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Hub4Circularity

A First of a kind Hub for circularity demonstrator for Attica and peripheral regions

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Publishable summary

This deliverable details the progress made in Task 5.5 within WP5 of the THESEUS project. It focuses on developing functional thin-film materials from recycled polymers enhanced with bioactive compounds, aiming to upgrade recycled low-density polyethylene (R-LDPE) into higher-value materials suitable for advanced applications such as active packaging. The work explores various processing strategies, including direct additive incorporation via extrusion, encapsulated systems to improve stability of sensitive compounds, and nanostructured coatings produced by electrospinning, all aligned with circular economy principles and efficient use of secondary raw materials. Results show that the performance of each approach depends heavily on the nature of the additives and processing conditions. For instance, inorganic ZnO particles were well suited to melt processing and achieved high entrapment efficiency due to their thermal stability and non-volatility. Conversely, adding wild thyme essential oil directly resulted in significant losses during extrusion, revealing the limitations of incorporating volatile, thermolabile compounds at high temperatures. Encapsulation with HPβCD was highly effective before processing, confirming the potential of host–guest inclusion systems, but performance declined after extrusion, indicating limited thermal and mechanical stability. Electrospun PLA-based systems showed enhanced encapsulation efficiency and structural control, highlighting the potential of electrohydrodynamic techniques for sensitive bioactive compounds. Overall, the findings emphasize the importance of choosing suitable material–process combinations depending on the target functionality. They confirm that melt processing is effective for stable additives, while encapsulation and electrospinning are promising for volatile compounds, thereby supporting the THESEUS goals of material upcycling, functionalizing recycled plastics, and developing innovative circular value chains.

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Abbreviations

Abbreviations	Full name
DSC	Differential Scanning Calorimetry
EO	Essential Oil
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas-Chromatography
HPβCD	Hydroxypropyl-beta-cyclodextrin
PLA	Poly-Lactic Acid
R-LDPE	Recycled Low-Density Polyethylene
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
ZnO	Zinc Oxide

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1 Introduction

1.1 Purpose of the deliverable

This deliverable presents the progress made in Task 5.5 (WP5), which focuses on developing functional thin-film materials from recycled polymers infused with bioactive compounds via extrusion, encapsulation, and electrospinning. It details the materials used, the processing methods applied, and the initial characterization of the produced materials.

More specifically, the deliverable focuses on developing recycled polymer systems with added functionality, aligning with the THESEUS goal of transforming secondary raw materials into higher-value packaging and related products. The work involves directly adding active compounds to recycled LDPE during extrusion, incorporating pre-encapsulated systems into recycled polymers via extrusion, and producing thin electrospun coatings containing encapsulated bioactive ingredients. Overall, this demonstrates innovative material-processing techniques that promote circular economy principles, enhance the use of recycled plastics, and support the THESEUS strategy of integrating material flows and upcycling packaging.

1.2 Materials involved in the deliverable

1.2.1 Recycled Low-Density Polyethylene (LDPE)

This study used recycled polyethylene (R-LDPE) supplied by Thrace Poly, sourced from post-industrial waste, including trimming residues and off-spec materials generated during plastic film production. As part of sustainability and circular economy goals, these materials were used as secondary raw materials to upcycle them into higher-value functional products. Future phases will also investigate the use of post-consumer polymers from Blue Bin collection systems, together with post-industrial materials, to further improve circularity.

In industrial applications where LDPE is extensively used, particularly in packaging, significant quantities of post-industrial scrap are continuously produced (Devra et al., 2024). These materials are typically reprocessed or blended with virgin polymers. However, in the present work, the recycled LDPE pellets are directly valorized through functionalization, demonstrating their potential for advanced applications beyond conventional reuse.

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Polyethylene, the most widely used synthetic plastic worldwide, consists of a linear hydrocarbon backbone characterized by a highly hydrophobic and chemically inert structure (Ghatge et al., 2020). This molecular configuration makes LDPE particularly resistant to chemical reactions and biological degradation, contributing to its durability but also to its environmental persistence.

1.2.2 Wild Thyme essential oil

Wild thyme essential oil (Thymus capitatus) was selected as a natural bioactive compound for its strong potential to confer antioxidant and antimicrobial properties to the developed materials. Its incorporation into polymeric matrices aims to enhance the functionality of LDPE-based systems, particularly for applications where inhibition of oxidation and microbial growth is critical. The high bioactivity of this essential oil is mainly attributed to its major phenolic components, such as carvacrol and thymol, along with compounds like p-cymene (Tagnaout et al., 2022). These molecules are known for their ability to scavenge free radicals and disrupt microbial cell membranes, leading to strong antioxidant and antibacterial effects. According to the literature, wild thyme essential oil exhibits one of the highest antioxidant activities among natural oils (Wińska et al., 2019).

However, its practical application presents challenges due to its high volatility and thermal sensitivity, especially under extrusion conditions. For this reason, this work explores various encapsulation strategies to enhance stability and maximize retention within the polymeric matrix, thereby ensuring sustained functionality in the final material.

1.2.3 Zinc-Oxide particles (ZnO)

ZnO is an inorganic metal oxide used in polymeric systems due to its multifunctional behavior, particularly its antimicrobial, antioxidant, and UV-protective properties (Maurya et al., 2026). In Task 5.5.1, ZnO was incorporated into recycled LDPE to enhance the functionality of the resulting materials. Its antimicrobial activity is primarily associated with the generation of reactive oxygen species (ROS) and the release of Zn^{+2} ions, which can disrupt microbial cell membranes and inhibit the growth of a wide range of microorganisms. Also, ZnO can contribute to oxidative stability by interacting with free radicals, thus supporting both the preservation of packaged goods and the durability of the polymer matrix itself (Dey et al., 2025).

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The key advantage of ZnO compared to essential oils is its high thermal stability and non-volatile nature. Those properties make it particularly suitable for melt-processing techniques such as extrusion, as it does not degrade or evaporate, allowing it to remain effectively entrapped within the polymer matrix. Furthermore, its inorganic nature enables long-term functionality and makes it a robust additive for functional polymer systems, as its activity is maintained over time without significant loss.

