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Effect of Reprocessing of Polyester/ Montmorillonite Nanocomposites

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The problem to be solved

Unknown properties of recycled nanocomposites.

Aim of the research

- Study the **effect of recycling** on the morphology, mechanical and thermal properties of MMT-nanocomposites with different polyester matrices.

Practical part

Types of polyesters

Petroleum-based

- Polyethylene terephthalate (PET)
- Polybutylene Terephthalate (PBT)

Bio-based

- Polybutylene succinate (PBS)
- Polylactic acid (PLA)

Montmorillonite (MMT)

Practical part

Test samples

1- After drying I compounded the nanocomposites adding 6 wt.% of MMT to each of PET, PBS, PBT and PLA using a twin screw extruder (1x extr.)

2- I repeated the extrusion for the reprocessed samples (2x extr.)

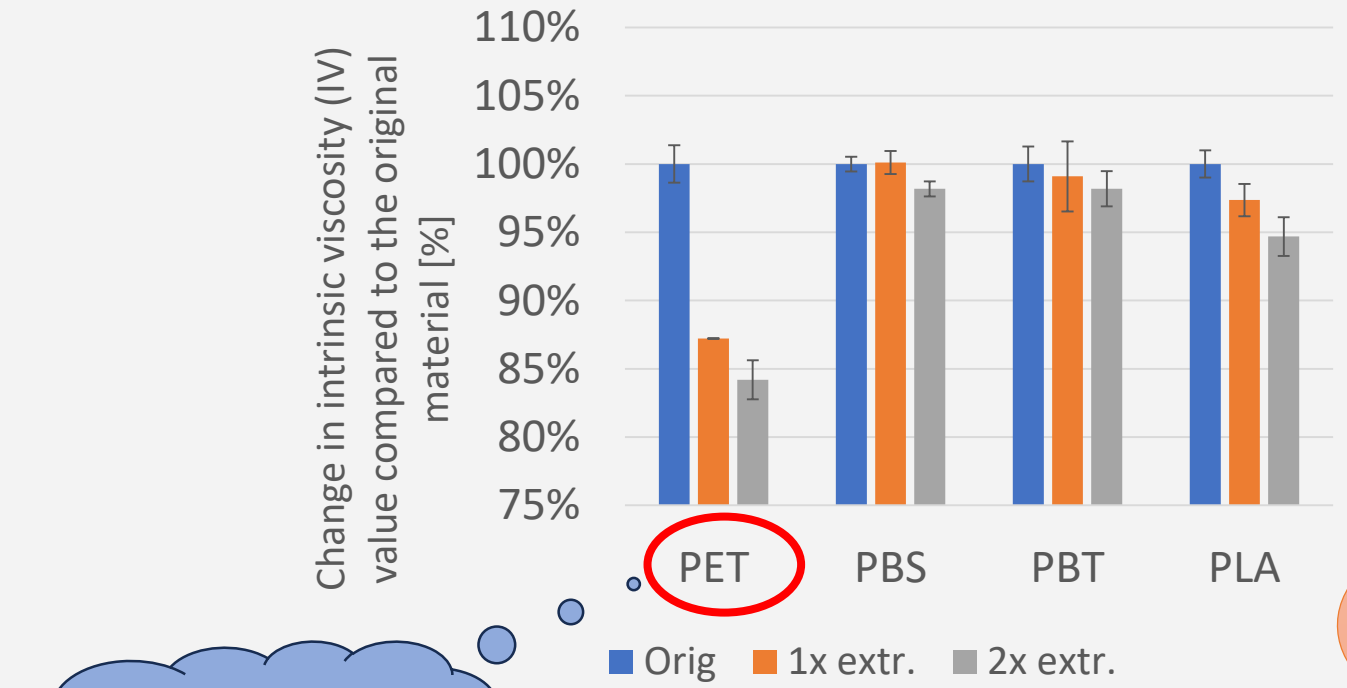
3- I dried all nanocomposite materials in an oven.

4- I used injection molding to make the test samples.

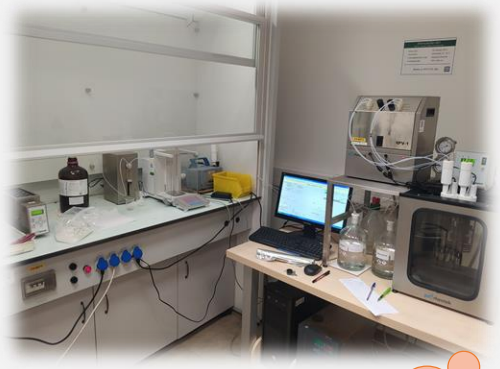
Practical part

Intrinsic viscosity (IV)

- Effect of recycling on the molecular weight of PET, PBS, PBT and PLA.



