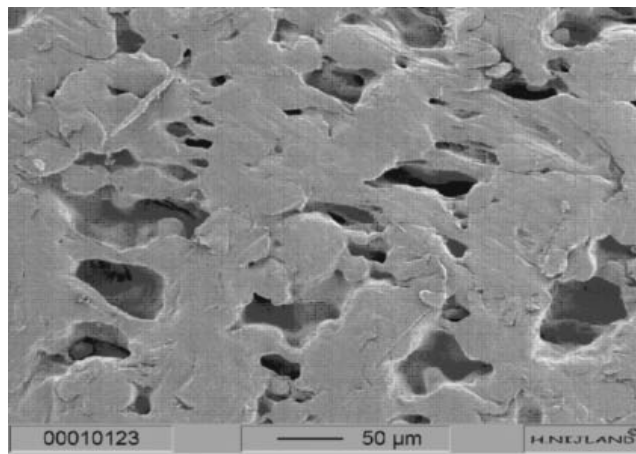
Biobased plastics produced on the basis of **renewable resources**

- sugar family
- vegetable oils and animals fat
- proteins
- chitosan
- etc.

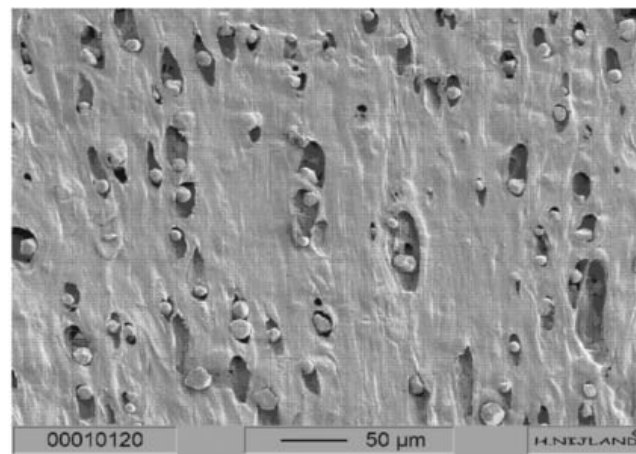
Bioplastic based on polycaprolactone (PCL) and starch



PCL-starch blends



a.



b.

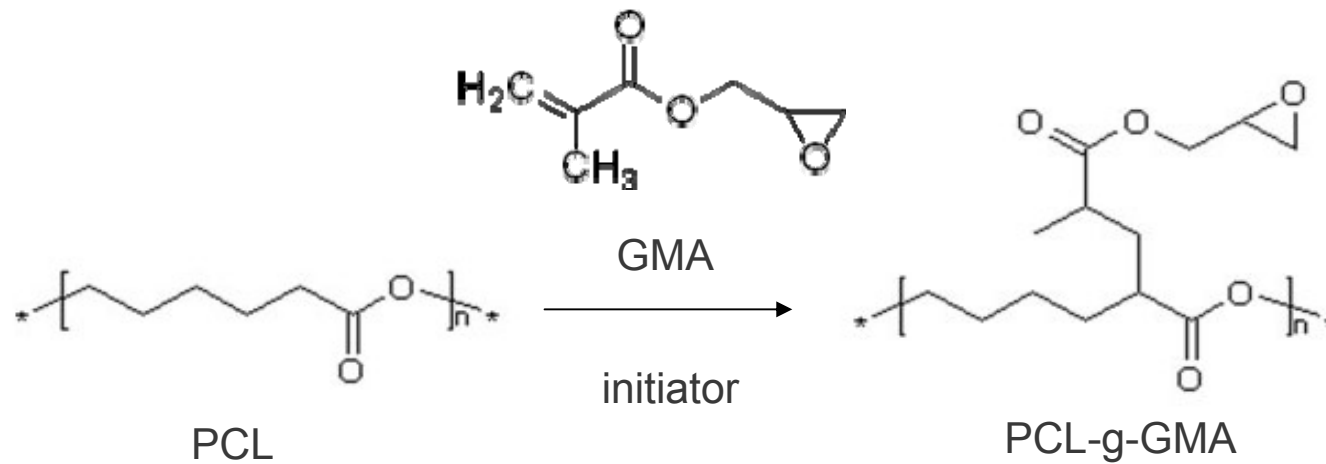


c.

