Óbuda University
Doctoral School of Materials Science and Technologies

EFFECT OF REPROCESSING ON POLYESTER/ MONTMORILLONITE NANOCOMPOSITES

-PHD THESIS-

PREPARED BY

ENG: ZOUBEIDA TAHA TAHA

MECHANICAL ENGINEERING (BSC)

MATERIALS SCIENCE AND ENGINEERING (MSC)

Supervisors

Dr. Andrea Ádámné Major, PhD

College professor

Dr. Ferenc Ronkay, Dsc

Professor

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Introduction

Modern industries need materials that have properties which are not found among the traditional materials used, so the manufacture of materials with special specifications has raised the interest of researchers in recent years [1–4]. Different types of polyester materials have started to be widely used, since these polymers are commonly used in most applications due to their low cost, adaptability and high mechanical properties such as strength and moisture resistance [5, 6]. Polyester can be classified into two main types depending on the raw materials used in their production. One of them is bio polyester, which is extracted from renewable resources such as microorganisms and plants like sugarcane and corn, the most important of which are polylactic acid (PLA) and polybutylene succinate (PBS) [7, 8]. The other type is called petroleum-based polyesters, which can be obtained from petrochemical raw materials, including polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [9, 10].

Composite materials have gained a significant position within the field of engineering materials due to their fitness for many industrial uses. They combine the features of two or more materials while relieving the disadvantages of each material. Furthermore, they provide the ability to control their characteristics, whether by altering the types and proportions of their component materials or by modifying their design and production techniques [2–4]. Nanocomposites differ from traditional composites due to their high aspect ratio which leads to the difference in structure thus the properties, where the material behaves differently from its state when it is normal size [11–13]. The properties of the matrix material are greatly affected in the reinforcement. They offer improved hardness without affecting either the toughness or optical clarity. The reinforcing material can consist of fibers (like carbon nanotubes), particles (like metals) or sheets (like clay) [14–16].

One of the ongoing challenges with polyester materials is their recyclability, especially in maintaining mechanical and thermal properties after multiple recycling cycles. For petroleum-based polyesters, physical recycling is more common, while for bio-polyesters, composting is often used at the end of the life cycle. However, bio-polymer can also be recycled by physical recycling, conserving the energy invested in the production of the material [17, 18]. As MMT can positively influence certain properties of these polyesters, its use is becoming more widespread, but its influence on the recyclability and long-term performance of polyester nanocomposites remains unexplored.

This research aims to investigate how MMT reinforcement affects the physical and mechanical properties of both petroleum-based and bio-based polyesters during repeated physical recycling. By evaluating key properties such as shrinkage, crystallinity, flexural strength, and impact resistance, thus discovering whether MMT promotes or accelerates the degradation of properties in recycled polyester.

The novelty of this work lies in its dual focus on improving material performance and promoting sustainable practices. It provides an approach to address challenges in plastic waste management by bridging the gap between nanomaterial design and practical recyclability. The results have the potential to redefine how reinforcement strategies can be combined with recycling processes to achieve both improved material properties and environmental sustainability.

Materials and methods

Materials

The following Table 1 shows the type and main properties of the two petroleum-based polyesters and two bio-based polyesters tested.

Table 1. *Tested polyesters*

Name	*Origin*	*Type (Producer)*	*MFI parameters*	*MFI value*
PET	Petroleum-based	Neopet 80 (Neogroup)	260°C / 1.2 kg	21 g / 10 min
PBT	Petroleum-based	Pocan B1305 (Lanxess)	250°C / 2.16 kg	47 cm^3 / 10 min
PLA	Bio-based	Ingeo 3100HP (Natureworks)	210°C / 2.16 kg	24 g / 10 min
PBS	Bio-based	BioPBS FZ91PM (PTT MCC Biochem)	190°C / 2.16 kg	6 g / 10 min

Montmorillonite (MMT): Nanomer® nanoclays are high purity, surface compatibilized montmorillonites. Nanomer type I.30P treated with octadecyl ammonium was used, as it provides high heat stability up to 280 ºC.

➢ **Preparation of samples**

All materials were carefully dried before the processing steps. The drying times/temperatures used were: for PET 160 °C/4 h; for PBS 80 °C/5 h; for PBT 120 °C/4h and for PLA 90 °C/5 hours. The MMT additive was also dried at 100°C/4 h before processing.

To prepare samples the materials were first processed with a Labtech 26-44 twin-screw extruder (Labtech Engineering, Thailand) with a screw diameter of 26 mm and an L/D ratio of 48 was used, with melt temperatures ranging between 250-270 °C for PET, 240-250 °C for PBT, 150-170 °C for PBS and 180-190 °C for PLA and a screw speed of 55 rpm in all cases. The extrusion step was repeated again to simulate reprocessing (1X extr and 2X extr specimens).

After that, injection moulding was used to make morphological and mechanical test specimens (60×60×2 mm^3). A 50 MEtII electric injection moulding machine (Mitsubishi, Japan) was used with the following parameters: mould temperature: 60 °C; injection speed: 60 - 65 mm/s, holding pressure 50 bar for 10 sec. The zone temperatures were between 260-280 °C for PET, 250-260 °C for PBT, 160-170 °C for PBS and 190-200 °C for PLA as shown in Figure 1.