The highest degradation



Mark-Houwink

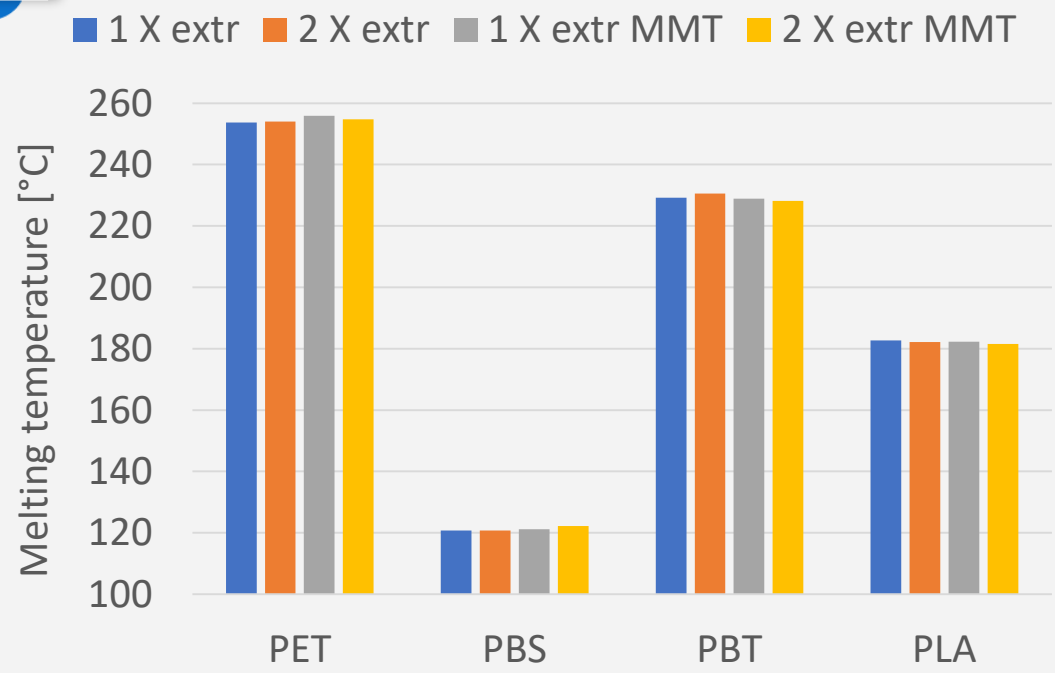
$$[\eta] = K M^{\alpha}$$

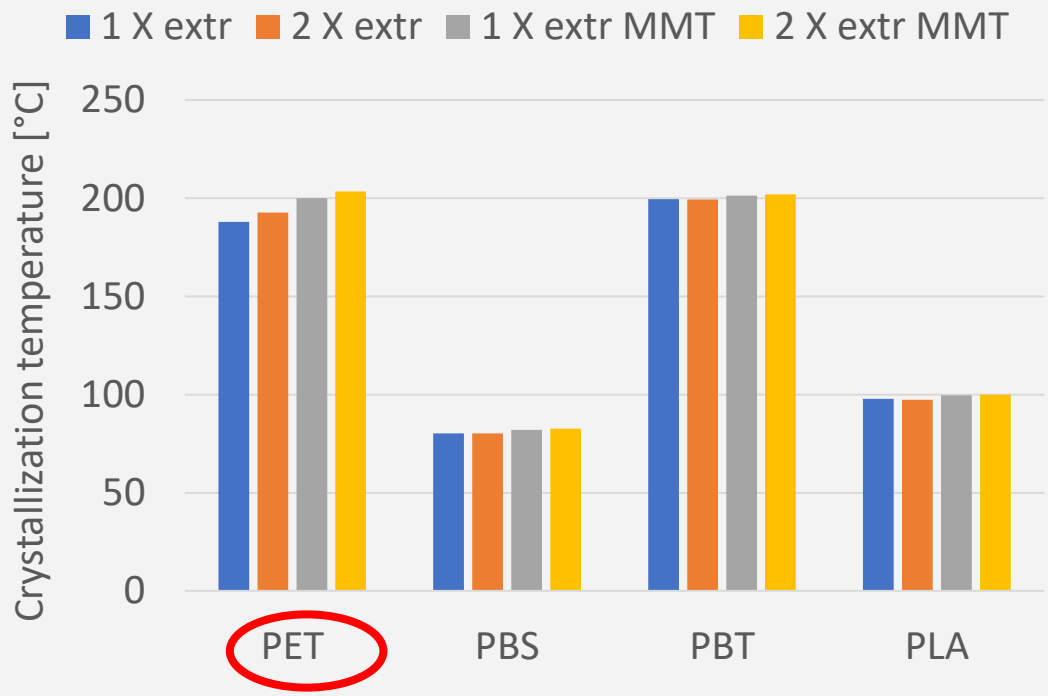
η: Intrinsic viscosity.
M: molecular weight.
K, α: constants.

Practical part

Non-Isothermal crystallization of PET, PBS, PBT and PLA

I scanned them by using a DSC during the following cooling rates 2.5, 5, 10, 20, 40°C/ min to determine the crystallization and melting temperature.



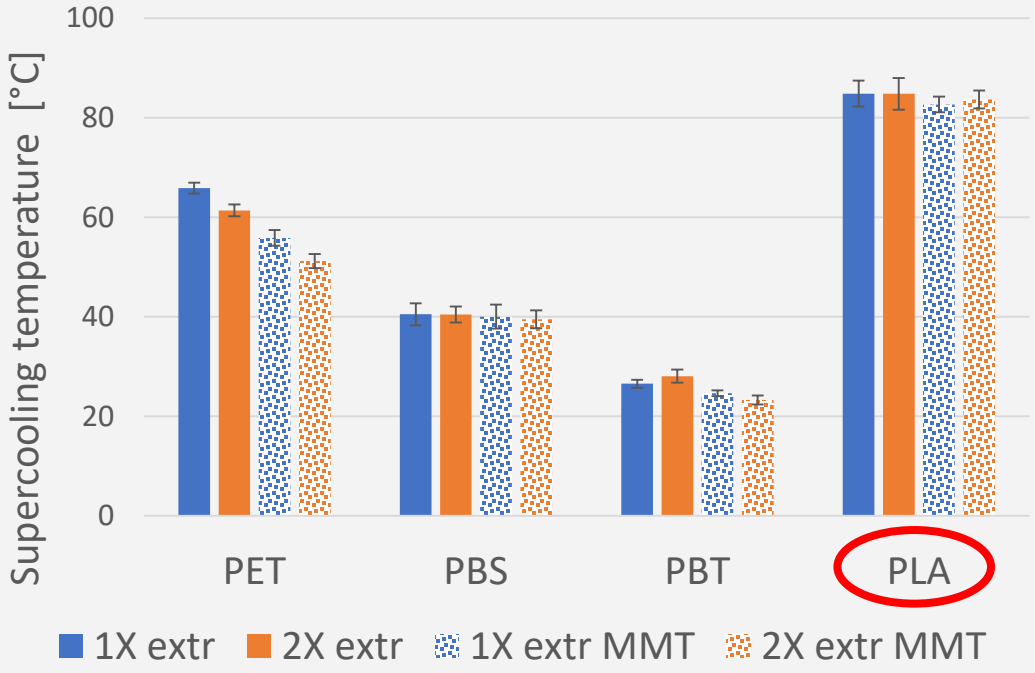


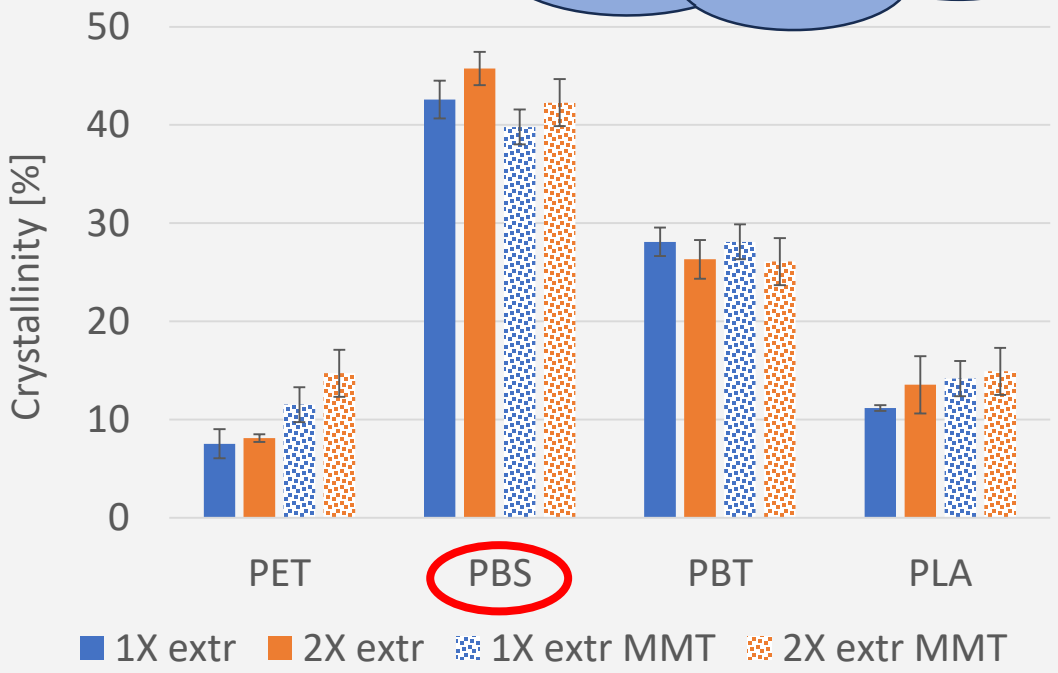
- T_m: **no** change significantly with reprocessing and MMT.
- T_c → By reprocessing → **no** change, except **PET**↑ :Lower M_w so higher crystallinity.
  → By adding MMT → ↑ of all polyesters, Nucleation effect.