Morphology of starch/PCL binary blends. (a) S/PCL 10/90, (b) S/PCL 20/80
Blend process is using a (c) Brabender batch-mixer

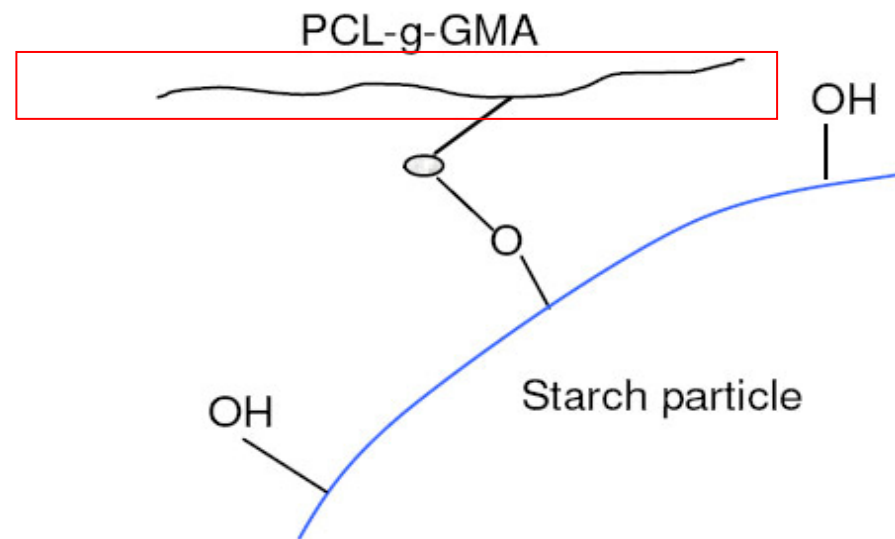
- PCL interacts poorly with starch
- compatibilizer is required to improve the interaction

Compatibilizer precursor for PCL-starch blends



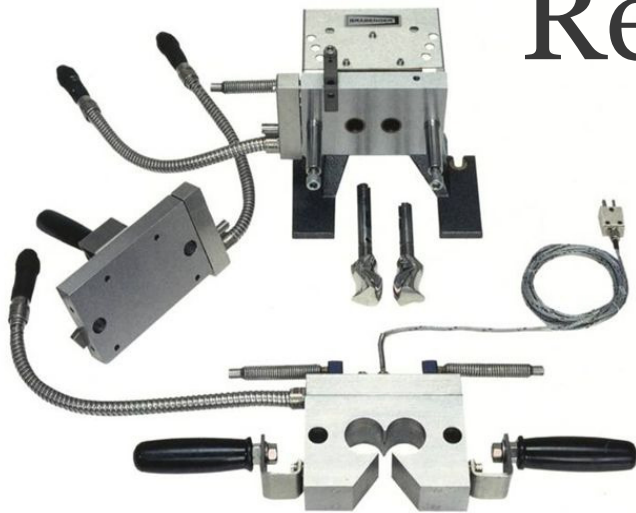
- PCL grafted by glycidyl methacrylate (GMA) is used as compatibilizer precursor

Ternary blends of PCL-compatibilizer-starch



- Grafted monomers site interacts with starch
- PCL backbone of the compatibilizer interacts with PCL

Research strategy



- Thermal degradation of PCL backbone occurred during the grafting process (batch-kneader mixing)



- Grafting under supercritical CO₂ at a lower temperature !!!