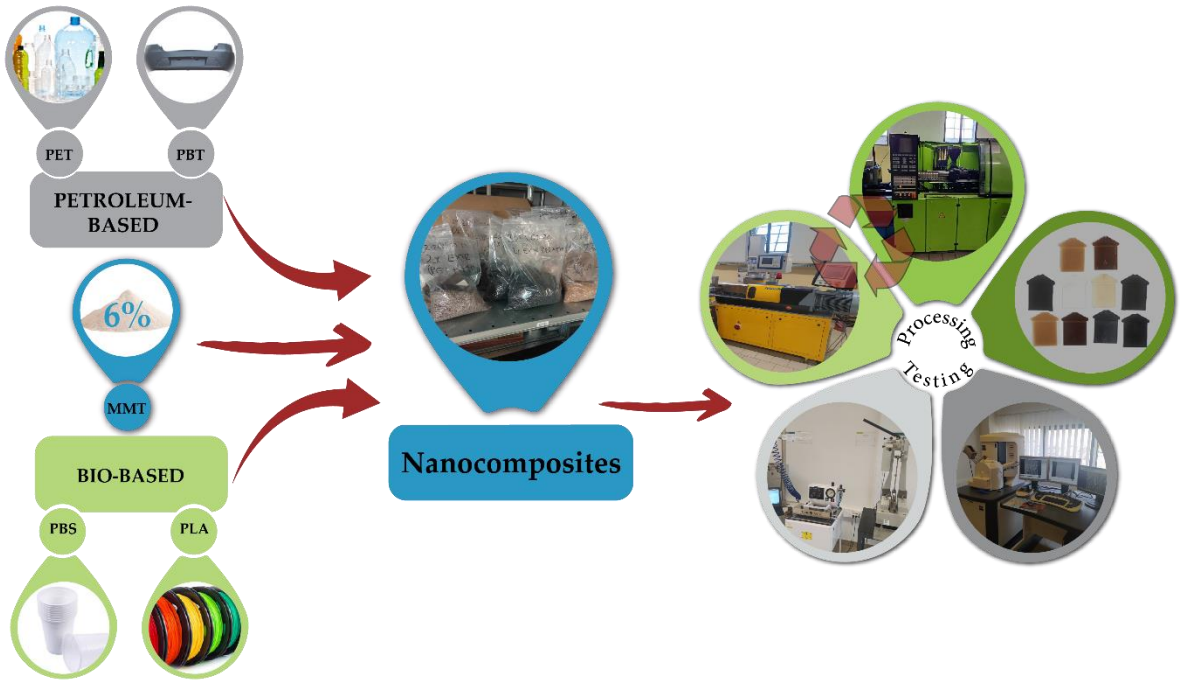


Figure 1. *Sample preparation*

➢ **Characterization methods**

Analytical techniques included Intrinsic viscosity (IV), Melt flow index (MFI), Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM), Wide-Angle X-ray Diffraction (WAXD), Izod impact test, 3-point-bending test, rheometer and Dynamic Mechanical Analysis (DMA).

Results

1- Degradation and dimensional stability

IV measurements were performed before and after the extrusion steps to monitor the material degradation during multiple reprocessing. The results shown in Table 2 showed that the smallest degradation for PBS and PBT was only about 2% after the second extrusion step. Also, the degradation was 3% after the first processing and 5% after the second for PLA. While PET showed the highest degradation, with a 13% decrease in IV after the first extrusion and a 16% decrease after the second extrusion.

Table 2. *Effect of reprocessing on the intrinsic viscosity of PET, PBS, PBT and PLA*

Name	***original***	***1X extr.***	***2X extr.***
PET	1.49 ± 0.01	0.69 ± 0.01	0.67 ± 0.01
PBS	1.49 ± 0.01	1.49 ± 0.01	1.46 ± 0.01
PBT	0.84 ± 0.01	0.83 ± 0.02	0.82 ± 0.01
PLA	1.24 ± 0.02	1.20 ± 0.01	1.17 ± 0.02

When measuring the mould shrinkage parameters measured for the injection moulded plate specimens as shown in Figure 2. The results showed that PBS and PBT had higher shrinkage than PET and PLA. Recycling and addition of MMT had an effect on shrinkage in both directions (transverse direction (TD) and flow direction (FD)). Reprocessing reduced the shrinkage of the polyesters without MMT materials in both FD and TD as well as volumetric shrinkage. It was also observed that addition of MMT resulted in a decrease in linear shrinkage . After 2x extrusion, the linear shrinkage of different polyesters decreased except for PLA where the shrinkage increased

in the flow direction and decreased in the transverse direction. The difference in shrinkage in the in-plane directions *indicates anisotropy.*

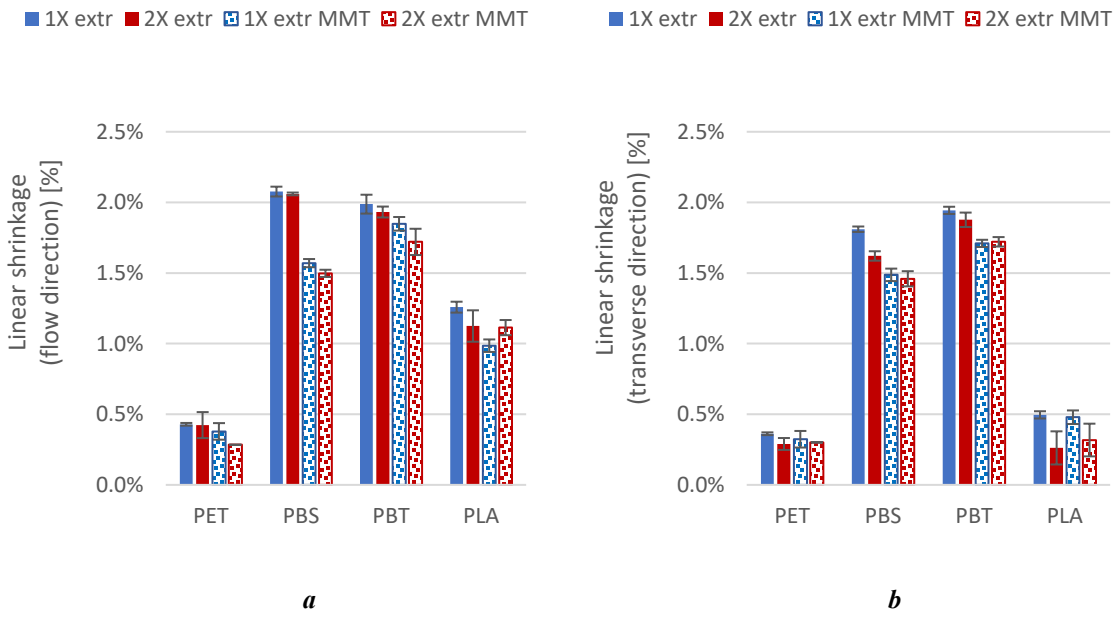


Figure 2. *Injection mould shrinkage of the polyesters and polyester/MMT-nanocomposites after 1x and 2x reprocessing (a: flow direction (FD); b: transverse direction (TD)*