Practical part

Crystallinity of composites PET, PBS, PBT and PLA

Supercooling ↔ CRF



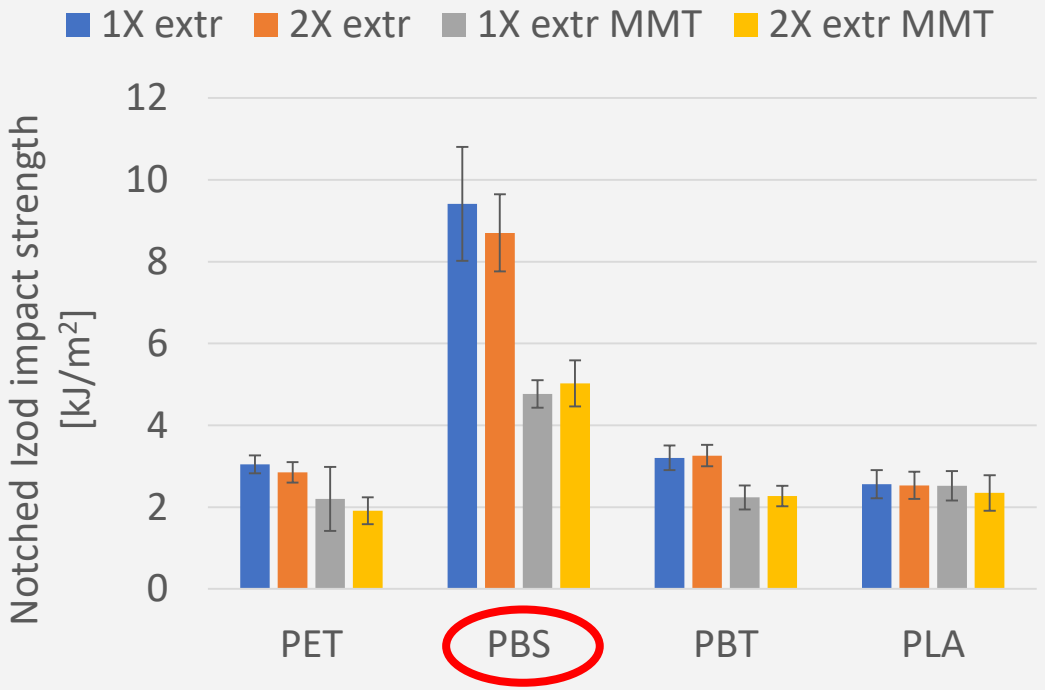


- Supercooling temperature = T_m - T_c.
- It depends on the type of polyester: **PLA** is the highest , higher cooling rate.
- $T_{Supercooling}$ → By reprocessing: ↓**PET**, ↑**PBT, no** effect **PLA and PBS** .
  → Adding MMT ↓in all cases, **except** for **PBS,** Prevent the order of chains(↓crystalline fractions).
- **PBT** and **PBS** have higher crystallization rates due to higher molecular mobility**.**

Practical part

Izod impact strength of composites (PET, PBS, PBT, PLA / MMT)

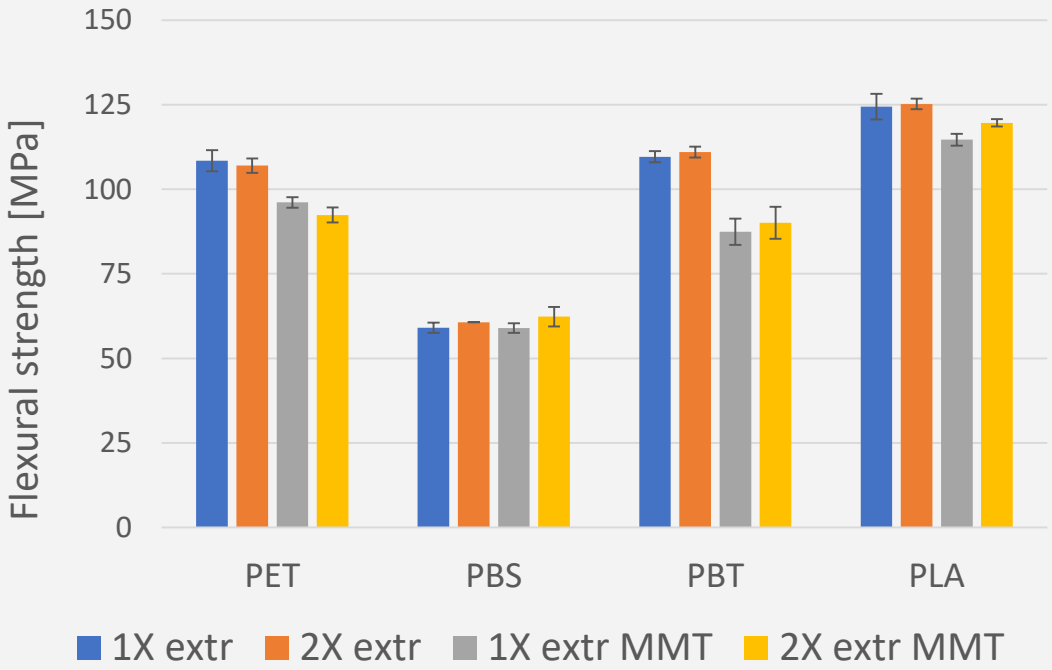
The effect of adding MMT and recycling on Izod impact strength of composite materials.

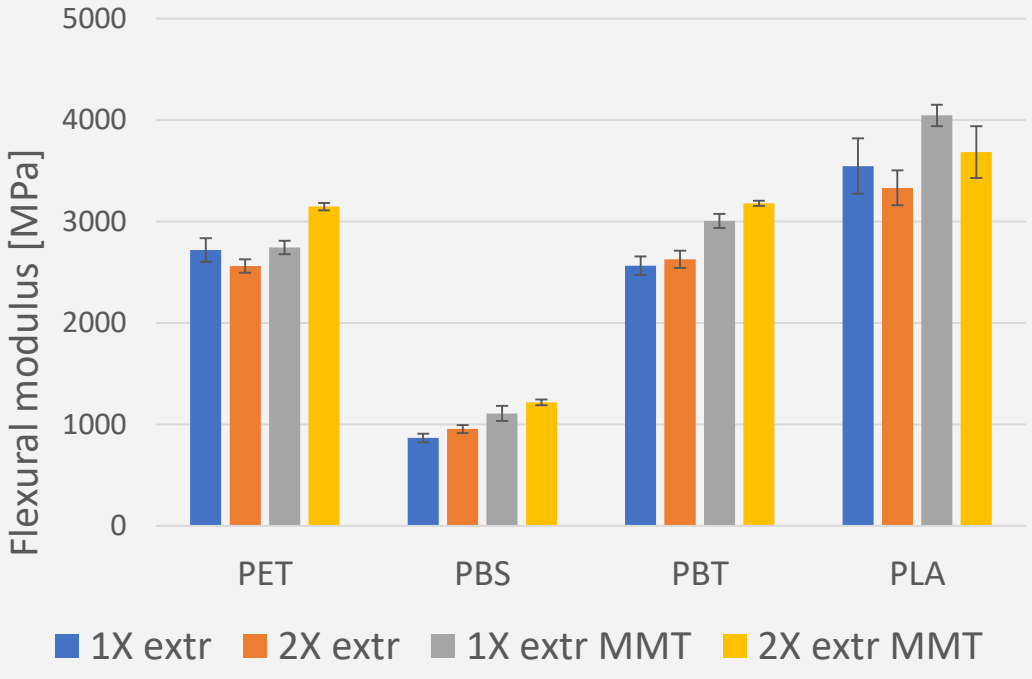


- **PBS** has the **highest** impact strength, **PET** and **PLA** are the lowest
- Recycling → **no** effect on **PBT** and **PLA, decrease** for **PET** and **PBS (**degradation+↑ crystalline)
- 1X extr MMT → **decrease** in all samples, especially for **PBS** because of the agglomerates.
- 2X extr MMT → **decrease** for **PET** and **PLA.**
  → **increase** for **PBT** and **PBS** , Improved distribution + size of aggregates

Practical part

Flexural strength and flexural modulus of composites (PET, PBS, PBT, PLA / MMT)





- 1X extr MMT → decrease in all samples except for **PBS**, where MMT had no effect.
- 2X extr & 2X extr MMT: **no** effect the **flexural strength** of polyesters and their nanocomposites.
- **PLA/MMT** is the stiffest while **PBS** is the most flexible
- Reprocessing did not lead to a significant change in the **flexural modulus** of polyester.
- 1X extr MMT → **increase** in the stiffness of all polyesters**,** increased crystallinity**.**
- 2X extr MMT → **increase** for **PET**, **PBS** and **PBT.**
  → **decrease** for **PLA.**