1.2.4 Poly-Lactic Acid (PLA)

PLA is a bio-based polymer derived from renewable resources such as corn starch or sugarcane, making it particularly suitable for applications aligned with sustainability and circular economy principles. PLA was utilized as a carrier matrix for the encapsulation of bioactive compounds in tasks 5.5.2 and 5.5.3, due to its ability to form both nanofibers and nanoparticles at different concentrations with electrohydrodynamic techniques (Maleki et al., 2022; Shao et al., 2022). These properties enable the formation of stable microparticles and nanofibrous structures that can entrap sensitive compounds such as essential oils, thereby protecting them against volatilization and degradation. PLA also allows for the uniform distribution of encapsulated compounds within its structure and can support controlled-release behavior. However, its thermal stability must be carefully considered, as PLA may degrade at elevated temperatures, potentially compromising the integrity of the encapsulated systems during subsequent melt-processing steps such as extrusion.

1.2.5 Hydroxypropyl-beta-cyclodextrin (HPβCD)

HPβCD is a cyclic oligosaccharide widely used as an encapsulant due to its unique molecular structure, which features a hydrophilic outer surface and a relatively hydrophobic internal cavity (Procopio et al., 2024). This amphiphilic architecture allows HPβCD to act as a host molecule that forms inclusion complexes with lipophilic compounds by incorporating them into its central cavity via non-covalent interactions, including van der Waals forces and hydrophobic interactions (Nicolaescu et al., 2025). In this way, hydrophobic bioactive molecules are effectively “trapped” within the cyclodextrin structure, leading to improved solubility, stability, and protection against environmental factors such as heat, light, and oxidation. In this deliverable, HPβCD was used in task

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5.5.2 to encapsulate wild thyme essential oil, thereby reducing its volatility and enhancing its stability during subsequent extrusion processing (Rakmai et al., 2018).

2 Experimental Trials

2.1 Direct encapsulation of compounds in the polymeric matrix through extrusion

The extrusion experiments were carried out using a laboratory-scale twin-screw extruder (Hartek Technologies Co., Ltd., Guangzhou, China), as shown in Figure 1. The system consists of a horizontally aligned processing unit equipped with intermeshing screws enclosed within a segmented, temperature-controlled barrel. The barrel is divided into multiple independently controlled heating zones, enabling a tailored thermal profile along the extrusion path, which is essential for the progressive melting and homogenization of the polymeric material. The extruder includes a primary feeding system for solid raw materials, such as polymer pellets or powders, and additional feeding ports along the barrel, enabling the introduction of additives at different stages of the process. This configuration is particularly advantageous for incorporating temperature-sensitive compounds, as it allows their addition in downstream zones, thereby reducing their exposure to high temperatures and limiting thermal degradation. The system is further complemented by a downstream cooling and pelletizing unit, ensuring continuous processing and the production of uniform pellets with controlled morphology and size.

Twin-screw extruders are widely used in polymer processing due to their superior mixing efficiency and operational flexibility compared to single-screw systems. The intermeshing screw design supports distributive and dispersive mixing, ensuring a uniform distribution of additives within the polymeric matrix and improving the overall homogeneity of the final material. Additionally, the modular screw configuration, which typically includes conveying elements, kneading blocks, and mixing sections, allows customization of processing conditions to meet the specific requirements of the material system. This level of control is particularly important when working with complex formulations, such as those involving bioactive compounds, where both sufficient mixing and controlled thermal exposure are critical.

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Figure 1. Lab-scale extruder

The extrusion process involves multiple interdependent parameters that must be carefully adjusted to ensure stable and continuous operation. Prior to incorporating any bioactive compounds, it was necessary to optimize the processing conditions using pure recycled LDPE to establish a reliable baseline. Key parameters such as the temperature profile along the barrel, the screw speed, the feeder rate, and the downstream cooling and pelletizing conditions must be synchronized to achieve a steady material flow and consistent pellet formation. In particular, the feeding rate must be in accordance with the screw rotation speed and the system's cooling capacity, so that the extruded strand solidifies properly before pelletization.

After systematically evaluating different processing conditions, the optimized parameters for pure R-LDPE were established as follows:

- The temperature was set to 200 °C across all barrel and die zones,
- The extruder twin-screw speed was operated at 30 rpm

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- The feeder speed was set to 15 rpm, corresponding to a throughput of approximately 0.62 kg/h.
- The conveyor belt was set to 1 rpm, and air-cooling fans were used for strand solidification
- The pelletizer cutter was operated at 10 rpm to produce uniform pellets.

These conditions provided stable, continuous extrusion and were subsequently used as the reference for all subsequent experiments involving additive incorporation.

2.1.1 Extrusion with essential oils as bioactive compounds

To incorporate wild thyme essential oil into the R-LDPE matrix, various feeding strategies were initially evaluated. In the first approach, the essential oil was added directly through the main feeder together with the polymer pellets. However, due to the essential oil's high volatility and thermal sensitivity, this method resulted in significant losses during processing. The oil remained exposed to elevated temperatures for an extended residence time in the extrusion barrel, leading to evaporation and potential thermal degradation, thereby reducing its retention within the polymer matrix.



Figure 2. Peristaltic pump and produced filament

To address this limitation, a second approach was implemented using a peristaltic pump (BT100FC, Chonry, China), as shown in Figure 2. In this case, the essential oil was introduced in the final zone of the extruder, where the polymer is already fully molten. This strategy significantly reduces the time the essential oil is exposed to high temperatures, thereby minimizing volatilization losses and

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preserving its functional properties. The use of a peristaltic pump also enables precise, controlled dosing of the liquid additive, ensuring stable, reproducible processing conditions.