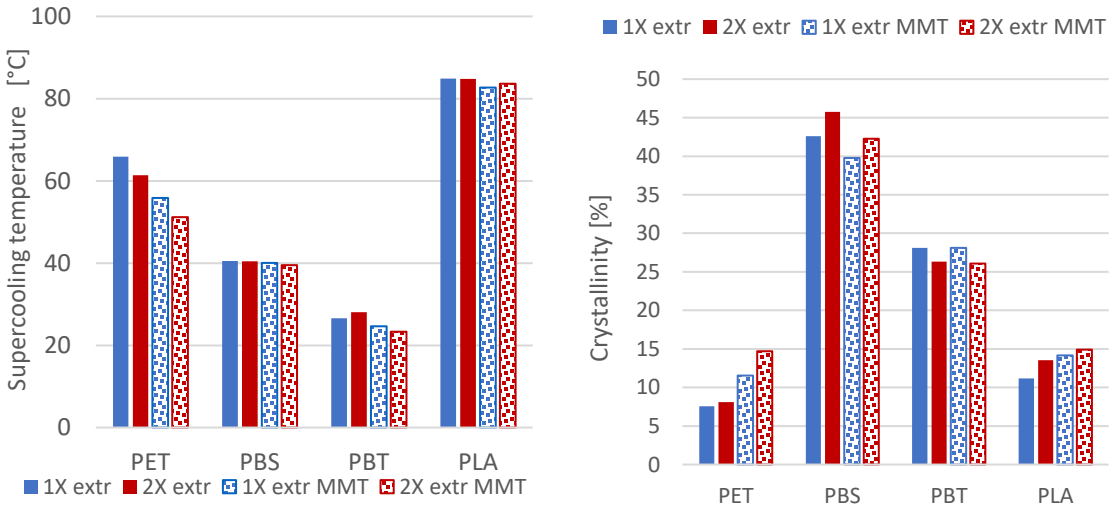
2- Crystallization behaviour of samples

A DSC was used to evaluate the melting and crystallization temperatures of different polyesters with and without nano reinforcing (Table 3). According to results, adding MMT and reprocessing did not significantly affect the melting temperature (T_m). The crystallization temperature (T_c) during cooling of the melt did not change with reprocessing for PBS, PBT, and PLA, but increases by 5°C for PET, indicating that the tendency of the molecular chains to order increases with a decrease the intrinsic viscosity of this polyester. The addition of MMT also increased the crystallization temperature, indicating its role as a nucleation agent.

Table 3 *Melting temperatures (T_m) from heating and crystallization temperatures (T_c) from cooling DSC curves*

	1X extr		***2X extr***		***1X extr MMT***		***2X extr MMT***	
	T_m [°C]	***T_c [°C]***	***T_m [°C]***	***T_c [°C]***	***T_m [°C]***	***T_c [°C]***	***T_m [°C]***	***T_c [°C]***
PET	253.8	187.9	254.0	192.6	255.9	200.0	254.7	203.5
PBS	120.7	80.2	120.8	80.3	121.1	81.1	122.2	82.7
PBT	229.2	202.7	230.6	202.5	228.9	204.3	228.2	204.9
PLA	182.7	97.8	182.2	97.4	182.3	99.6	181.6	97.9

While using T_m-T_C to calculate the supercooling temperature at 10°C/min. The results indicated that its valuable is primarily dependent on the type of polyester, with PLA had the highest value because of its higher molecular mobility. The supercooling temperature decreased for PET and increased for PBT when reprocessing without MMT, but PBS and PLA showed no noticeable difference. All polyesters examined, with the exception of PBS, showed a decrease in supercooling temperature following MMT application, indicating MMT's effect of promoting crystallization. Also, the addition of MMT led to an increase in crystallinity for PET and PLA, it decreased for PBS because it prevented the order of the molecular chains, while there was no effect on PBT. as shown in Figure 3.



a ***b***

Figure 3. *a: Supercooling temperature; b: Crystallinity of polyesters and polyesters/MMT nanocomposites*

3- Mechanical performance of polyesters and polyesters/MMT samples

Figure 4 shows the effect of MMT addition and recycling on the impact strength and modulus of PET, PBS, PBT and PLA composites. PBS showed the highest impact strength, while PET and PLA had the lowest. Reprocessing without MMT reduced impact strength in PET and PBS due to degradation and higher crystallinity, with minimal effect on PBT and PLA. Adding MMT reduced impact strength variation across all samples, though PBS saw the largest drop due to clay agglomeration. Upon reprocessing in the presence of MMT, the impact strength decreased slightly in PET and PLA, but improved it in PBS and PBT due to better clay dispersion (Figure 4/a).

Flexural modulus results of the injection moulded samples indicated PLA/MMT as the stiffest and PBS (without MMT) as the most flexible. Reprocessing did not cause a significant change in the flexural modulus of the polyesters, while the incorporation of MMT increased the stiffness of all polyesters. Stiffness further improved for PBS, PBT, and PET nanocomposites after reprocessing, but slightly declined for PLA (Figure 4/b).