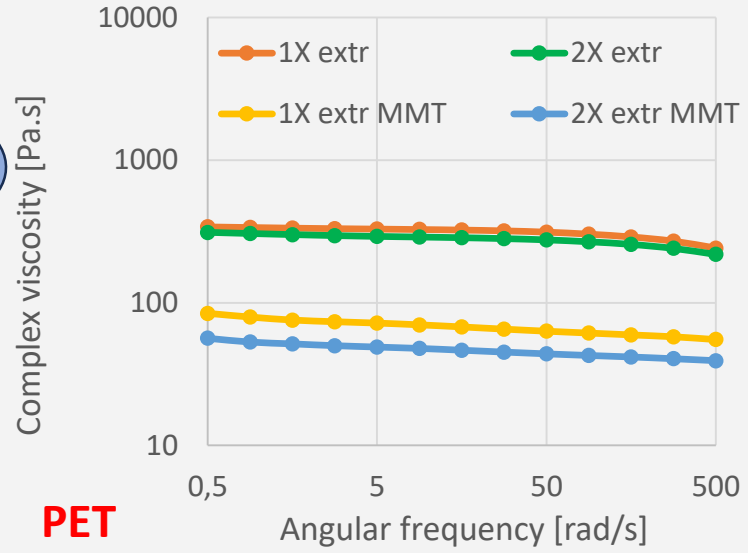
Time- and temperature-dependent properties of MMT/polyester nanocomposites

Practical part

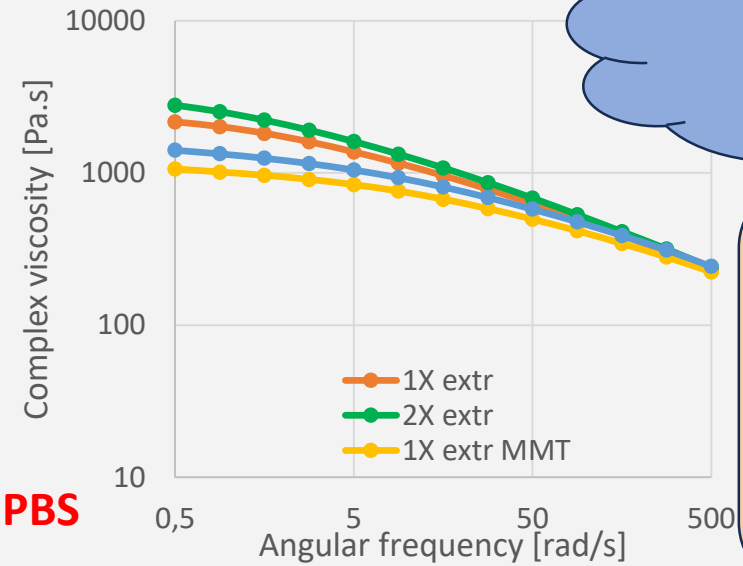
I measured the complex viscosity of polyesters and polyesters/MMT using Rheometer.

Shear thinning behaviour

- Addition of MMT and sample recycling have an effect on complex viscosity.



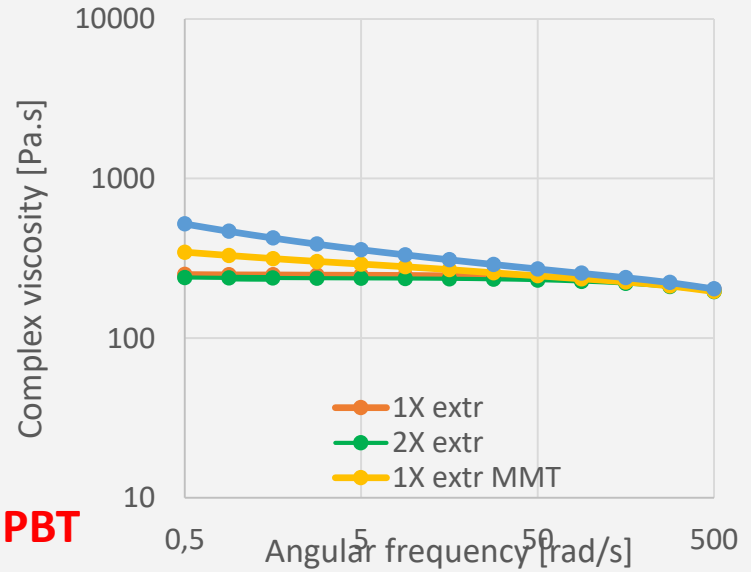
PET



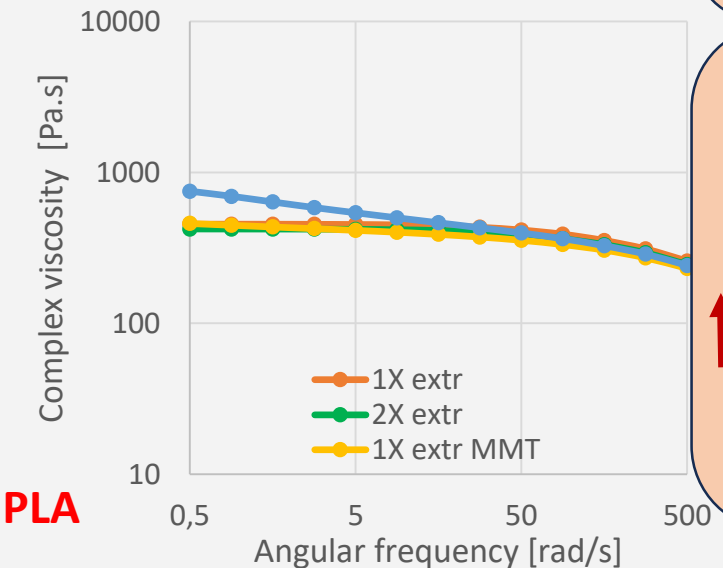
PBS

- **PBS**: The viscosity values of all samples are close to each other

- **PET:** MMT and recycling → viscosity → degradation



PBT



PLA

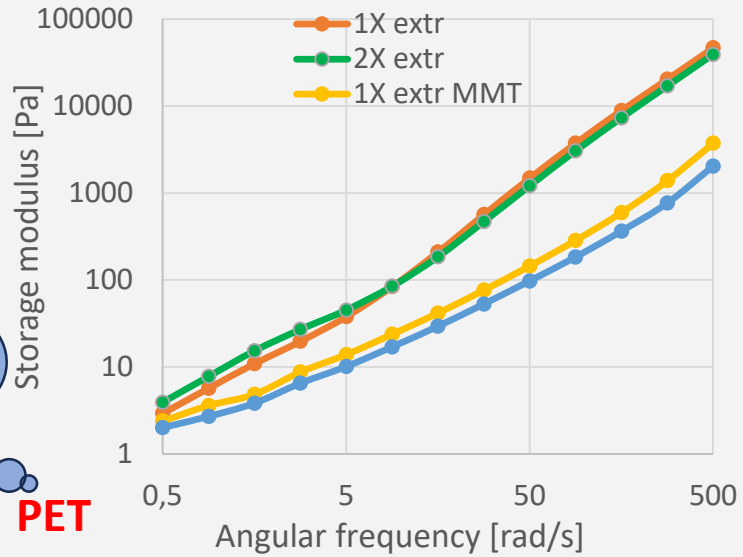
- **PBT&PLA:**
  - -MMT → viscosity
  - - 2X extr MMT → viscosity (good dispersion)