The peristaltic pump was operated under three different pulsed-feeding conditions to evaluate the effect of essential oil concentration on the final material. Specifically, the pump was set to deliver 100 µL, 200 µL, and 300 µL per second, each followed by a 1-second pause. This intermittent feeding mode enabled the controlled introduction of the essential oil without disturbing the extrusion flow, while also improving dispersion within the polymer melt. Using this methodology, various oil-to-polymer ratios were achieved, enabling further investigation of their effects on encapsulation efficiency and the functional performance of the resulting pellets.

2.1.1 Extrusion with ZnO particles

To incorporate ZnO particles into the R-LDPE matrix, the additive was introduced directly via the main feeder, along with the polymer pellets, as a dry mixture. Specifically, ZnO was added at a concentration of 5% w/w relative to the R-LDPE pellets, and the components were physically premixed prior to extrusion in order to achieve an initial homogeneous distribution. This method is particularly suitable for inorganic additives such as ZnO, which exhibit high thermal stability and are not susceptible to volatilization or degradation under the applied processing conditions. During extrusion, the twin-screw configuration promotes both distributive and dispersive mixing, enabling effective dispersion of ZnO particles throughout the polymer melt, while the feeder ensures that the additive is subjected to the full mixing length of the screws (Figure 3). As a result, ZnO remains within the polymer matrix during processing, leading to high retention and efficient incorporation into the final pelletized material, thereby providing a simple and robust approach for developing functional R-LDPE composites with enhanced antimicrobial and antioxidant properties.

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Figure 3. ZnO 5% w/w together with R-LDPE

2.2 Extrusion of encapsulated systems with recycled polymers

Electrospraying was carried out in uniaxial mode using a TL-Pro-BM system (Tongli Tech Co., Ltd., Shenzhen, China), as shown in Figure 4. The formulations were delivered by a syringe pump through a 19-gauge stainless-steel needle at a fixed flow rate for each experiment. A high positive voltage was applied to the needle while the rotating drum collector was charged with a high negative voltage to create the electric field necessary for fiber formation. As the electric field at the needle tip overcame the liquid's surface tension, the solution formed a Taylor cone, and a thin, charged jet was projected toward the collector. During its travel, the jet was stretched and progressively thinned, and solvent evaporation produced nanoparticles prior to deposition.

The experimental work is currently underway and focuses on developing encapsulated bioactive systems that can be incorporated into recycled LDPE via extrusion to improve the stability of thermally sensitive compounds. In this approach, the essential oil is first encapsulated in a carrier matrix, forming powder systems that can be directly fed into the extruder along with the polymer pellets, enabling processing under conventional extrusion conditions. Two different matrices are currently being investigated, namely PLA and HPβCD, due to their ability to form stable encapsulation systems via electrospraying and their distinct mechanisms of interaction with the bioactive compound. The electrospraying process is being optimized by testing different solution concentrations and operating parameters to achieve stable particle formation and effective

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incorporation of the essential oil into the carrier system. So far, an HPβCD-based encapsulated system has been successfully produced, containing wild thyme essential oil at 5% w/w relative to HPβCD, yielding a powder that can be handled and processed with the polymer. This encapsulated system is currently being used in extrusion trials at a 5% w/w concentration relative to R-LDPE to evaluate its behavior during processing and assess its potential to enhance essential oil retention compared with direct addition. At the same time, further work is underway to develop PLA-based encapsulated systems and optimize electrospraying conditions, with the overall aim of identifying the most effective encapsulation strategy for incorporation into recycled polymer matrices.



Figure 4. Electrospraying process

2.3 Development of thin film coatings via electrospinning

The development of thin-film coatings via electrospinning is underway, focusing on fabricating functional nanofibrous layers on recycled LDPE films supplied by Thrace Poly, with the aim of enhancing surface functionality while preserving the substrate's bulk properties (Figure 5). In this approach, PLA is used as the carrier polymer due to its processability and compatibility with electrospinning, while wild thyme essential oil is incorporated as a bioactive agent to introduce antioxidant and antimicrobial properties. The electrospinning technique is particularly suitable for this application, as it enables the formation of ultrafine fibers with high surface area and porosity, which can facilitate both the encapsulation and potential controlled release of the active compounds. The overall objective is to develop a coating system that can be applied onto recycled films, contributing to their upcycling into higher-value materials.

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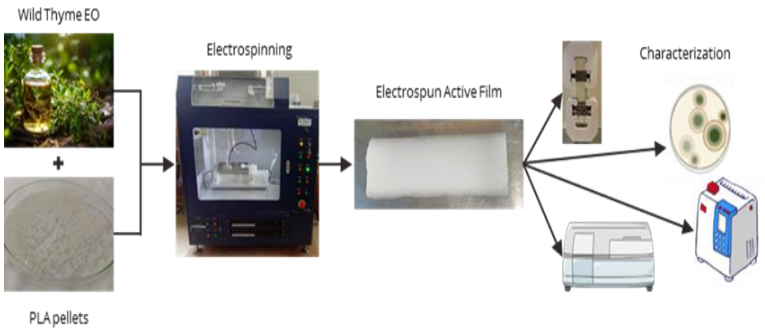


Figure 5. Development of electrospun thin-films

To systematically investigate the influence of processing parameters on electrospinning performance and encapsulation behavior, a Box–Behnken Design (BBD) experimental plan has been implemented (Table 1), comprising 29 experimental runs and additional center points to estimate experimental error and detect curvature effects. The main response variable selected for the study is the encapsulation efficiency, while the independent variables include polymer concentration, applied voltage, solution flow rate, and oil-to-polymer ratio, each examined at three different levels. This design allows for a structured evaluation of both the individual and combined effects of the parameters, enabling the identification of optimal processing conditions and providing a statistical basis for understanding the system behavior. The use of such a design also reduces the total number of experiments required while still ensuring reliable and meaningful results.