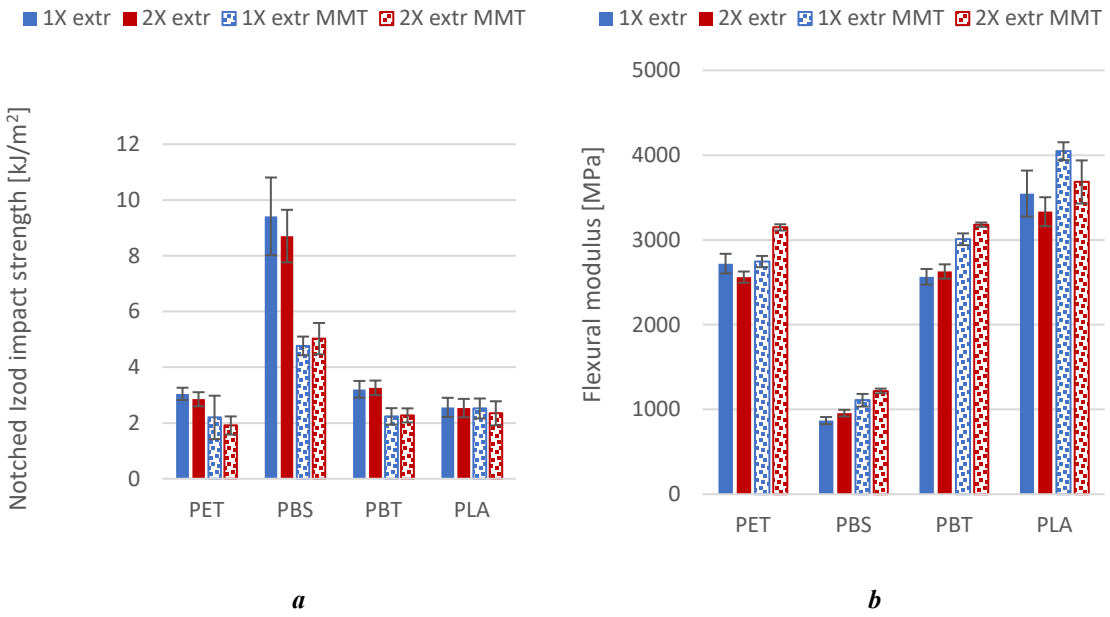


Figure 4. *Effect of MMT and recycling (1X, 2X) on a: Impact strength; b: Flexural modulus of PET, PBS, PBT and PLA*

4- Structure of polyester/MMT nanocomposites

When MMT was added to the polyester matrix, there were two possible nanoclay distribution (Figure 5): either agglomerates, detected using scanning electron microscopy or intercalation, where X-rays were used to clarify their distribution.

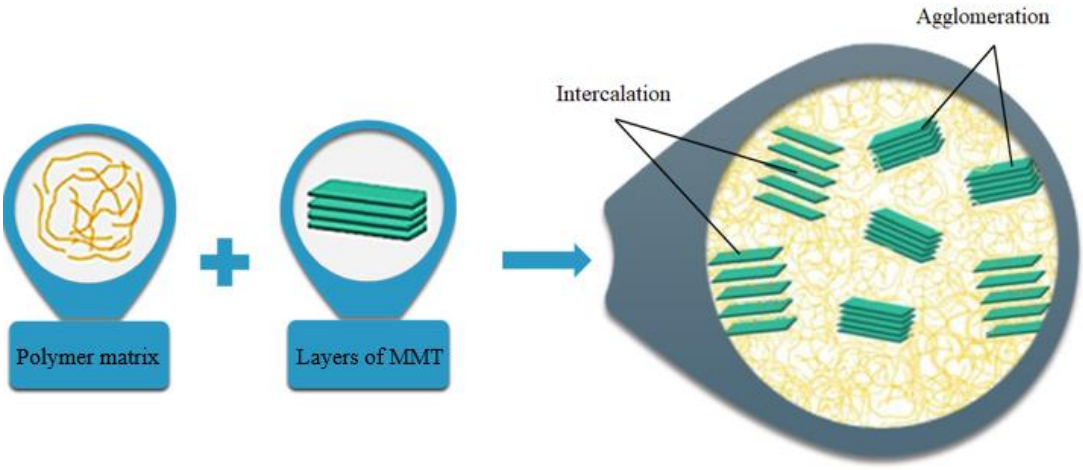


***Figure 5**. Structural morphologies in polyester/MMT nanocomposites*

5- Rheological behaviour

When the injected samples were tested using a rotational rheometer, the results showed that MMT addition and recycling influenced the complex viscosity of the polyesters as shown in Figure 6. All samples exhibited shear thinning, with viscosity decreasing as frequency increased. Pure PET had the highest complex viscosity, while MMT addition reduced it by 10–20% due to the degradation that resulted in the reduction of the molecular weight of PET. Recycling lowered PET viscosity. For PBS, viscosity changes were minimal, but MMT and recycling slightly increased viscosity at low frequencies. In PBT and PLA, MMT enhanced the viscosity at low frequencies, with recycling further increasing this effect due to better MMT dispersion.