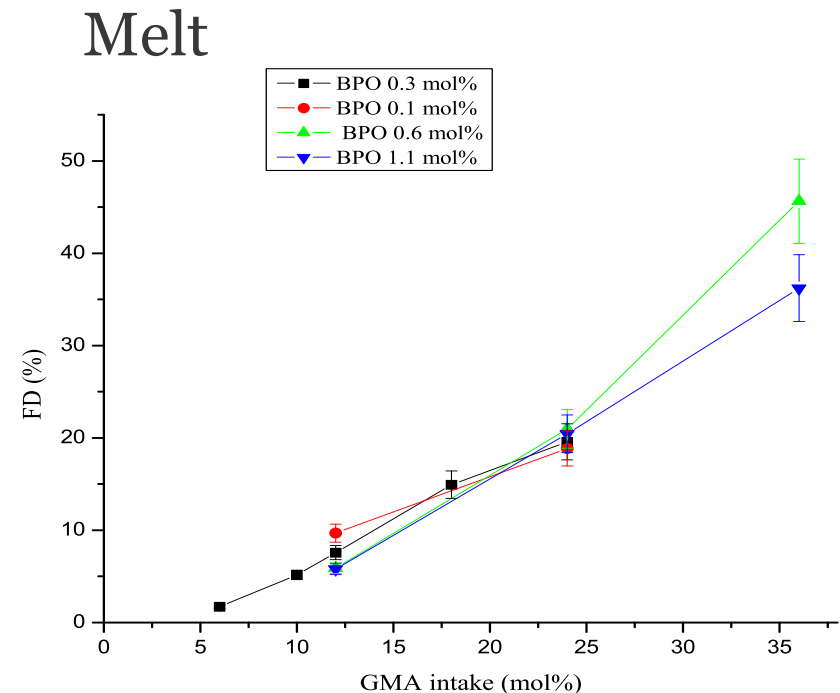
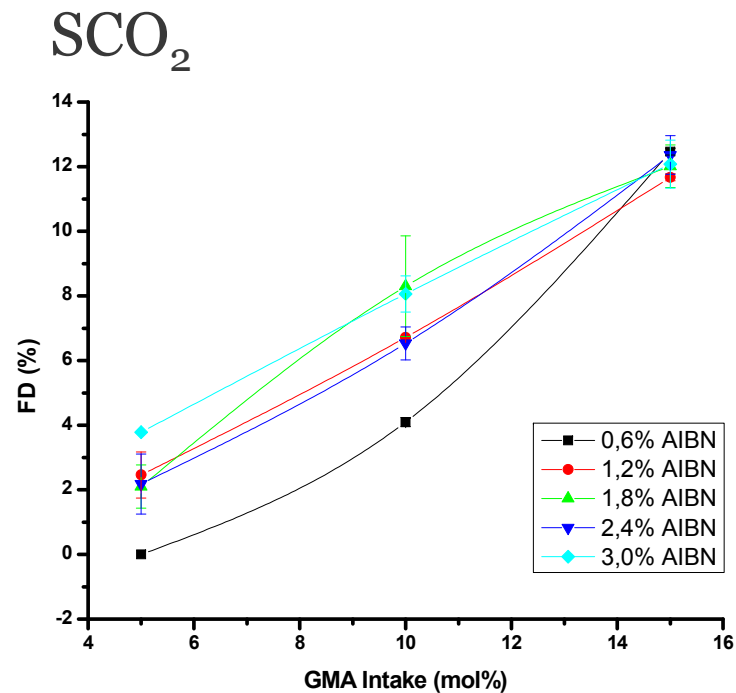
Results and discussions

PCL-g-GMA synthesis

Methods	T (°C)	P (bar)	t (min)	Stirring (rpm)	initiator
Melt	130	-	15	80	benzoyl peroxide
Supercritical CO ₂	97	90	40	900	azobisisobutyronitrile

- Grafting process of GMA onto PCL has been performed using two approaches, normal melt processing and under **supercritical CO₂ (new method)**.
- Grafting at lower temperature lowers thermal degradation of PCL backbone