Time- and temperature-dependent properties of MMT/polyester nanocomposites

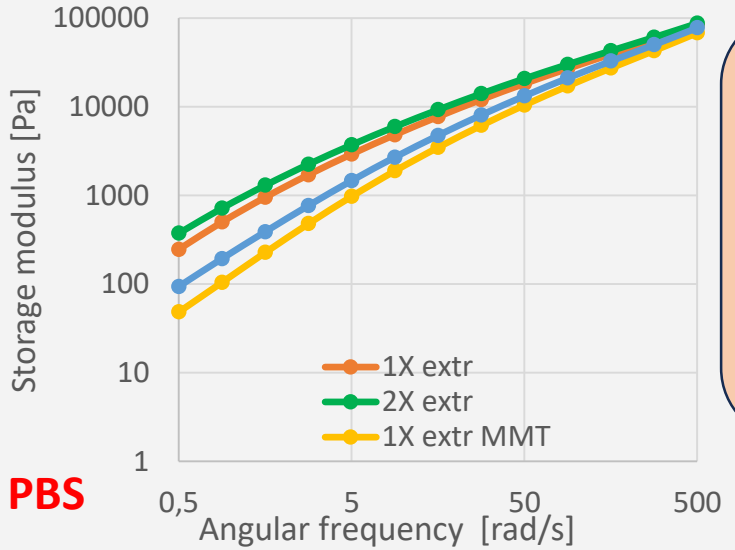
Practical part

I measured the storage modulus (G´) of polyesters and polyesters/MMT.

- All curves are almost identical for polyesters



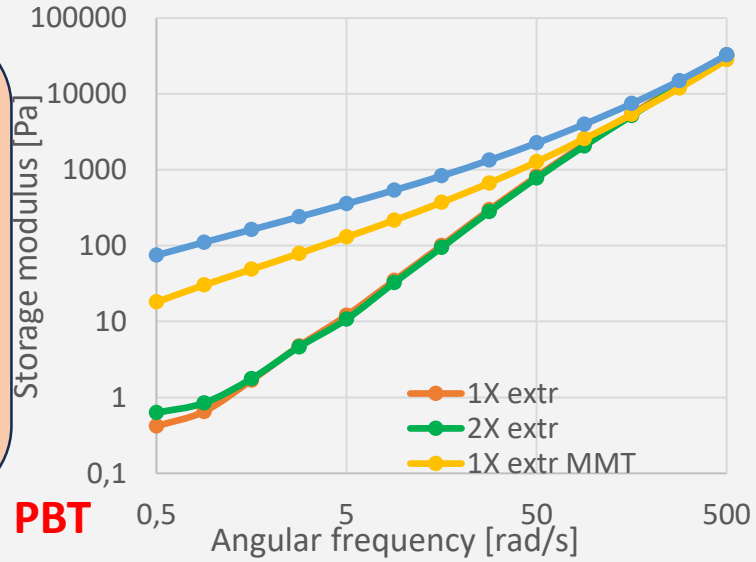
PET



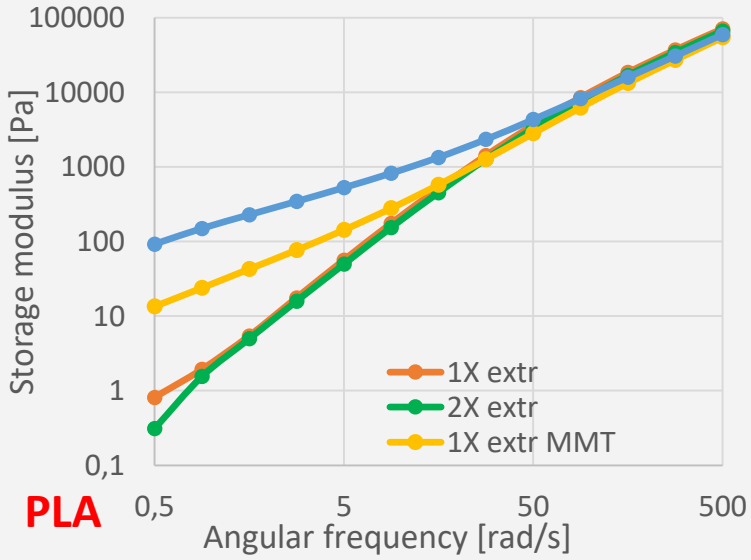
PBS

➢ **PET&PBS:**
-1X & 2X extr : the highest G´.

➢ **PBT& PLA:**
- MMT → ↑G´
- 2X extr MMT: the highest G´, (improved MMT dispersion)



PBT

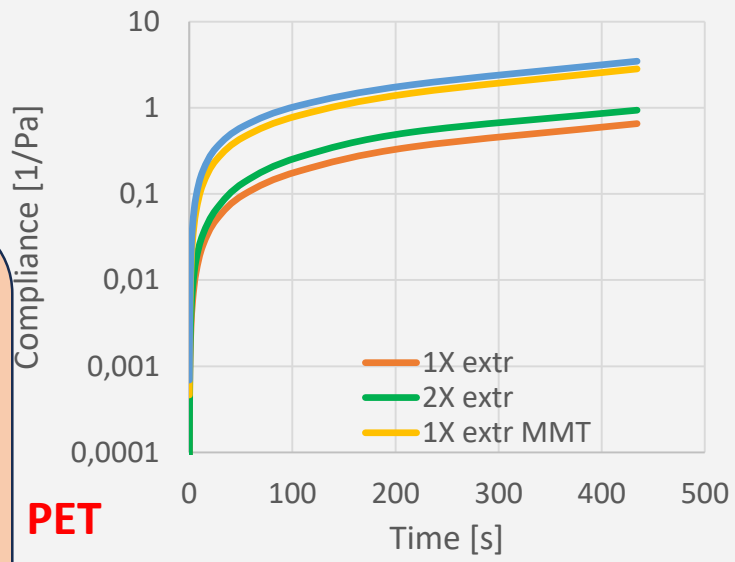


PLA

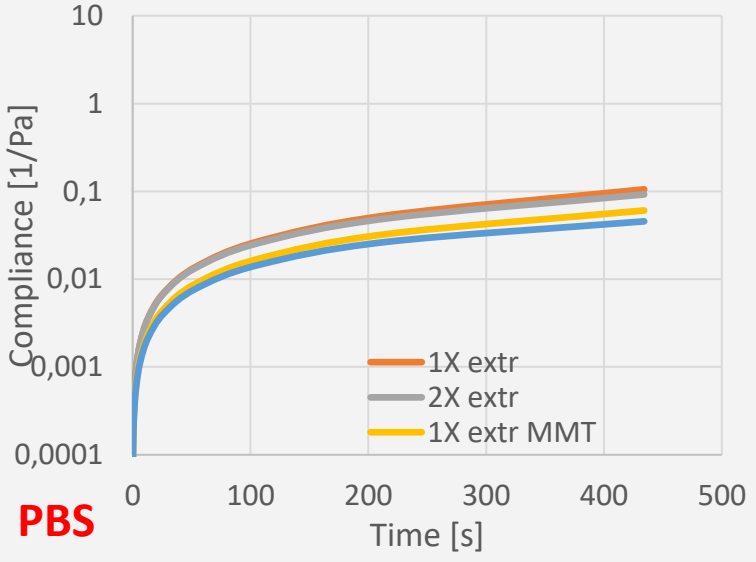
Time- and temperature-dependent properties of MMT/polyester nanocomposites