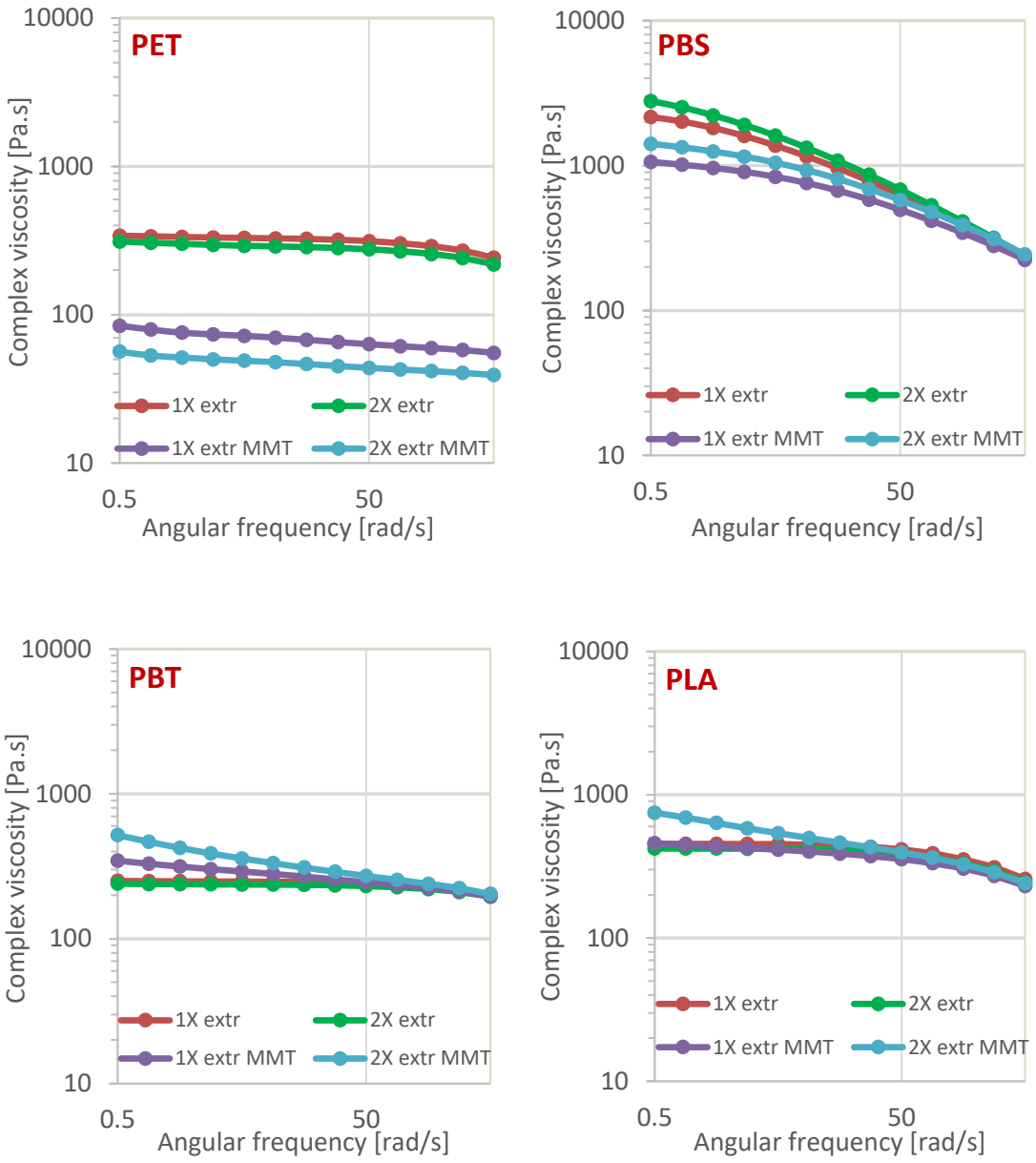


Figure 6. *Complex viscosity of injection moulded polyesters*

Figure 7 illustrates how recycling and MMT addition affect the storage modulus (G') of polyesters. In the case of PLA and PBT, G' increased notably in MMT-reinforced and recycled their samples, suggesting improved clay dispersion. Conversely, unreinforced PET and PBS showed higher G' values, indicating a different interaction with MMT. Overall, MMT contributed to the formation of a physical network that enhanced the storage modulus, while reprocessing further promoted the dispersion effect of MMT.

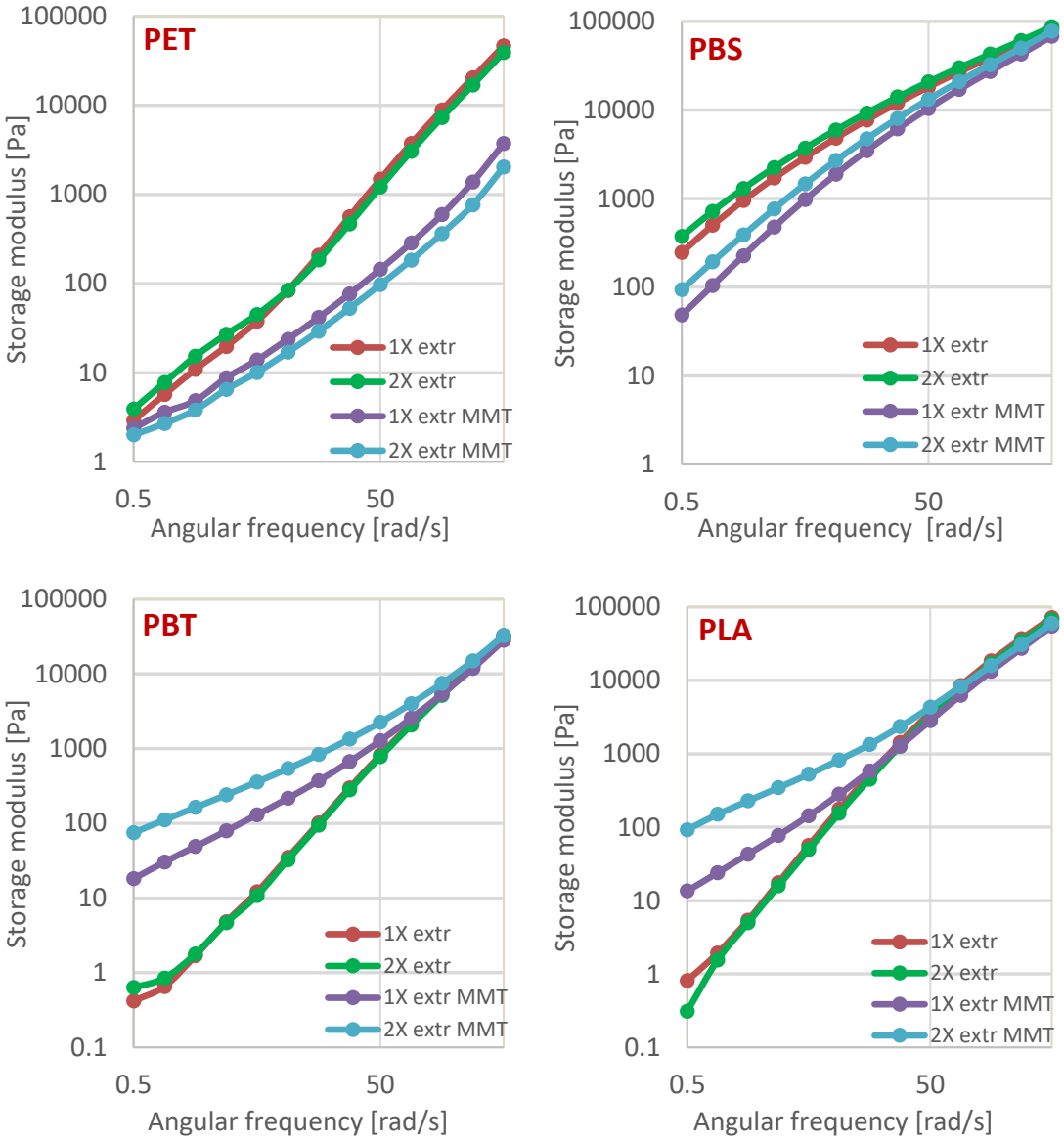


Figure 7. *Effect of reprocessing on storage modulus of polyesters and polyester/MMT*

The creep compliance of several polyesters and their nanocomposites is shown in Figure 8. MMT addition decreased creep compliance for PBS, PBT, and PLA, suggesting increased elasticity and greater MMT dispersion, which is particularly apparent in recycled samples. This indicates improved reinforcing of the structure. On the other hand, PET showed higher creep compliance with MMT, indicating a different interaction due to its significant degradation. These results validate that the time-dependent deformation behaviour of polyesters is influenced by both MMT and recycling.

