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LIFE CYCLE ASSESSMENT OF POLYMER MATRIX PRODUCTION OF NANO-ZNO ANTIMICROBIAL PACKAGING MATERIALS

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ABSTRACT
Petroleum-based polymers offer beneficial packaging properties, but their environmental impact necessitates a shift to bio-based alternatives. The study analyzes the "cradle-to-gate" life cycle assessment (LCA) of polymer matrices of ZnO nanoparticles/low-density polyethylene (LDPE), ZnO nanoparticles/ethylene vinyl acetate copolymer (EVA), and ZnO nanoparticles/polylactic acid (PLA). Results indicate that PLA produced from renewable biomass requires more water consumption than LDPE and EVA produced from petroleum feedstocks. PLA production's dependence on water-intensive agricultural processes contributes to its water footprint. In addition, a comparative analysis of energy demand showed that the production of LDPE and EVA is significantly dependent on non-renewable fossil energy sources, while the production of PLA is more dependent on renewable biomass and alternative energy sources. Findings from environmental impact categories such as eutrophication, global warming potential, and ecotoxicity highlight the various environmental concerns associated with PLA and the need for sustainable production methods. The study highlights the importance of LCA when selecting materials for future manufacturing, advocating the use of polymers with a lower environmental impact.
Keywords: Life cycle assessment, Antimicrobial packaging, Environmental impact, Polymer, Polyethylene, Ethylene vinyl acetate, Polylactic acid.

Introduction

The sustainable design of nanocomposites made from petroleum and bio-based polymers as antimicrobial packaging is currently the focus of researchers. The advantage of petroleum-based polymers is that they have traditional processability (blown film or cast film), high tensile strength, suitable elasticity, flexibility, and high heat resistance. Antimicrobial packaging usually uses petroleum-based polymers, and attempts are being made to replace them with bio-based polymers whenever possible. Because the production of petroleum-based polymers consumes 65% more energy and emits 30-80% more greenhouse gases than the production of bio-based polymers [1]. The design of new polymer-based materials can be achieved by incorporating nanoparticles (NPs) into the polymer matrix. The application of zinc oxide nanoparticles (ZnO NPs) in improving the properties of polymer packaging such as barrier, mechanical, and antimicrobial properties is known [2]. ZnO NPs/polymer nanocomposites designed by encapsulating ZnO NPs in a polymer matrix inhibit the growth of bacteria and fungi and prevent spoilage by increasing product shelf life [2].

As the application of ZnO NPs/polymer nanocomposites in food packaging increases, the study of the life cycle assessment (LCA) of these materials also becomes important. In the preparation of antimicrobial packaging ZnO NPs/polymer nanocomposites, petroleum-based polymers such as low-density polyethylene (LDPE), polyethylene terephthalate, polypropylene, polyvinyl chloride, ethylene-vinyl acetate (EVA) and biologically based polymers such as polylactic acid (PLA), polycaprolactone, polyglycolic acid, polybutylene succinate-co-adipate, polyhydroxyalkanoates, and polyhydroxybutyrate are used [1].

The study is about an investigation of the “cradle-to-gate” LCA of polymer matrices of ZnO NPs/LDPE [2], ZnO NPs/EVA [3], and ZnO NPs/PLA [4] nanocomposites known in the literature for use in packaging and showing antimicrobial properties. The purpose of choosing these nanocomposites is that nanocomposites with these matrices can be prepared by extrusion. Nanocomposites are designed via the extrusion method, blending the polymer with a specific quantity of ZnO nanoparticles in a twin-screw extruder [2–4]. In general, if the synthesis process is the same for all three composites, the LCA of the materials will depend on the matrix production.

LDPE is ideal for food packaging due to its water vapor resistance and gas permeability. EVA, a blend of polyethylene and polyvinyl acetate, is preferred for refrigerated food packaging due to its low vapor permeability, flexibility, and transparency. PLA, derived from biomass like corn, is biodegradable but has limited gas permeability, restricting its use in food packaging. Despite this, PLA's non-toxic and biocompatible nature often leads to its use, sometimes in blends with other polymers [5]. Fig. 1 shows LDPE, EVA, and PLA structures.