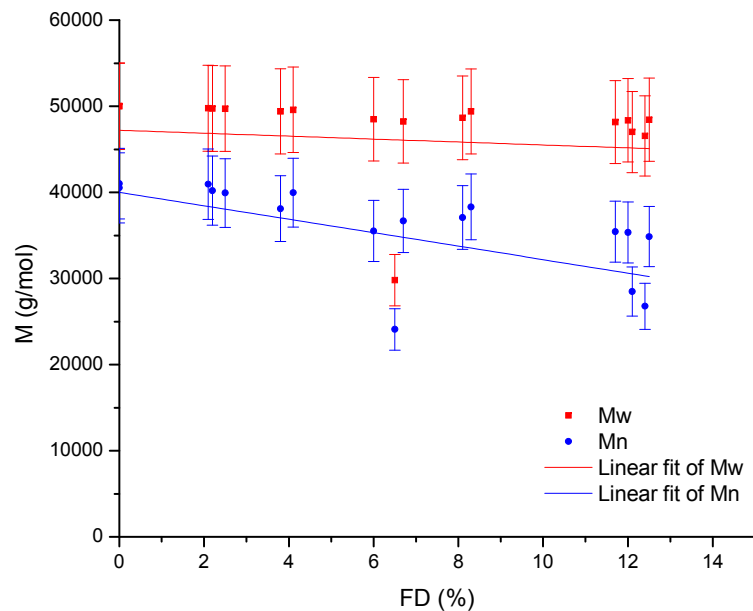
FD as function of GMA intakes



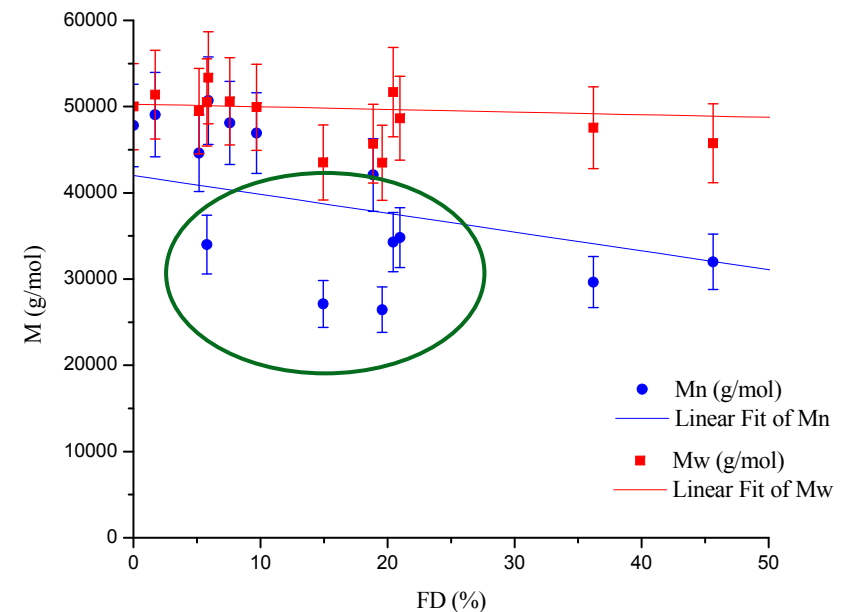
- FD increases along with the GMA
- After a certain amount, initiator intake gives a low effect to the FD
- Different FD and compatibilizer intakes were used to investigate changes in mechanical properties of the blends