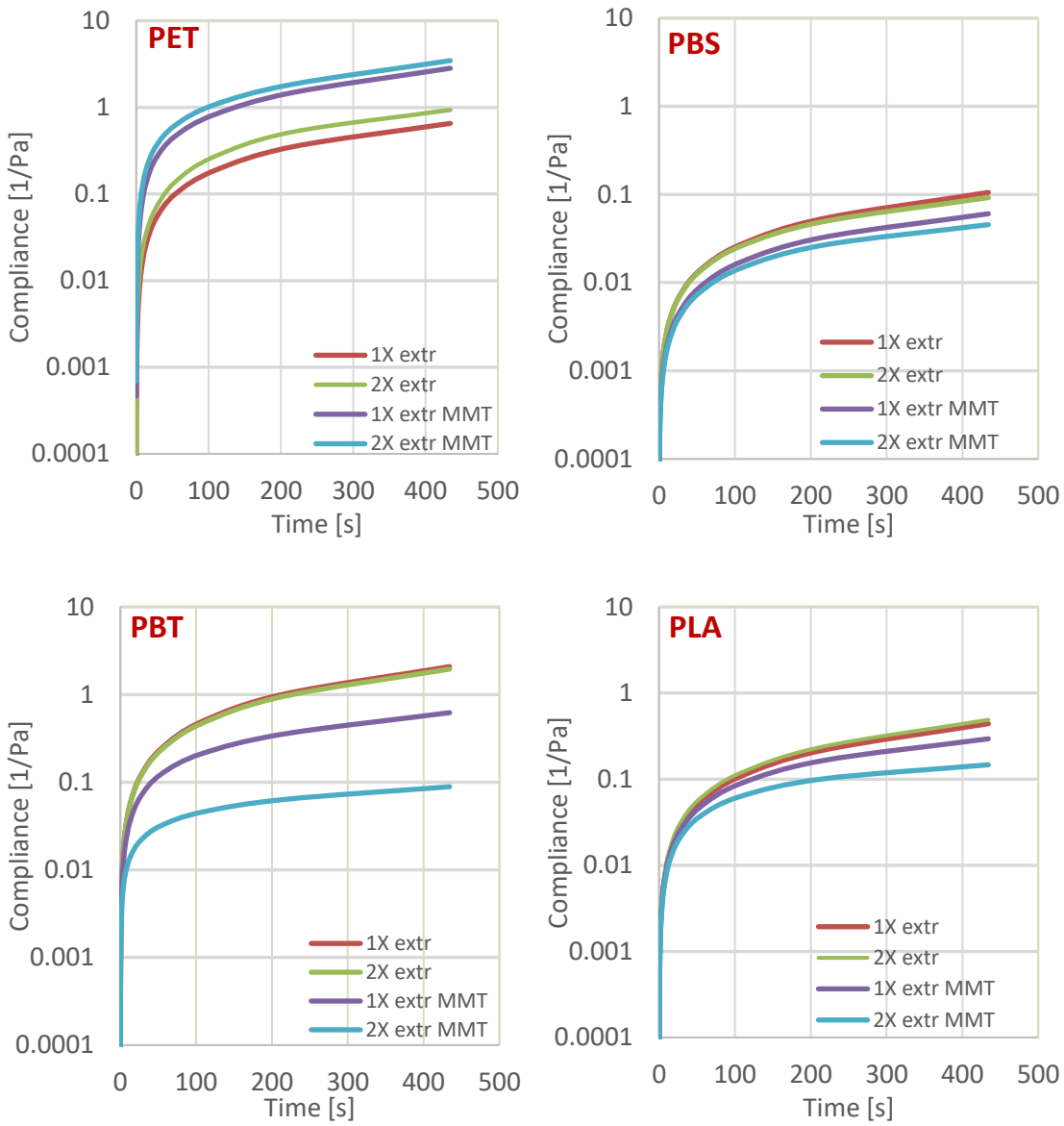


Figure 8. *Creep of polyesters and polyester/MMT nanocomposites before and after recycling*

6- Dynamic mechanical properties of the injection moulded specimens

The glass transition temperature (T_g) of the polyesters was measured using DMA and is shown in Figure 9.

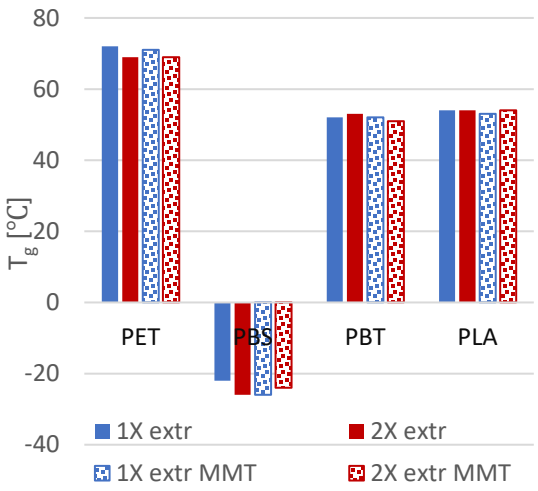
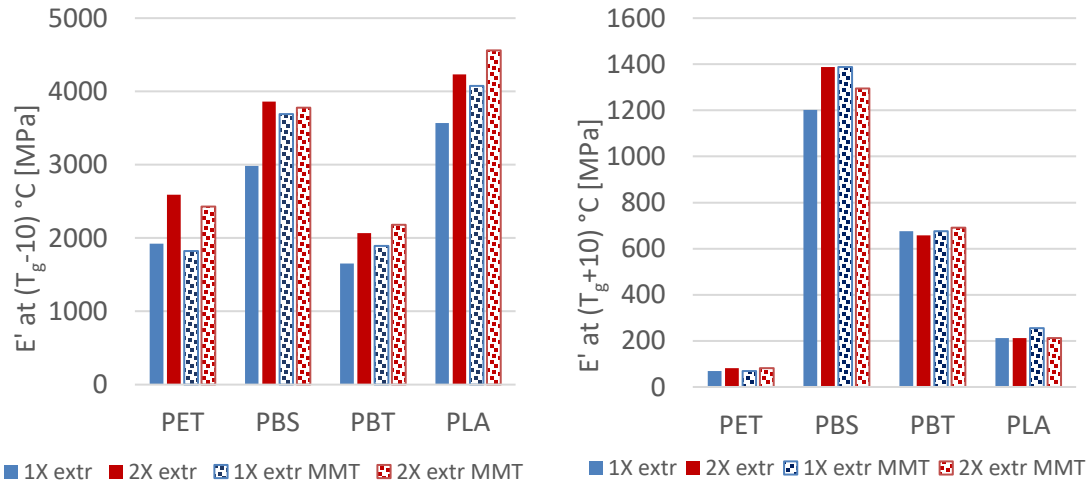