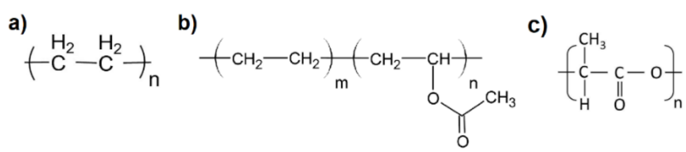

Fig.1. The structure of LDPE (a), EVA (b), and PLA (c) polymers.

Materials and Methods

The database in SimaPro 9.5.0 software (Demo version without additional data input), which contains the Ecoinvent 3 life cycle inventory databases was used to compare “cradle-to-gate” LCA of LDPE, EVA, and PLA with “AWARE”, “Cumulative energy demand” (CED), and “CML-IA baseline” methods. For comparison, 1 kg of 'Polyethylene, low density, pellet {RER}| production | Cut-off, S', 1 kg of 'Polyethylene, low density, pellet {RER}| production | Cut-off, S', 1 kg 'Polylactide, granule {GLO}| production | Cutting, S' and 1 kg of 'Ethylene vinyl acetate copolymer {RER}| production | Cut-off, S' processes are selected. It is known that input (energy, water, raw materials, and ancillary materials) and output (emissions, waste, wastewater, and products) materials define the boundaries of LCA for each stage of polymer production [6]. For LDPE, EVA, and PLA, the functional unit is 1 kg.

The “cradle-to-gate” analysis involves evaluating the life cycle of a product from the extraction of resources used in its production (cradle) to the point just before its delivery to the consumer (factory gate) [7]. Freshwater eco-factors are currently identified using the "AWARE" method, which measures the relative amount of water remaining in watersheds after both human and ecosystem needs have been met. CED reflects the total amount of primary energy consumed during the life cycle of a product or service. The "CML" method, provides versatility by allowing the assessment of both intermediate and end points [7].

Results and Discussion

Water Consumption

Fig.2 illustrates that PLA production consumes more water than LDPE and EVA production, based on the AWARE/Characterization method in SimaPro 9.5.0 [7, 8]. Differences in water footprints, production processes, and raw materials contribute to variances among PLA, LDPE, and EVA copolymer. Several factors explain why producing 1 kg of LDPE and EVA may require more water than 1 kg of PLA: 1) Raw material distinctions: PLA is typically derived from renewable resources like corn or sugarcane, necessitating significant water for biomass growth. The agricultural phase in PLA production notably impacts water pollution. Conversely, LDPE and EVA are commonly derived from fossil fuels, such as ethylene from natural gas or oil. Although water is also essential for fossil fuel extraction and processing, biomass-based materials like PLA can have a higher water footprint; 2) Processing methods and stages: Production processes for different polymers involve varying levels of water consumption. For instance, PLA production entails multiple steps like sugar fermentation, extraction, and polymerization, each potentially requiring water for cooling, cleaning, or other purposes [9].

While LDPE and EVA manufacturing processes are also water-intensive, they can be simpler and less water-intensive compared to the complex PLA manufacturing process. Efficient water management, including recycling and reuse, further contributes to reducing water consumption. Particularly, LDPE and EVA production often feature advanced water recycling systems, decreasing overall water usage per production unit. However, it's crucial to note that water consumption may vary among polymer types, influenced by diverse production practices across different enterprises and regions. Additionally, technological advancements and evolving manufacturing processes may alter water requirements in polymer production over time. Efforts are underway to mitigate the environmental impact of polymer production, including minimizing water usage through sustainable materials development.

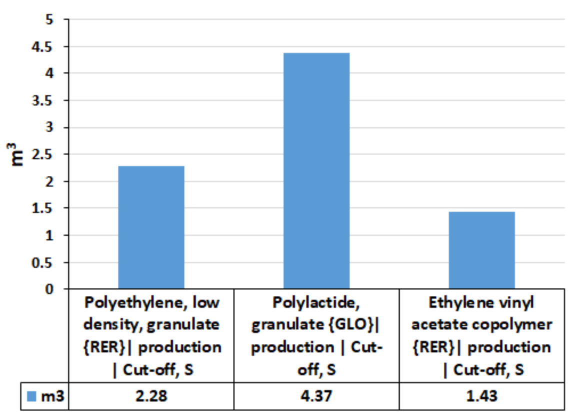

Fig.2. Comparison of water use during the synthesis of 1 kg of the LDPE, EVA, and PLA by the

AWARE/Characterization method (SimaPro 9.5.0) [7]

Water-intensive stages in PLA production include sugar cane cultivation, sugar milling, lactic acid production, lactide production, and various PLA production stages, with lactic acid fermentation being the most water-consuming. Notably, water consumption in sugar factories is relatively low as treated water from the mill is often reused for irrigation nearby. Despite PLA production's overall higher water demand compared to LDPE and EVA, many PLA facilities can fulfill most water needs from industrial complex reservoirs, collecting rainwater and wastewater [9].