Thermal degradation study of PCL-g-GMA

SCO₂

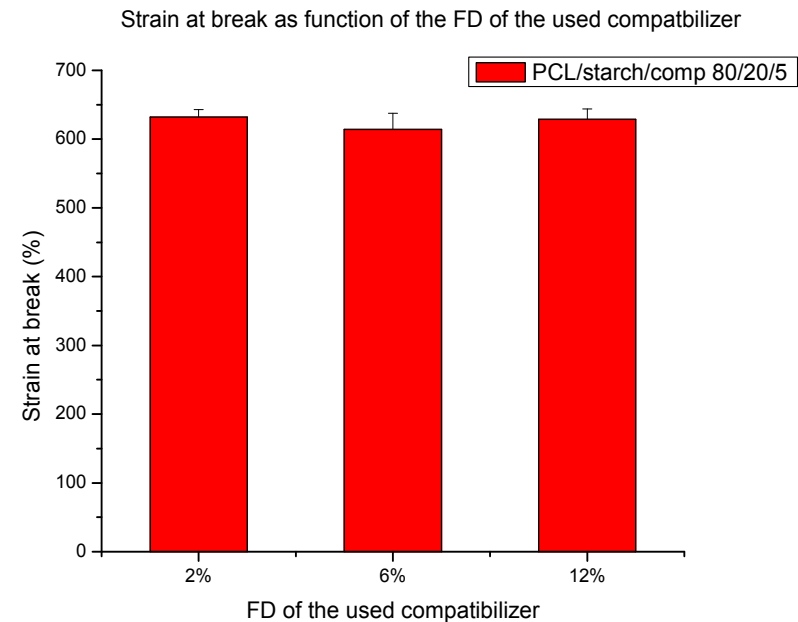
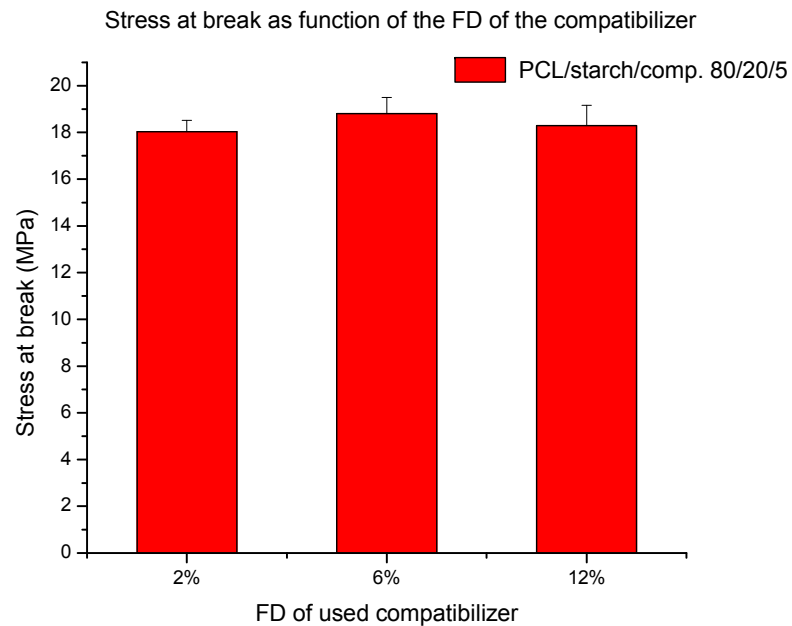