Figure 9. *The glass transition temperature of different polyesters*

Storage modului varied with MMT addition and reprocessing, as shown in Figure 10. Below the glass transition temperature (T_g), the modulus increased in most cases due to the significant influence of the amorphous phase on stiffness, while above T_g, the crystalline phase became dominant. MMT enhanced stiffness below T_g in PBT, PBS and PLA, but reduced it in PET. Reprocessing also contributed to higher storage modulus in the amorphous phase by promoting molecular orientation. Polyesters with higher crystallinity, such as PBS and PBT, retained more stiffness above Tg, whereas PET and PLA, with greater amorphous content, exhibited larger decreases—up to 95%.



a ***b***

Figure 10. *Storage moduli 10°C below (a) and above (b) T_g*

Figure 11 (Cole-Cole plots) shows the dispersion of MMT within the polyester nanocomposites and their structural stability during recycling. Most plots appear semi-circular, with a slightly flattened shape for PBT, indicating generally homogeneous MMT dispersion, with minor variations depending on the polyester type. Reprocessing had only a slight effect on MMT dispersion, suggesting good structural stability throughout the recycling process.

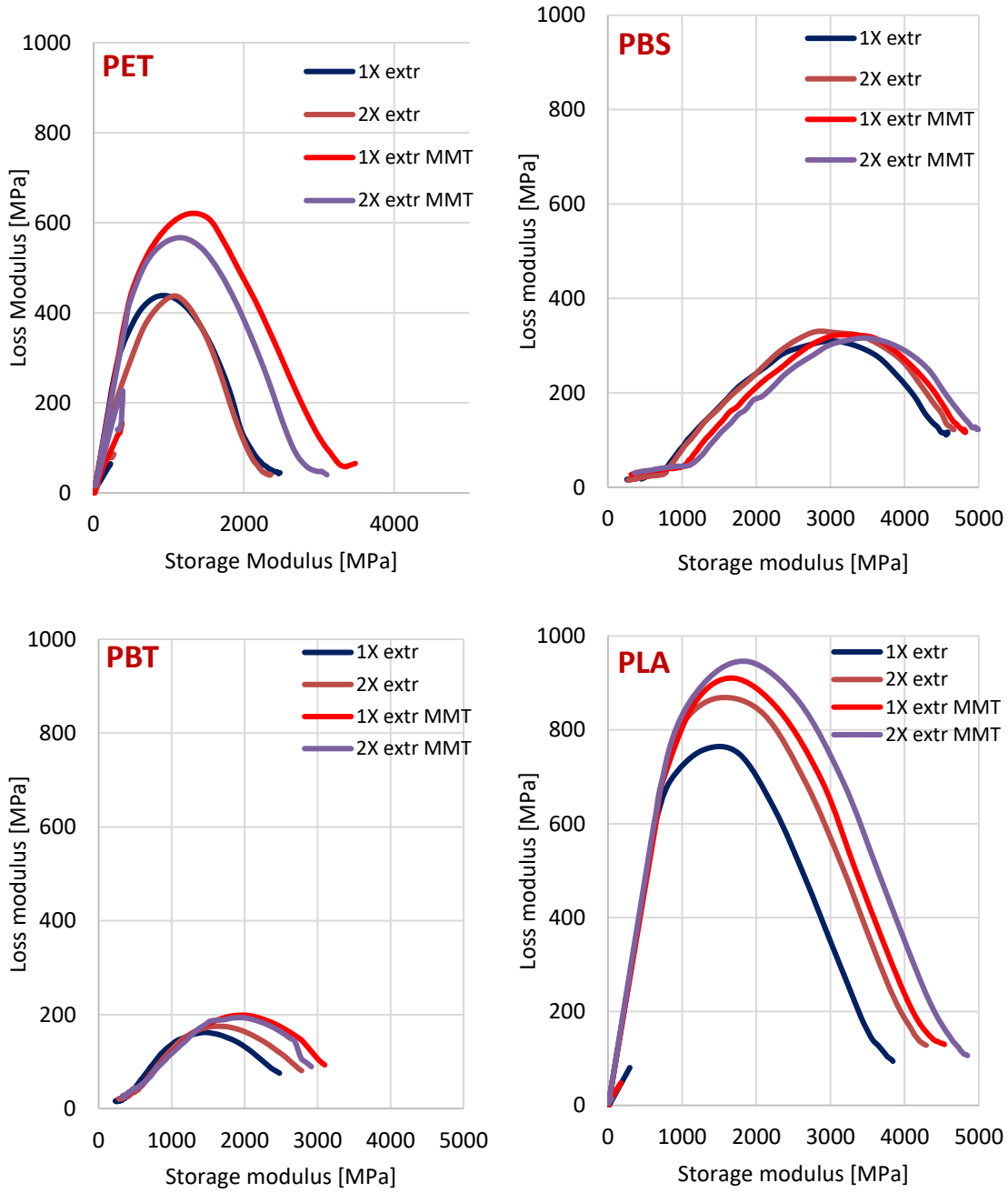


Figure 11. *Cole-Cole diagrams of the sample*

Theses - New scientific results

✓ *1st thesis: About recycling of bio- based polyesters [III, IV, V, VI]*

In my research, I demonstrated that bio-based polyesters (PLA and PBS) can be mechanically reprocessed similarly to petroleum-based ones (PET and PBT). After two extrusion cycles, PET showed a 13% decrease in intrinsic viscosity, while PLA dropped by only 4%, and PBS by just 1.5%. The presence of MMT in the nanocomposites intensified degradation, particularly in PET and PLA, due to the acidic decomposition of the ammonium-based surface modifier. Shrinkage and mechanical properties were most affected in PLA, whereas PBS exhibited only minor changes. The increase in crystallinity during reprocessing (PLA: + 95%, PBS: minimal) limited amorphous chain mobility and influenced elasticity. Tensile and impact strength showed moderate variation: a slight decrease was observed in PBS, while PLA remained virtually unchanged.