Comparative CED

Table 1 presents the comparative total energy requirements for producing 1 kg of LDPE, PLA, and EVA, reported in percentage points across various energy-related categories. Notably, LDPE and EVA exhibit the largest impact in the “Non renewable, fossil” category, indicating their reliance on non-renewable fossil energy sources. The primary non-renewable fossil energy sources in LDPE and EVA production typically involve fossil fuels like natural gas and oil. LDPE, derived from ethylene, is synthesized via steam cracking of hydrocarbons like ethane or naphtha, derived from natural gas or oil. Similarly, EVA copolymer, also based on ethylene, utilizes fossil fuels, mainly natural gas or petroleum feedstock, for ethylene production. Additionally, the production of vinyl acetate, used as a co-monomer in EVA production, also relies on fossil fuels [10]. Consequently, the “Non renewable, fossil” category is more pronounced in EVA production (100%) compared to LDPE (99.8305%). The extraction, processing, and conversion of fossil fuels into ethylene, and subsequently into LDPE or EVA copolymer, contribute to the generation of non-renewable fossil energy sources associated with their production. The high-energy intensity of fossil fuels and the dependency of LDPE and EVA production on these resources underscore their reliance on non-renewable sources [11].

Table 1. Comparative CED in percentage points (%) of production 1 kg LDPE, EVA, and PLA using SimaPro 9.5.0 (Characterization) [7, 11]

Impact category	LDPE, granulate {RER}| production | Cut-off, S	PLA {GLO}| production | Cut-off, S	EVA {RER}| production | Cut-off, S
Non renewable, fossil	99.8305	51.7984	100
Non-renewable, nuclear	100	62.3835	63.0124
Renewable, biomass	1.6707	100	1.8678
Renewable, wind, solar, geothermal	76.0352	100	40.9973
Renewable, water	55.9332	100	39.8359

Furthermore, in Table 1, the “Non-renewable, nuclear” category exhibits the lowest value for PLA, with LDPE production showing the highest value (100%). Nevertheless, significant values are also observed in PLA (62.3835%) and EVA (63.0124%) production. Nuclear energy, often utilized in electricity generation, is integrated into the LCA when energy for raw material extraction, transportation, and polymer processing originates from non-renewable nuclear sources. This impact is reflected in the “Non-renewable, nuclear” category, contributing to the overall

LCA analysis.

PLA production demonstrates the highest impact level (100%) in the “Renewable, biomass” category compared to LDPE (1.6707%) and EVA (1.8678%) production. Commonly used biomass sources in PLA production include: 1) Corn Starch – derived from corn kernels, corn starch undergoes microbial fermentation to produce lactic acid, which is then polymerized into PLA; 2) Sugarcane – rich in fermentable sugars, sugarcane can be fermented to yield lactic acid, which polymerizes into PLA; 3) Cassava – this root crop, abundant in starch, serves as a biomass source for PLA production. Cassava starch is converted into lactic acid and subsequently polymerized into PLA; 4) Sugar Beet – another source of fermentable sugar, sugar beet, can also be utilized in PLA production; 5) Other Biomass – additional sources like millet, wheat, and barley are also used in PLA production [9, 12].

In the “Renewable, wind, solar, geothermal” category, PLA exhibits the highest impact score, indicating its reliance on renewable energy sources such as wind, solar, and geothermal energy. The higher value of the "Renewable, water" category in PLA production compared to LDPE and EVA is attributed to the increased utilization of collected rainwater and purified water in its production process.

CML-IA baseline method

Fig.3 shows the environmental impact of LDPE, EVA, and PLA polymers according to the basic CML-IA method: values are normalized on a scale from zero to 100, with 100 indicating the highest environmental impact.