Practical part

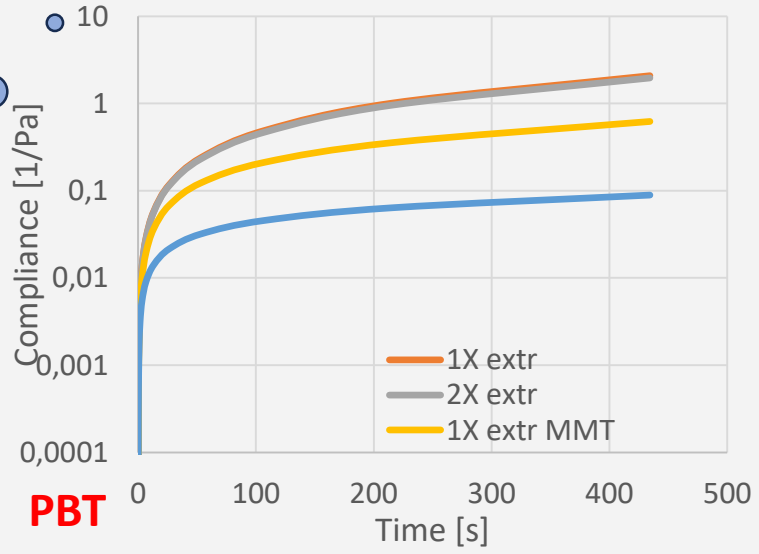
Creep compliance



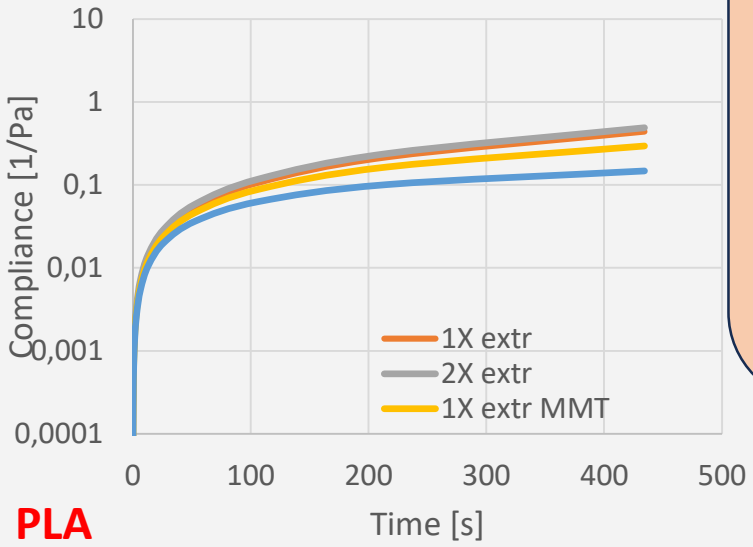
PET



PBS



PBT



PLA

➢ **PET:**

-1X & 2X extr MMT → ↑ creep (its big degradation)

- All curves are almost identical for polyesters

➢ **PBS,PBT&PLA**

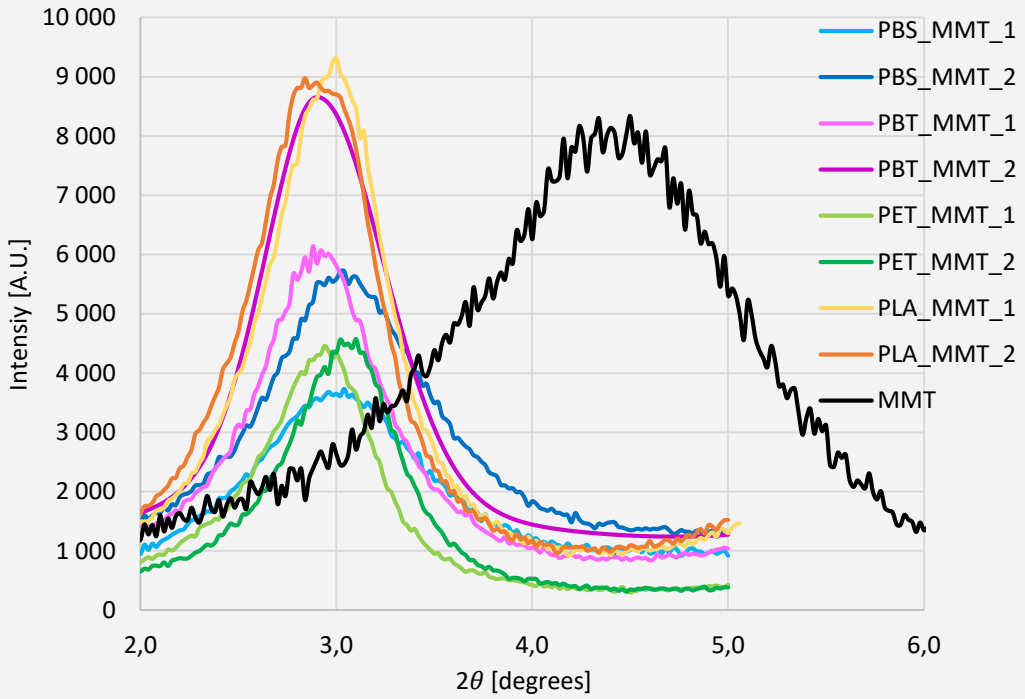
- 2X extr: **Slight effect** on creep (M_w has no effect)

-MMT → ↓ creep, elastic behaviour and dispersion of MMT.

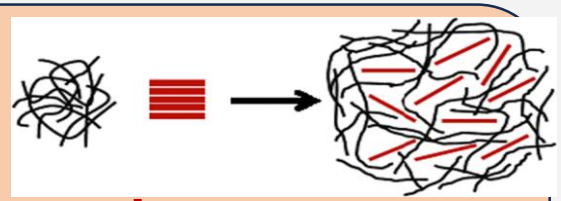
- 2X extr MMT: Improve dispersion

Practical part

Nanocomposites structure by using Wide-angle X-ray diffraction (WAXD)



- MMT → >2θ
- 2X extr MMT:



PLA&PET: ↓intensity(↓crystallinity & ↓dispersion)

PBT&PBS: slight changes , stability.

- Recycling **reduced** the layer thickness → **increased** layer stacking due to the aggregation of MMT layers.

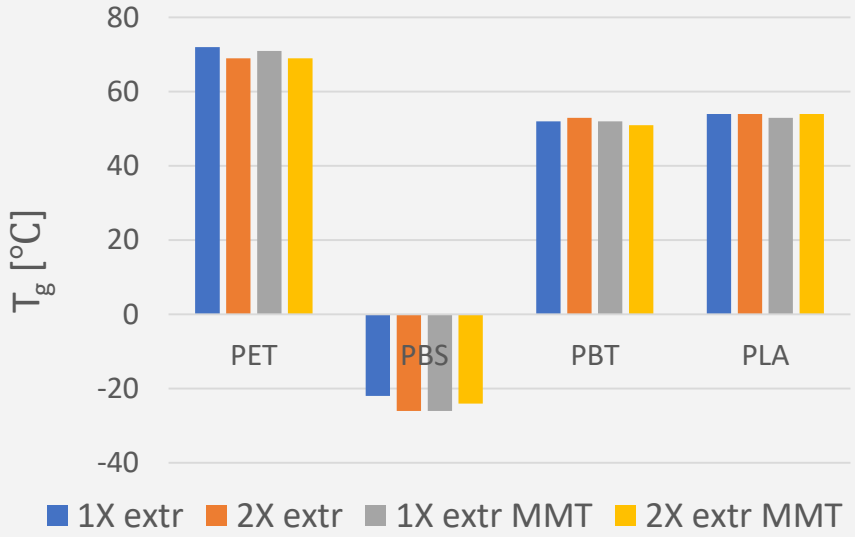
***Table**: Layer thickness (d_{001}), crystalline size (D), full width at half maximum (β) and number of layers (N)*

	d_{001} [nm]	β [°]	D [nm]	N
MMT	1.98	____	____	___
PBS_MMT_1	3.02	0.85	9.35	3.1
PBS_MMT_2	2.92	0.86	9.24	3.2
PBT_MMT_1	3.03	0.73	10.88	3.6
PBT_MMT_2	3.04	0.72	11.03	3.6
PET_MMT_1	2.99	0.65	12.22	4.1
PET_MMT_2	2.86	0.65	12.22	4.3
PLA_MMT_1	2.97	0.71	11.19	3.8
PLA_MMT_2	2.86	0.72	11.03	3.9

Practical part

Time- and temperature-dependent properties of MMT/polyester nanocomposites

I measured the glass transition temperature (T_g) of polyesters and polyesters/MMT using DMA.