✓ *2nd Thesis - About the effect of MMT on crystallinity during recycling of bio- and petroleum-based materials [IV, V, VI]*

Using non-isothermal crystallization experiments, I investigated how MMT influences crystallization during reprocessing in different polyesters. I introduced two parameters — undercooling ($\Delta T_{c,1}$) and change in crystallinity ($\Delta X_{m,1}$) — to better evaluate these effects. MMT reduced ΔTc,1 in PET and PBT (e.g., PET: from 9.4 to 3.7 °C), but increased it in PLA and PBS, suggesting distinct crystallization behaviors. PLA showed the most significant increase in crystallinity upon reprocessing (+ 95%), while PBT and PBS exhibited slight decreases. These differences confirm that the interaction between MMT and the polymer matrix strongly influences crystallization kinetics during recycling.

✓ *3rd Thesis- About the effect of MMT on mechanical properties during recycling (bio- and petroleum-based materials) [IV, V, VI]*

Using Izod impact tests and three-point bending tests, I have demonstrated that 6 wt.% MMT nano-reinforcement affects the physical recycling of various polyesters differently:

The impact strength decreased when recycled in the presence of MMT in the case of PBS/MMT by about 42 %, while it was 33 % for PET/MMT, 30 % for PBT/MMT, and 8 % for

PLA/MMT. I have noted that MMT did not have a significant effect on the flexural strength in all cases during recycling. Furthermore, I have observed from the values of the flexural modulus, that the incorporation of nanoclay increased the stiffness of the nanocomposites during recycling by 5- 14 %, except for PLA/MMT, which decreased the flexural modulus by 8 %.

The reason for this is that based on SEM images and X-ray diffractograms, I have found that MMT is located in the polymer matrices in two different ways: intercalated and agglomerated structures. During the reprocessing, the intercalated structures (layer spacing, stack number) do not change significantly, but the size of the agglomerates became smaller due to the improved distribution and fragmentation into smaller ones as a result of the high shear forces in the twin-screw extruder. Thus, the dispersion state of MMT plays a crucial role in the mechanical property recovery of recycled nanocomposites. Furthermore, degradation also plays a major role in influencing the mechanical properties, especially in PET. PET showed clear degradation that affected its molecular weight and viscosity, resulting in a more brittle fracture. The interaction between PET and organically modified MMT increases the degradation rate because of the elevated number of acidic sites on the clay plates.

- ✓ ***4th Thesis- About the correlation between the rheological behaviour and the reprocessing cycles in nanocomposites [V, VI]***

By conducting rheological analysis on reprocessed polyester/MMT nanocomposites, I have observed that the viscosity behaviour differs between polyesters. PET exhibited shear thinning with a significant decrease in viscosity upon recycling. This was attributed to its greater susceptibility to chain scission as this behaviour is related to the low molecular weight of PET and the influence of MMT, which could not counteract the degradation. Whereas PBS, PLA and PBT demonstrated a smaller decrease in viscosity after multiple reprocessing cycles, indicating their molecular structures and interactions with MMT provide better stability against shear and thermal degradation due to stronger intermolecular interactions and the enhancing effect of MMT. This confirms that the polymer matrix structure and MMT dispersion influence the long-term processability of these materials.

Utilization of results

This research was motivated by industrial needs, particularly those of Jász-Plasztik Kft., a leading plastic processor in Hungary. The study focused on the processability and recyclability of PLA and PBS nanocomposites. The Findings highlight that MMT enhances the recyclability of both bio- and petroleum-based polyesters. Key results include improved structural stability, enhanced mechanical properties, reduced shrinkage variation, and strong performance retention after reprocessing. These results are applicable to industries requiring dimensional precision and material integrity, such as automotive, electronics, packaging and medical devices.

Overall, the thesis provides valuable insights into the development of recyclable, high-performance nanocomposites and establishes a foundation for further research in polymer sustainability.

My publications

I. Zoubeida Taha Taha, Andrea Ádámné Major: A review on MWCNTs: The effect of its addition on the polymer matrix, ***Gradus***, 10 (2023). pp 1-14 https://gradus.kefo.hu/archive/2023-1/2023_1_ENG_012_Taha.pdf.

II. Zoubeida Taha Taha, Andrea Ádámné Major: Investigating the Effect of Adding Multiwalled Carbon Nanotubes on the Morphological Properties of Polybutylene Terephthalate. In: Kovács, T.A., Nyikes, Z., Berek, T., Daruka, N., Tóth, L. (eds) Critical Infrastructure Protection in the Light of the Armed Conflicts. HCC 2022. **Advanced Sciences and Technologies for Security Applications.** ***Q4*** Springer, Cham. *2024, Paper, Chapter 41, pp 473-482* https://doi.org/10.1007/978-3-031-47990-8_41

III. Zoubeida Taha Taha, Andrea Ádámné Major, Ferenc Ronkay, Effect of Reprocessing on the Crystallization of Different Polyesters, ***Acta Technica Jaurinensis***, ***Q3*** 17(2023) pp. 1-7, 2023 https://acta.sze.hu/index.php/acta/article/view/723/620.

IV. 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, Q3,*** 79(2024), https://www.mdpi.com/2673-4591/79/1/48.

V. 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, Q3 IF: 1.6***, 2025 https://doi.org/10.1177/14777606241313078.

VI. Zoubeida Taha Taha, Attila Bata, Béla Molnár, Ferenc Ronkay, Impact of Montmorillonite Reinforcement on the Physical Recyclability of Biobased and Petroleum-Based Polyesters, ***Heliyon, Q1 IF: 3.6*** 11(2025), e43022 https://doi.org/10.1016/j.heliyon.2025.e43022.

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