Melt



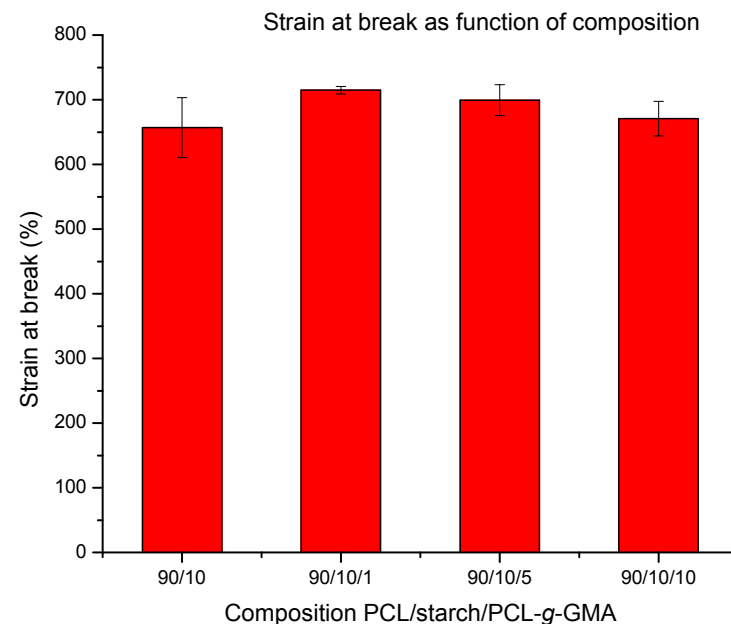
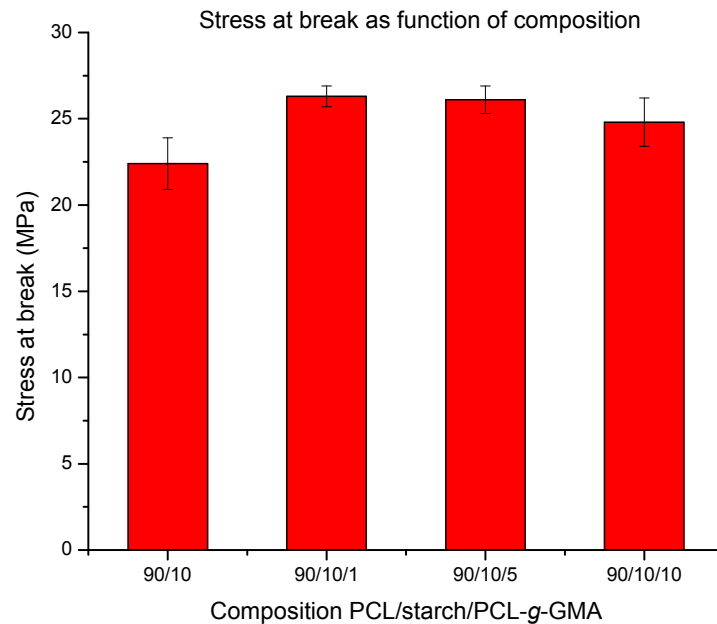
- There was no significant degradation/cross linking observed from the reactions in supercritical carbon dioxide, some changes were observed from reactions in the melt.

The effect of compatibilizer FD to the blends mechanical properties



- Functionalization degree of the compatibilizer does not significantly affect the mechanical properties.

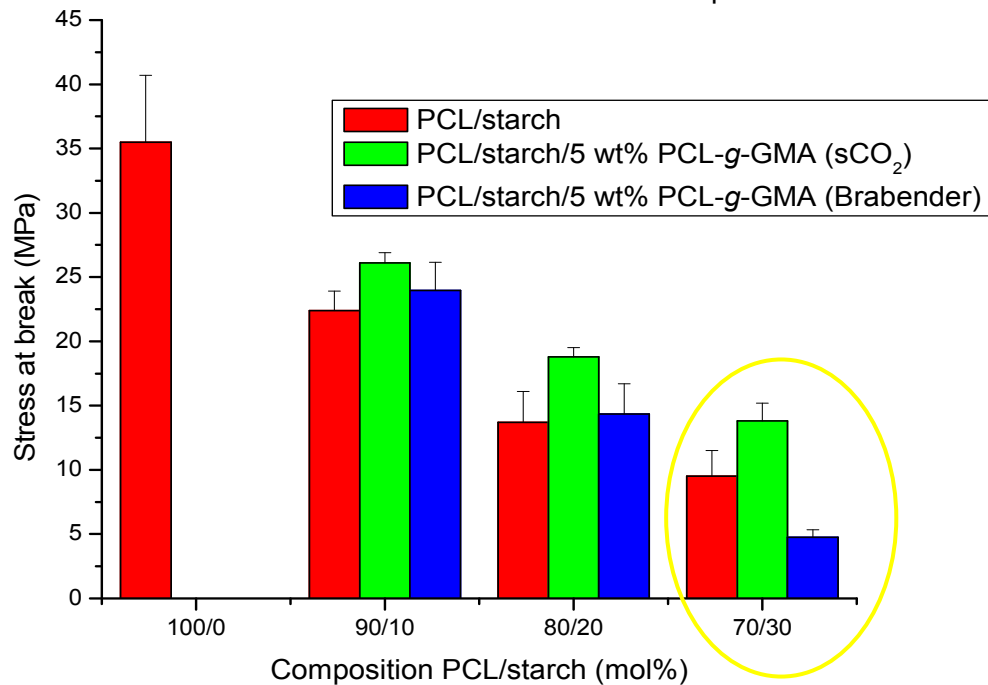
The effect of compatibilizer amount to the blends mechanical properties