Table 1. Box–Behnken Experimental Design

Factor	Description	Levels
A	Polymer Concentration (% w/v)	8, 10, 12
B	Voltage (kV)	18, 24, 30
C	Flow Rate (mL/h)	2, 5, 8
D	Oil to Polymer Ratio (w/w)	0.05, 0.1125, 0.175

The process of electrospinning works in a similar way as electrospraying. The main difference

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Electrospinning operates on the same fundamental principles as electrospraying, since both processes subject a polymer solution to a high electric field that induces jet formation and subsequent solvent evaporation. However, the key distinction between the two techniques lies in the concentration and viscoelastic properties of the polymer solution, which directly influence jet stability. In electrospinning, the higher polymer concentration leads to increased chain entanglements, preventing the breakup of the jet into droplets. As a result, instead of forming discrete nanoparticles as in electrospraying, the jet remains continuous and elongates into fibers.

The stability of the jet, the absence of bead formation, and the encapsulation efficiency are key parameters currently being evaluated, as they directly influence the morphology and performance of the final coating. At the same time, efforts are underway to control the thickness and coverage of the deposited layer and to improve adhesion between the electrospun fibers and the LDPE substrate.

In parallel with the processing experiments, characterization activities are underway to evaluate the properties of the electrospun films and coatings produced. Scanning electron microscopy is used to examine fiber morphology, diameter distribution, and structural uniformity, while tensile testing is performed to assess the mechanical properties of the electrospun films. Additionally, gas chromatography is used to analyze the presence and retention of key essential oil components, providing insight into encapsulation performance. These efforts are ongoing and focus on correlating processing parameters with material properties to support the development of thin-film coatings with enhanced functionality for potential applications in active packaging systems.

3 Characterization of the produced materials

3.1 Characterization of extrusion pellets

The pellet samples exhibited distinct visual characteristics depending on the additive, indicating variations in dispersion and phase distribution within the polymeric matrix (Figure 6). Pure R-LDPE exhibited a uniform, semi-transparent morphology typical of polyethylene, whereas the addition of essential oil produced darker pellets, indicating partial absorption and possible phase separation due to incompatibility between the hydrophobic polymer and the volatile oil components. In contrast, ZnO-filled samples exhibited a homogeneous, lighter appearance, suggesting effective

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distribution of the inorganic phase, whereas the HPβCD-based system showed slight heterogeneity, likely due to the presence of solid encapsulated particles within the melt. These observations provide a first qualitative indication of the interaction between the additives and the polymer during melt processing. Such macroscopic differences are often correlated with microstructural dispersion and can influence final material properties. This visual variability also suggests differences in interfacial interactions between each additive and the polymer matrix.

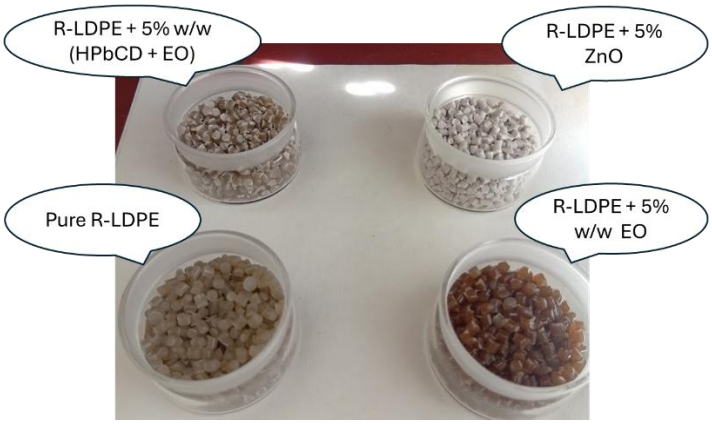


Figure 6. Pellets produced with the extruder

Thermogravimetric analysis (TGA) of pure R-LDPE (Figure 7a) confirmed a single-step thermal degradation mechanism, characteristic of polyolefins, with negligible residue, indicating the absence of inorganic fillers or thermally stable additives. Upon incorporation of ZnO at 5% w/w, a residual mass of approximately 4.9% was observed at high temperatures, corresponding closely to the initial loading, thereby confirming the thermal stability of ZnO and its complete retention during processing (Figure 7b). Based on this result, the entrapment efficiency was calculated to be approximately 94%, demonstrating that inorganic particles are not affected by volatilization or thermal degradation under extrusion conditions. This behavior highlights the suitability of inorganic fillers for incorporation into polymer matrices via melt processing. Furthermore, the unchanged degradation onset temperature suggests that ZnO does not significantly catalyze polymer degradation under the applied conditions. This stability indicates that ZnO can maintain its functional properties after processing.

The TGA profile of samples with directly added essential oil showed an additional mass loss at lower temperatures, typically below 150 °C, attributed to the evaporation of volatile compounds, such as monoterpenes, present in wild thyme oil (Figure 7c). However, the magnitude of this mass loss was

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significantly lower than the theoretical oil content, indicating that a large fraction of the essential oil was lost during extrusion due to its high vapor pressure and low thermal stability. Consequently, the entrapment efficiency was estimated at approximately 26%, highlighting the limitations of directly incorporating volatile bioactive compounds into polymer melts. This result emphasizes the strong influence of processing temperature and residence time on the retention of thermolabile substances. It also suggests that diffusion of volatile components through the polymer melt plays a critical role in their loss during processing. The results further indicate that even late-stage addition does not fully prevent volatilization losses.

In the case of the HPβCD-based encapsulated system, the TGA curves exhibited multi-step degradation, with an intermediate weight loss around 300 °C, attributed to cyclodextrin decomposition and the release of encapsulated compounds (Figure 7d). Despite HPβCD's known ability to form inclusion complexes with hydrophobic molecules via host–guest interactions, the retained fraction of the essential oil after extrusion remained low, with an estimated entrapment efficiency of approximately 8%. This indicates that the encapsulation system, although effective at ambient conditions, is not sufficiently stable under the combined effects of temperature and shear during melt processing. The mechanical stresses within the extruder may further disrupt the inclusion complexes, contributing to the premature release of the active compounds. Additionally, the hydrophilic nature of HPβCD may limit its compatibility with the non-polar LDPE matrix, affecting dispersion and retention. This incompatibility may also promote phase separation during melt flow.