- **PBT& PLA:**

- Reprocessing or addition of MMT did not significantly affect T_g.

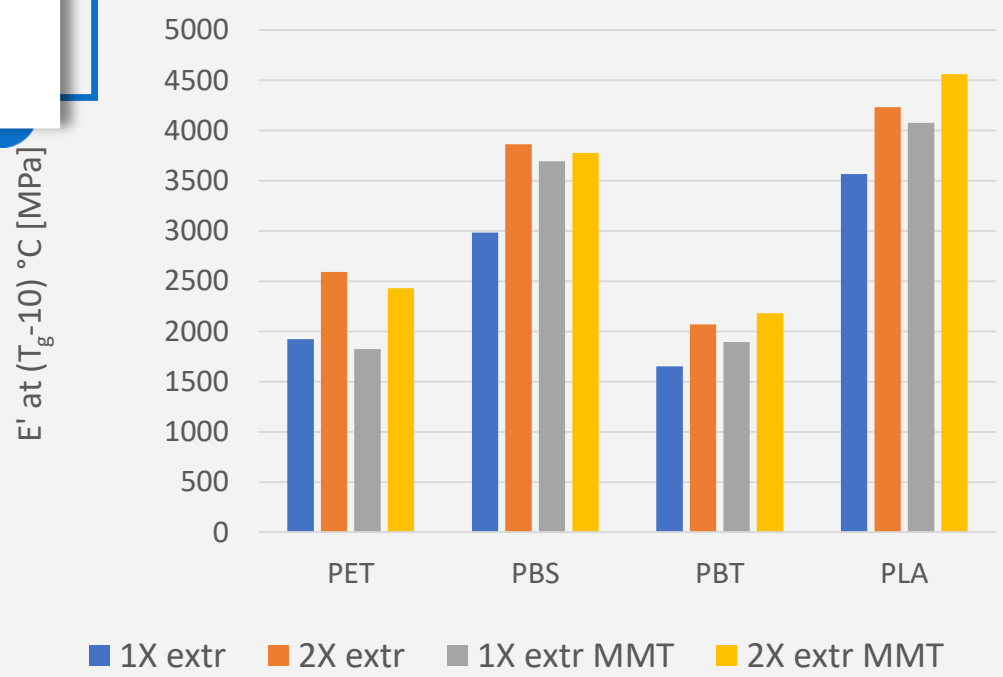
- **PET&PBS:**

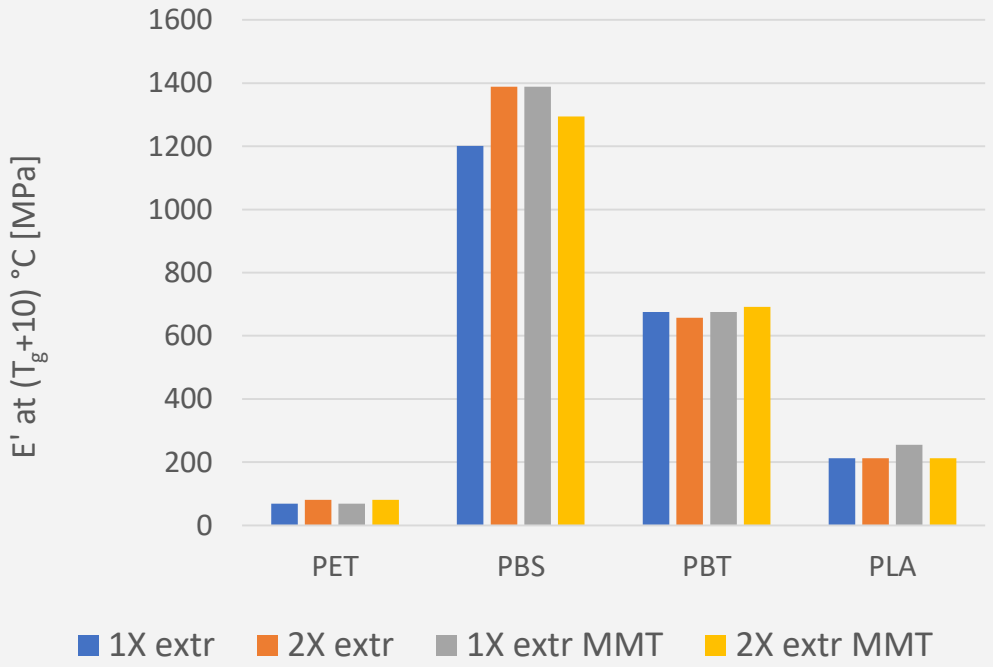
- 2X extr: **slight decreases** in T_g.

Practical part

Time- and temperature-dependent properties of MMT/polyester nanocomposites

I measured the Storage moduli (E´) (below and above the T_g)of polyesters and polyesters/MMT using DMA.

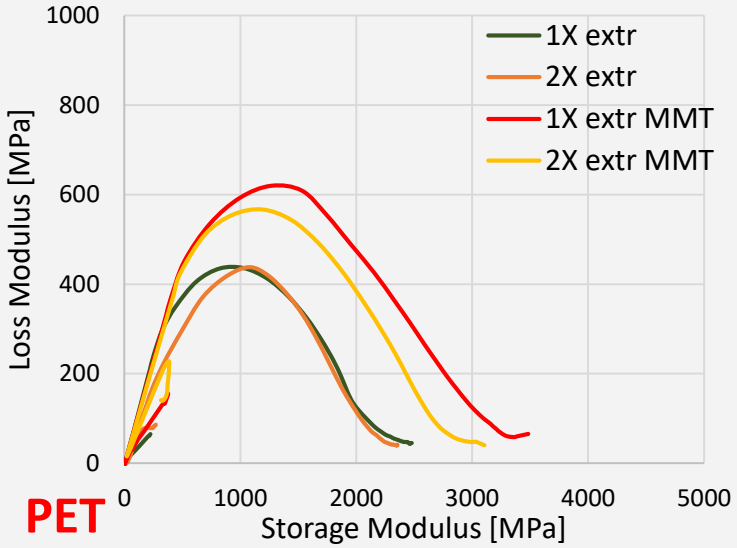




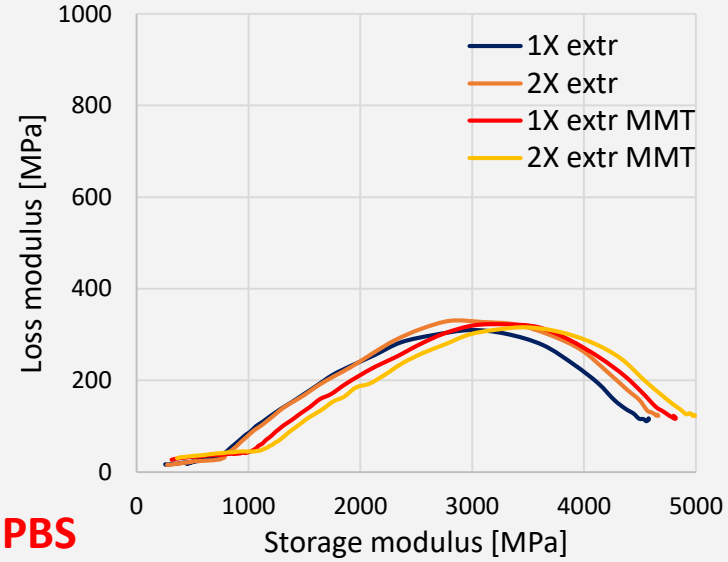
- Below T_g:
- MMT ⟶ **improved** E´ for **PBT, PBS, and PLA** but decreased it for **PET**.
- Recycling **increased** E´ in all cases, the degraded chains in the amorphous phase enhance stiffness.
- Above T_g:
- For **PBS and PBT: a small decrease** in E´, higher crystalline fractions.
- For **PET and PLA: larger decreases,** higher amorphous content**.**