Analyzing the data reveals that PLA, scoring 100, exhibits the highest impact in most categories (excluding “Photochemical Oxidation” and “Abiotic Depletion (fossil fuels)”). In LDPE production, ethylene plays a crucial role in photochemical oxidation, a phenomenon occurring under specific atmospheric conditions like sunlight, low humidity, nitrogen oxides, and volatile organic compounds (VOCs). Ethylene, a VOC released during LDPE (and EVA) production, contributes to the formation of photochemical oxidants, aligning with conditions favoring their formation [14].

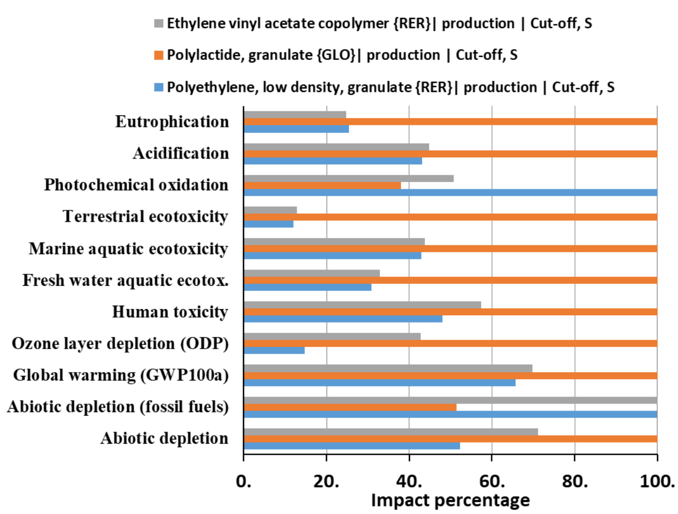

Fig.3. Comparative LCA results of 1 kg LDPE, EVA, and PLA production by CML-IA baseline/ Characterization method (SimaPro 9.5.0) [13]

PLA's biomass starch significantly impacts “Eutrophication” due to the high Chemical Oxygen Demand (COD) in wastewater. Additionally, PLA's “Eutrophication” impact peaks during cultivation due to agrochemical usage like fertilizers and pesticides, enhancing eutrophication potential. PLA biopolymer production notably exhibits higher effects in categories like “Abiotic depletion”, “Global warming potential (GWP100a)”, “Ozone layer depletion (ODP)”, “Human toxicity”, “Freshwater aquatic ecotoxicity”, “Marine aquatic ecotoxicity”, “Terrestrial ecotoxicity”, and “Acidification” compared to LDPE and EVA polymer production. This discrepancy primarily arises from increased SO_2 and NO_x formation in sugar production, as well as SO_2 emissions from sulfuric acid production in the lactic acid production process [15].

Limitations and Future Directions

Limitations of the study affecting result interpretation and application include: 1) The study employs a “cradle-to-gate” analysis, focusing on the manufacturing stage of LDPE, EVA, and PLA polymers. Neglecting other life cycle steps (transportation, usage, disposal, and end-of-life) restricts the environmental impact assessment's comprehensiveness. Future research could explore a more holistic “cradle-to-grave” analysis for a complete polymer life cycle understanding; 2) The study assumes a single production scenario for LDPE, EVA, and PLA polymers, based on software data. Differences in production methods, regional disparities, and evolving technologies can alter environmental impacts. Considering various scenarios would provide a more accurate representation; 3) While environmental impact is highlighted, the study offers limited information on the antimicrobial efficacy of ZnO NPs/polymer nanocomposites; 4) Primarily comparing two petroleum-based polymers with bio-based PLA overlooks other biodegradable polymers with varying environmental impacts. Further research on alternative polymers could enhance understanding of eco-friendly options.

Determining these limitations and taking them into account in future research is crucial to determining directions for future research. Addressing some of the limitations in future research may improve our understanding of the environmental impacts associated with the design and use of new antimicrobial packaging materials.

Conclusion

In conclusion, LCA studies of the polymer matrices of ZnO NPs/LDPE, ZnO NPs/EVA, and ZnO NPs/PLA nanocomposites provide important insight into the environmental impacts associated with these materials. Given the current emphasis on reducing the environmental impact of industrial processes, finding sustainable packaging solutions is critical. The study shows the environmental impact of producing two petroleum-based polymers (LDPE and EVA) and one bio-based PLA on water consumption, cumulative energy demand, and environmental toxicity. PLA exhibits significant biodegradability, requires greater water consumption to produce, and is a biomass-dependent renewable energy source. In many impact categories, the environmental impact of LDPE and EVA is almost similar.