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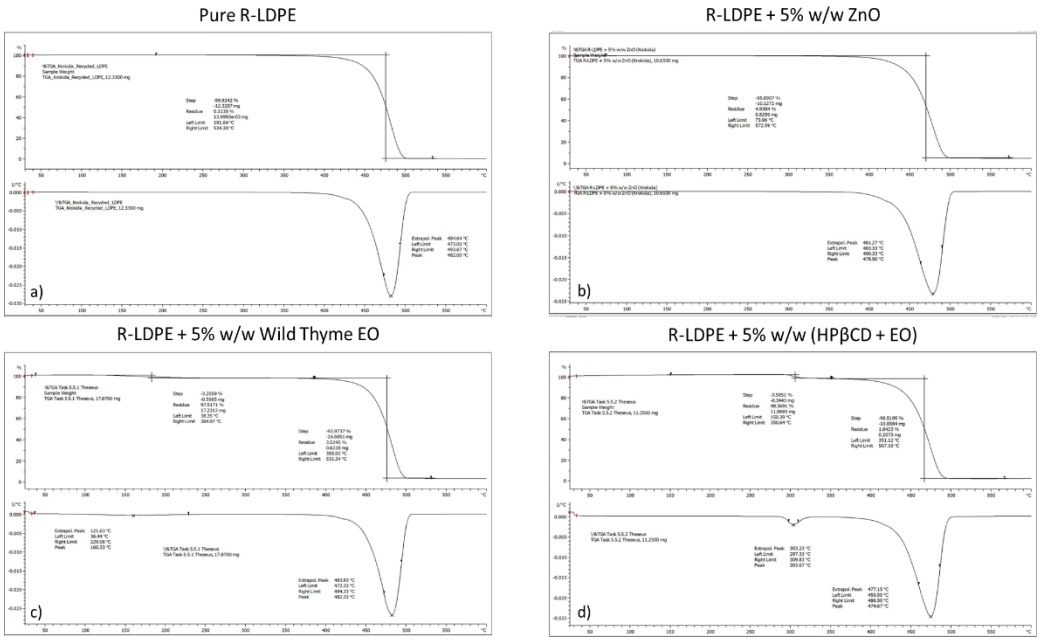


Figure 7. TGA of extrusion samples for a) Pure R-LDPE, b) R-LDPE + 5% w/w ZnO, c) R-LDPE + 5% w/w Wild Thyme EO and d) R-LDPE + 5% w/w (HPβCD + EO)

FTIR analysis provided further insight into the chemical composition of the samples with direct extrusion, confirming the presence of characteristic absorption bands associated with the essential oil, including peaks corresponding to aliphatic C–H stretching and aromatic ring vibrations (Figure 8). These bands were detected with low intensity in the modified samples, indicating limited retention of the oil within the polymer matrix. The absence of new peaks or significant spectral shifts suggests that no chemical bonding occurs between the polymer and the additives and that the system remains physically blended rather than chemically modified. This is consistent with the inert chemical nature of LDPE and its limited ability to interact with functional molecules. The results also indicate that the additives do not significantly alter the chemical structure of the polymer backbone. This confirms that any functional improvement is primarily due to physical incorporation rather than chemical modification.

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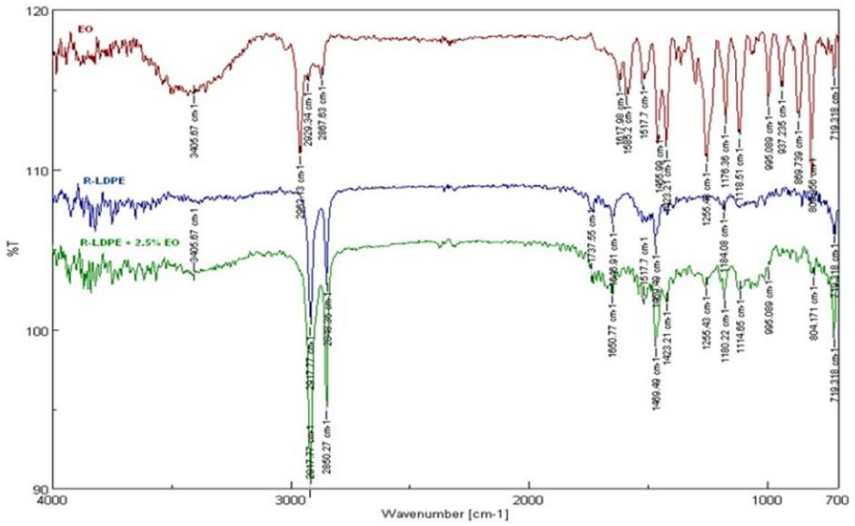


Figure 8. FTIR of pellets made with direct incorporation of wild thyme essential oil

Differential Scanning Calorimetry (DSC) analysis showed that the melting temperature of R-LDPE was only slightly affected by the presence of essential oil, with a minor decrease observed as the oil content increased, indicating a weak plasticizing effect (Figure 9). This behavior can be attributed to the presence of low-molecular-weight compounds that interfere with polymer chain packing, leading to a slight reduction in crystallinity. However, the overall thermal transitions remained largely unchanged, confirming that the crystalline structure of LDPE is not significantly disrupted at the studied concentrations. This suggests that the polymer's mechanical integrity is expected to be largely preserved. The small shift in melting temperature also indicates limited miscibility between the oil and the polymer matrix. This limited miscibility may restrict the uniform distribution of the oil within crystalline regions.