Cole-Cole plots of MMT/polyester nanocomposites

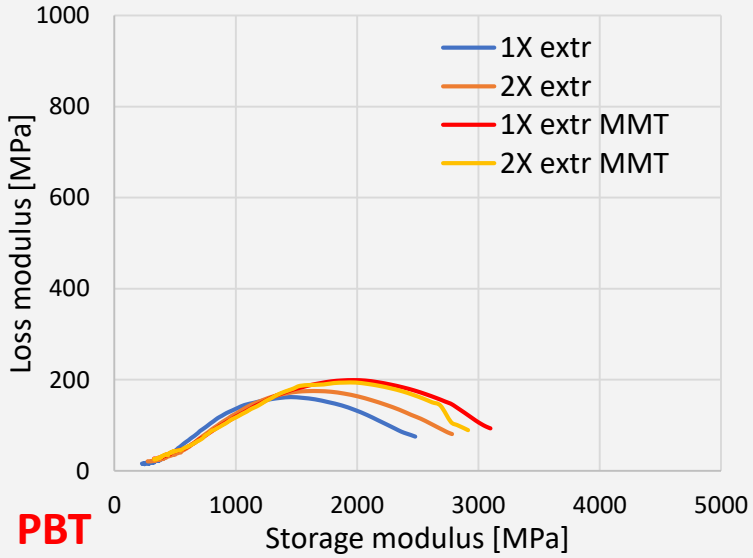
Practical part



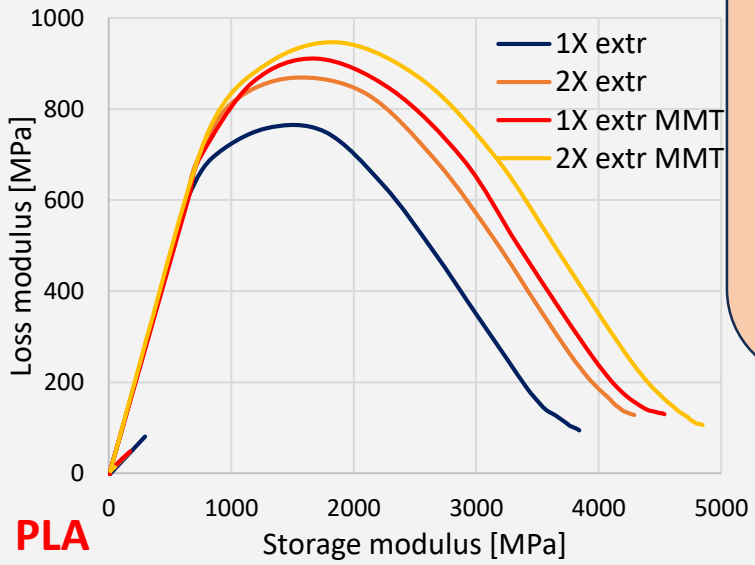
PET



PBS



PBT



PLA

- Small differences in the plots depend on the polyester type.

- The plots are **semi-circular** for most samples, homogeneous dispersion of MMT.
- Recycling did not significantly affect the dispersion of MMT, structural stability .

Conclusions:

The results

- The results indicate a change in the properties of polyesters as a result of **the following factors:** Adding MMT and recycling.
- Recycling → change in the distribution of MMT in the polyester matrix → change in the final properties of nanocomposites.
- The difference in the effect of MMT and recycling depends on the type of polyester used.

- MMT had a nucleation effect so the crystallization temperature of all composites increased when it was added.
- **PBS** had higher crystallinity, more flexibility and higher impact strength compared to other polyester materials used.
- **PET** had the highest degradation rate after recycling, while **PBS** and **PBT** showed minimal changes.
- DSC results showed that the changes were related to interphase interactions, physical network, and molecular weight changes.
- Rheological analysis showed shear-thinning behaviour in all materials, with **PET** exhibiting the highest viscosity, which decreased significantly after MMT addition and recycling.
- DMA revealed that storage modulus increased for **PLA** and **PBT** nanocomposites after reprocessing, while the increase was seen for unreinforced **PBS** and **PET**.
- MMT intercalation occurred in the polymer matrices, with decreased diffraction intensity and layer thickness after recycling in **PLA** and **PET**.
- T_g decreased slightly after reprocessing, and Cole-Cole plots showed stable and mostly homogenous dispersion of MMT across samples.
- Biodegradable polyester and its nanocomposites can be physically recycled in many cases with better efficiency than conventional petroleum-based polyester

Plans for the future

I will do the following

- finish all the evaluations of the results obtained

- Finalize writing the thesis.

List of publication

List of publications

- **First article :** *Zoubeida Taha Taha, Andrea Ádámné Major*, **A review on MWCNTs: The effect of its addition on the polymer matrix,** *Gradus*, https://gradus.kefo.hu/archive/2023-1/2023_1_ENG_012_Taha.pdf

- **Second article :** *Zoubeida Taha Taha, Andrea Ádámné Major*, **Investigating the effect of adding multiwalled carbon nanotubes on the morphological properties of polybutylene terephthalate,** Advanced Sciences and Technologies for Security Applications (1613-5113) : 2024 pp 473-482 Paper Chapter 41, https://link.springer.com/chapter/10.1007/978-3-031-47990-8_41.

- **Third article :** *Zoubeida Taha Taha, Andrea Ádámné Major, Ferenc Ronkay,* **Effect of Reprocessing on the Crystallization of Different Polyesters,** *Acta Technica Jaurinensis,* https://acta.sze.hu/index.php/acta/article/view/723/620 .

- **Fourth article:** *Zoubeida Taha Taha, Attila Bata, Béla Molnár, Ferenc Ronkay,* ***Impact of Montmorillonite Reinforcement on the Physical Recyclability of Biobased and Petroleum-Based Polyesters****, Heliyon,* **(under review).**

List of publication

List of publications

- **Fifth article :** *Zoubeida Taha Taha, Andrea Ádámné Major and Ferenc Ronkay*, **Effect of Reprocessing on the Viscosity and Mechanical Properties of PLA and PLA/MMT Nanocomposites ,** *Engineering proceedings*, https://www.mdpi.com/2673-4591/79/1/48.

- **Sixth article :** *Zoubeida Taha Taha, Péter Gerse, Attila Bata, Béla Molnar, Emese Slezák, Ádámné Major Andrea, Ferenc Ronkay*, **Influence of recycling on different polyesters and their MMT nanocomposites: Effects on morphology, mechanical properties, and rheological behaviour,** *Progress in Rubber Plastics and Recycling Technology, IF: 1.1, https://doi.org/10.1177/14777606241313078.*

List of publication

Conferences

- **AGTECO: 23.11.2021**
- **AGTECO: 24.11.2022**
- **Óbuda: “Fiatal Diplomások Fóruma 2022” 10.12.2022.**
- **III. International Architectural Sciences and Applications Symposium (İksad Institute Conference) 14-15.9.2023.**
- **Sustainable Mobility and Transportation Symposium 2024, 14-16. 10. 2024.**
- **AGTECO 2024, 28. 11. 2024.**

Semester Activities

Semester Activities

- I have finished the measurements.
- I evaluated the results.
- I have submitted three articles for publication.
- I participated in two conferences.
- I started writing my thesis.

THANK YOU for YOUR ATTENTION!