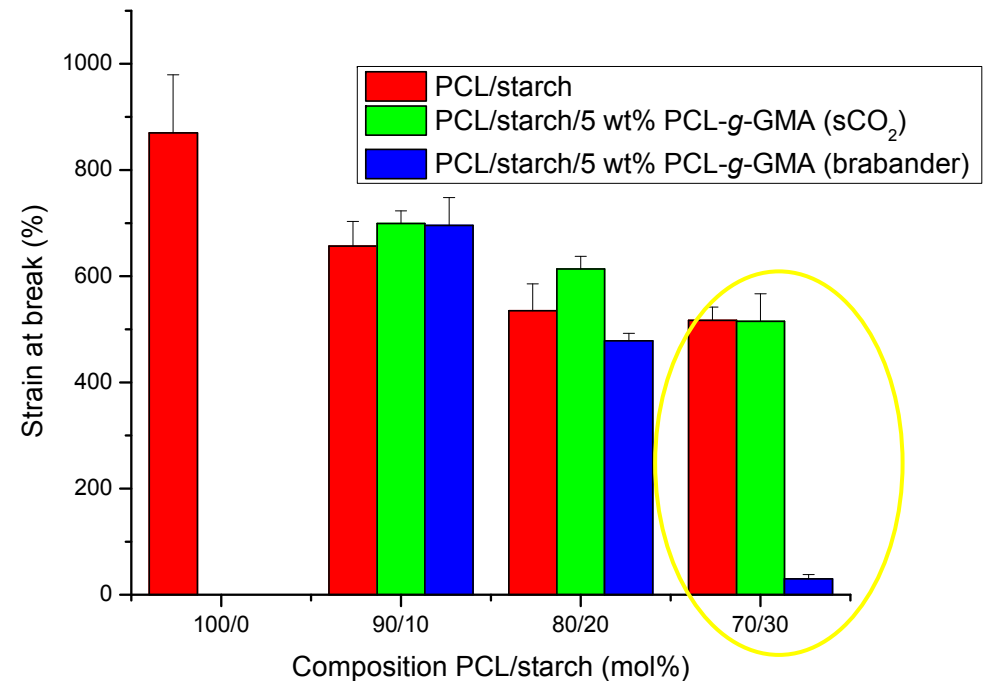
- Intake of the compatibilizer does not significantly affect the mechanical properties.

Ternary blend comparison

Stress at break as function of the composition



Strain at break as function of composition.



- Blends with compatibilizers prepared in supercritical carbon dioxide have better mechanical properties with respect to those with compatibilizers prepared in the melt.

Conclusions

- Grafting process of GMA onto PCL has been performed using two approaches, normal melt processing and under supercritical CO₂.
- There was no significant degradation/cross linking observed from the reactions in supercritical carbon dioxide, some changes were observed from reactions in the melt.
- The use of compatibilizers improves the mechanical properties of the blends.
- The amount and functionalization degree of the compatibilizer does not significantly affect the mechanical properties.
- Blends with compatibilizers prepared in supercritical carbon dioxide have better mechanical properties with respect to those with compatibilizers prepared in the melt.



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Discussions

Thank You