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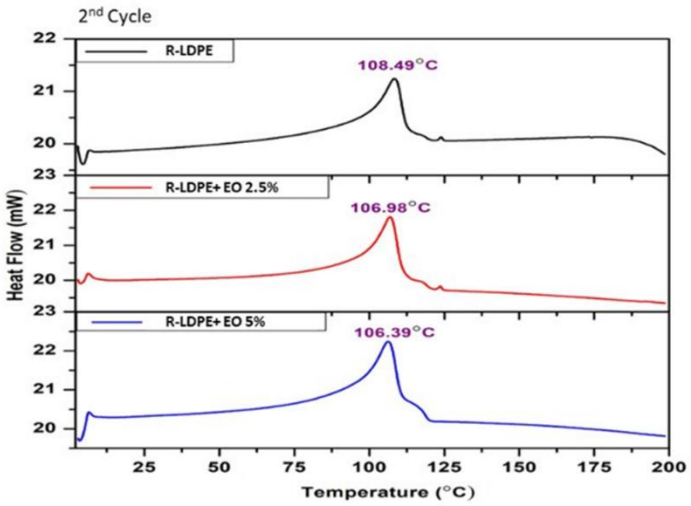


Figure 9. DSC of pellets made with direct incorporation of wild thyme essential oil

Scanning Electron Microscopy (SEM) analysis of the electrosprayed encapsulated systems revealed clear morphological differences between the PLA and HPβCD particles, reflecting the influence of matrix properties and processing conditions on particle formation (Figure 10). The PLA electrosprayed system exhibited relatively small, irregularly shaped particles that tended to agglomerate, indicating partial coalescence during solvent evaporation and limited droplet stabilization. The broad particle size distribution suggests that jet breakup and secondary droplet formation were not fully controlled under the selected parameters. In contrast, the HPβCD-based system exhibited larger, more spherical particles, often characterized by porous or partially collapsed surface structures, which can be attributed to rapid solvent evaporation and the formation of inclusion complexes within the cyclodextrin matrix. Despite the more defined morphology, significant aggregation between HPβCD particles was also observed, likely due to intermolecular interactions and insufficient repulsion during deposition. These morphological features are expected to influence the dispersion behavior of the encapsulated systems within the polymer matrix during extrusion, potentially leading to inhomogeneous distribution and localized release of the encapsulated essential oil.

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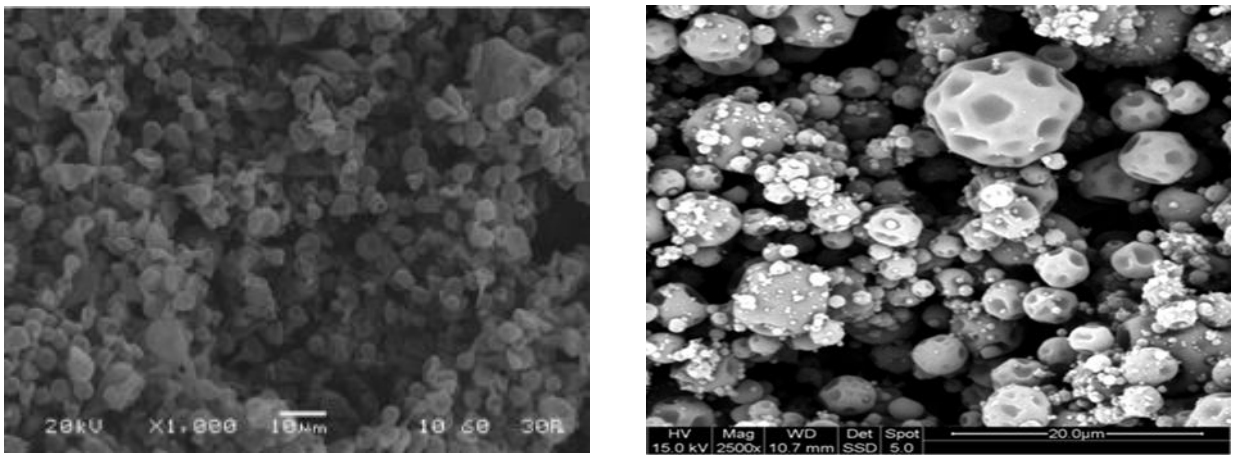


Figure 10. SEM images of a) PLA and b) HPβCD

Finally, it should be noted that the encapsulation efficiency of the HPβCD-essential oil system before extrusion was determined by GC–MS (Figure 11) and was approximately 90%, indicating the high effectiveness of the encapsulation process. The significant decrease in efficiency observed after extrusion demonstrates that the primary limitation arises during thermal processing, where the combined effects of temperature, shear forces, and residence time lead to partial release and volatilization of the encapsulated compounds. This highlights the need for alternative processing strategies or more thermally stable encapsulation systems for such applications. It further suggests that processing conditions must be carefully tailored to preserve the functionality of sensitive bioactive compounds. This discrepancy between pre- and post-processing efficiency underscores the challenges of transferring encapsulated systems into melt-based processes.



Figure 11. GC-MS system

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3.2 Characterization of thin nanofiber films made with electrospinning

3.2.1 PLA electrospun films with encapsulated essential oils

The encapsulation efficiency (EE%) of the essential oil within the electrospun PLA fibers was quantified using GC–MS analysis, following the previously described protocol, thereby enabling accurate determination of volatile compound retention. The results (Table 2) indicated that encapsulation efficiency strongly depends on processing parameters, with moderate voltage and flow rate favoring greater retention of the essential oil. Specifically, the highest encapsulation efficiency was experimentally determined to be 79.4%, corresponding to a polymer concentration of 10% w/v, a voltage of 24 kV, a flow rate of 8 mL/h, and an oil-to-polymer ratio of 0.05 w/w. This finding is consistent with the balance required between sufficient jet stretching and controlled solvent evaporation during electrospinning. It also suggests that excessive oil loading impairs encapsulation due to the instability of the polymer jet. The GC–MS chromatographic analysis confirmed the presence of key volatile compounds, such as carvacrol and thymol, validating successful encapsulation.