As the demand for antimicrobial packaging materials continues to grow, this type of research can provide valuable information to researchers and industries looking to choose more sustainable alternatives to balance environmental impact and address environmental issues.

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POLİMER MATRİSLİ NANO-ZnO ANTİMİKROB QABLAŞMA MATERİALLARININ İSTEHSALININ HƏYAT DÖVRÜNÜN QİYMƏTLƏNMƏSİ

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XÜLASƏ
Neft əsaslı polimerlər faydalı qablaşdırma xüsusiyyətləri təklif edir, lakin onların ətraf mühitə təsiri bio-əsaslı alternativlərə keçidi tələb edir. Tədqiqat ZnO nanohissəciklərinin/aşağı sıxlıqlı polietilenin (ASPE), ZnO nanohissəciklərinin/etilen vinil asetsopolimerinin (EVA) və ZnO nanohissəciklərinin/polilaktik turşunun (PLA) polimer matrislərinin "beşikdən qapıya" həyat dövrünün qiymətləndirilməsini (HDQ) təhlil edir. Nəticələr göstərir ki, bərpa olunan biokütlədən əldə edilən PLA, neft xammalından istehsal olunan ASPE və EVA-dan daha çox su istehlakı tələb edir. PLA istehsalının su tutumlu kənd təsərrüfatı proseslərindən asılılığı onun su izlərinə kömək edir. Bundan əlavə, enerji tələbatının müqayisəli təhlili göstərdi ki, ASPE və EVA istehsalı əhəmiyyətli dərəcədə bərpa olunmayan fosil enerji mənbələrindən, PLA istehsalı isə bərpa olunan biokütlədən və alternativ enerji mənbələrindən daha çox asılıdır. Evtrofikasiya, qlobal istiləşmə potensialı və ekotoksiklik kimi ətraf mühitə təsir kateqoriyalarından əldə edilən nəticələr PLA ilə bağlı müxtəlif ekoloji problemləri və davamlı istehsal üsullarına ehtiyacı vurğulayır. Tədqiqat gələcək istehsal üçün material seçərkən HDQ-nın əhəmiyyətini vurğulayır, ətraf mühitə daha az təsir göstərən polimerlərin istifadəsini müdafiə edir.
Açar sözlər: Həyat dövrünün qiymətləndirilməsi, Antimikrob qablaşdırma, Ətraf mühitə təsir, Polimer, Polietilen, Etilen vinil asetat, Polilaktik turşu.

ОЦЕНКА ЖИЗНЕННОГО ЦИКЛА ПОЛИМЕРНОЙ МАТРИЦЫ ПРОИЗВОДСТВА НАНО-ЗНО АНТИМИКРОБНЫХ УПАКОВОЧНЫХ МАТЕРИАЛОВ

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РЕЗЮМЕ
Полимеры на основе нефти обладают полезными упаковочными свойствами, но их воздействие на окружающую среду требует перехода на альтернативы на биологической основе. В исследовании анализируется оценка жизненного цикла (ОЗЦ) «от колыбели до ворот» полимерных матриц наночастицы ZnO/полиэтилен низкой плотности (ПЭНП), наночастицы ZnO/сополимер этиленвинилацетата (ЭВА) и наночастицы ZnO/полимолочная кислота (ПЛА). Результаты показывают, что ОЗЦ, произведенный из возобновляемой биомассы, требует большего потребления воды, чем ПЭНП и ЭВА произведенные из нефтяного сырья. Зависимость производства ПЭНП от водоемких сельскохозяйственных процессов увеличивает потребление воды. Кроме того, сравнительный анализ спроса на энергию показал, что производство ПЭНП и ЭВА существенно зависит от невозобновляемых ископаемых источников энергии, тогда как производство ПЛА в большей степени зависит от возобновляемой биомассы и альтернативных источников энергии. Результаты таких категорий воздействия на окружающую среду, как эвтрофикация, потенциал глобального потепления и экотоксичность, подчеркивают различные экологические проблемы, связанные с ПЛА, и необходимость в устойчивых методах производства. Исследование подчеркивает важность ОЗЦ при выборе материалов для будущего производства, пропагандируя использование полимеров с меньшим воздействием на окружающую среду.
Ключевые слова: Оценка жизненного цикла, Антимикробная упаковка, Воздействие на окружающую среду, Полимер, Полиэтилен, Этиленвинилацетат, Полимолочная кислота.