Table 2. Encapsulation efficiency of electrospun samples

RUN	Polymer Concentration (%w/v)	Voltage (kV)	Flow Rate (mL/h)	Oil to Polymer Ratio (w/w)	Encapsulation Efficiency
1	10	24	8	0.05	79.4
2	10	18	5	0.175	50.9
3	10	24	5	0.1125	76.8
4	8	24	5	0.175	35.1
5	10	24	5	0.1125	73.7
6	10	18	5	0.05	48.5
7	12	18	5	0.1125	69.9
8	8	18	5	0.1125	44.7
9	8	24	5	0.05	34.7

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10	10	24	5	0.1125	60.1
11	10	30	8	0.1125	55.7
12	10	24	5	0.1125	57.4
13	12	30	5	0.1125	43.9
14	10	30	5	0.175	61.7
15	10	18	2	0.1125	48.4
16	10	18	8	0.1125	42.7
17	10	30	5	0.05	51.7
18	10	24	8	0.175	36.7
19	10	24	5	0.1125	40.6
20	12	24	8	0.1125	43.6
21	12	24	5	0.175	37.7
22	12	24	5	0.05	53.4
23	8	24	2	0.1125	42.7
24	10	24	2	0.175	38.3
25	10	30	2	0.1125	35.2
26	8	24	8	0.1125	47.2
27	10	24	2	0.05	44.8
28	12	24	2	0.1125	35.1
29	8	30	5	0.1125	39.3

The experimental results further demonstrated that encapsulation efficiency exhibits nonlinear behavior with respect to the studied variables, reaching maximum values at intermediate parameter levels rather than at extreme conditions. Higher polymer concentrations increased matrix density and reduced porosity, thereby enhancing the physical entrapment of the essential oil within the fiber structure. However, excessively high viscosity can hinder proper jet formation, leading to

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defects and reduced encapsulation performance. Similarly, very high voltages may promote jet instability and increased evaporation of volatile compounds before deposition. This interplay highlights the importance of optimizing electrospinning parameters to achieve both structural integrity and functional performance. The observed trends agree with established electrohydrodynamic principles of fiber formation.

Scanning electron microscopy (SEM) analysis (Figure 12) revealed that the electrospun films possess a non-woven fibrous network composed of randomly oriented fibers with a relatively uniform diameter distribution. The absence of bead formation under optimized conditions suggests stable jet formation and favorable solution properties. Localized defects or droplets are likely attributable to partial phase separation or elevated oil content, both of which can alter the viscoelastic properties of the spinning solution. The resulting fibrous structure provides a high area-to-volume ratio, which is advantageous for applications requiring controlled release of active compounds. Additionally, fiber morphology plays a critical role in governing diffusion processes and the release rate of encapsulated substances. The observed microstructure demonstrates that electrospinning is an effective method for producing functional active packaging materials.

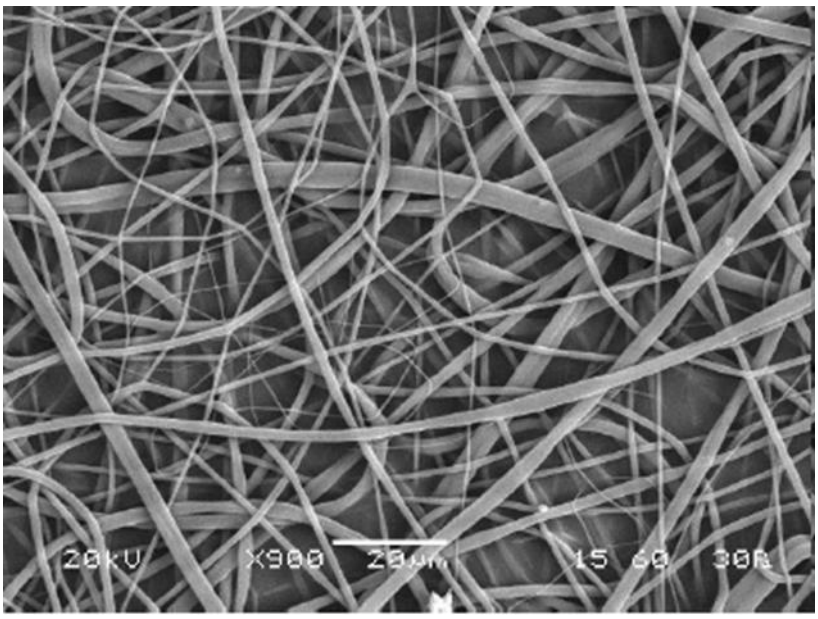


Figure 12. SEM of electrospun PLA with encapsulated wild thyme

The structural characteristics of the electrospun films are closely linked to their encapsulation performance, as the distribution of essential oil within the fiber matrix directly influences both retention and release. Uniform dispersion of the oil within the fibers enhances encapsulation

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efficiency and reduces the likelihood of surface evaporation during processing. In contrast, phase separation or accumulation of oil at the fiber surface can result in rapid loss of volatile compounds. SEM observations indicate that optimal processing conditions improve compatibility between the polymer and the encapsulated phase. This compatibility is essential for maintaining the stability of the encapsulated system and influences the material's long-term performance in practical applications. Further characterization will focus on evaluating the mechanical properties of the electrospun films, particularly through tensile testing, to determine their suitability for packaging applications. Initial findings suggest that the fibrous structure imparts adequate flexibility, although the incorporation of essential oil may decrease mechanical strength due to plasticization effects. Balancing encapsulation efficiency with mechanical performance is critical for developing effective materials. These assessments will provide valuable insights into the structural integrity of the films under mechanical stress, which is necessary for predicting material performance during handling and use.

4 Conclusions and Future Work

4.1 Conclusions

This deliverable presents the progress made in Task 5.5 toward developing functional materials from recycled polymers that incorporate bioactive compounds via extrusion, encapsulation, and electrospinning. The results demonstrate both the potential and the limitations of different material-processing strategies in the context of circular economy applications.

The direct incorporation of bioactive compounds into recycled LDPE via extrusion proved feasible but was highly dependent on the physicochemical properties of the additives. Inorganic ZnO particles exhibited excellent compatibility with the extrusion process, showing high retention (~94%) and uniform dispersion within the polymer matrix. Their thermal stability and non-volatile nature make them highly suitable for melt-processing applications, enabling the development of functional recycled polymers with enhanced antimicrobial and antioxidant properties.

In contrast, the direct addition of wild thyme essential oil led to significant losses during extrusion, with a low entrapment efficiency (~26%), despite the use of optimized feeding strategies. This behavior highlights the inherent limitations of incorporating volatile and thermolabile compounds into polymer melts, even when introduced at later stages of processing.

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Encapsulation strategies were therefore investigated to improve the stability and retention of the essential oil. While HPβCD-based systems achieved high encapsulation efficiency before extrusion (~90%), their performance declined significantly after processing (~8%), indicating that inclusion complexes are insufficiently stable under extrusion conditions. This result emphasizes the impact of thermal and mechanical stresses on encapsulated systems and the importance of matrix compatibility with the polymer phase.

In contrast, electrospun PLA-based systems demonstrated significantly higher encapsulation efficiencies (up to ~79.4%), confirming the suitability of electrohydrodynamic techniques for incorporating sensitive bioactive compounds. The ability to control fiber morphology and processing parameters enabled the development of nanostructured coatings with enhanced retention and potential for controlled release. Overall, the results indicate that:

- Melt-processing techniques are suitable for thermally stable additives (e.g., ZnO),
- Encapsulation is essential for volatile compounds but must be compatible with processing conditions,
- Electrospinning offers a highly promising alternative for incorporating sensitive bioactives into functional materials.

These findings contribute to the THESEUS objectives by demonstrating viable pathways to upcycle recycled polymers into higher-value functional materials, supporting both material circularity and advanced packaging applications.

4.2 Future Work/ Next Steps

Building on the current findings, the following activities are planned to optimize material performance further and advance the technology readiness level:

1. **Optimization of Encapsulation Systems**
    - Development and optimization of PLA-based encapsulated particles via electrospraying, focusing on improving particle stability during extrusion.
    - Exploration of hybrid encapsulation systems to enhance thermal resistance.
    - Investigation of encapsulation efficiency vs. release kinetics trade-offs.
2. **Improvement of Extrusion Processing Strategies**
    - Optimization of extrusion parameters (temperature profile, screw configuration, residence time) to minimize bioactive losses.

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- Evaluation of reactive extrusion or compatibilizers to improve interaction between LDPE and encapsulated systems.
- Study of alternative feeding strategies (e.g., micro-dosing, liquid injection systems with cooling zones).

3. **Advanced Material Characterization**

   Quantitative evaluation of:

   - Antioxidant performance,
   - Release kinetics of active compounds under simulated conditions.
   - Mechanical and barrier property assessment of both pellets and films:
   - Tensile strength, elongation, permeability.
   - Long-term stability studies of functionalized materials.

4. **Scale-Up and Process Integration**

   - Assessment of the scalability of electrospinning and electrospraying processes for industrial applications.
   - Integration of electrospun coatings into continuous film production lines.
   - Evaluation of compatibility with industrial extrusion systems.

References

Devra, R.S., Srivastava, N., Vadali, M., Arora, A., 2024. Recycling, thermophysical characterization, and assessment of low-density polythene waste as feedstock for 3D printing. Materials Today Sustainability 28.

Dey, S., Mohanty, D. lochan, Divya, N., Bakshi, V., Mohanty, A., Rath, D., Das, S., Mondal, A., Roy, S., Sabui, R., 2025. A critical review on zinc oxide nanoparticles: Synthesis, properties and biomedical applications. Intelligent Pharmacy.

Ghatge, S., Yang, Y., Ahn, J.H., Hur, H.G., 2020. Biodegradation of polyethylene: a brief review. Appl. Biol. Chem.

Maleki, H., Azimi, B., Ismaeilimoghadam, S., Danti, S., 2022. Poly(lactic acid)-Based Electrospun Fibrous Structures for Biomedical Applications. Applied Sciences (Switzerland).

Maurya, S., Anupam, Tripathi, S., Chaubey, S., Soni, A., 2026. Recent advances in the synthesis and applications of zinc oxide nanomaterials for healthcare energy and environmental systems. Discover Chemistry 3, 98.

Nicolaescu, O.E., Belu, I., Mocanu, A.G., Manda, V.C., Rău, G., Pîrvu, A.S., Ionescu, C., Ciulu-Costinescu, F., Popescu, M., Ciocîlteu, M.V., 2025. Cyclodextrins: Enhancing Drug Delivery, Solubility and Bioavailability for Modern Therapeutics. Pharmaceutics.

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This project has received funding from the European Union Horizon Research and Innovation programme under grant agreement No 101178059

Procopio, F.R., Brexó, R.P., Vitolano, L.E.S., Martins, M.E. da M., Astolfo, M.E. de A., Bogusz Junior, S., Ferreira, M.D., 2024. Development of essential oils inclusion complexes: a nanotechnology approach with enhanced thermal and light stability. Discover Nano 19.

Rakmai, J., Cheirsilp, B., Cid, A., Torrado-Agrasar, A., Mejuto, J.C., Simal-Gandara, J., 2018. Encapsulation of Essential Oils by Cyclodextrins: Characterization and Evaluation. In: Cyclodextrin - A Versatile Ingredient. InTech.

Shao, L., Xi, Y., Weng, Y., 2022. Recent Advances in PLA-Based Antibacterial Food Packaging and Its Applications. Molecules.

Tagnaout, I., Zerkani, H., Hadi, N., Moumen, B. El, Makhoukhi, F. El, Bouhrim, M., Al-Salahi, R., Nasr, F.A., Mechchate, H., Zair, T., 2022. Chemical Composition, Antioxidant and Antibacterial Activities of Thymus broussonetii Boiss and Thymus capitatus (L.) Hoffmann and Link Essential Oils. Plants 11.

Wińska, K., Mączka, W., Łyczko, J., Grabarczyk, M., Czubaszek, A., Szumny, A., 2019. Essential oils as antimicrobial agents—myth or real alternative? Molecules.

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