

Article

Green Plasticizer for Poly(vinyl chloride) Re-Granulate Production: Case Study of Sustainability Concept Implementation

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Abstract: The increase in waste polymer recycling has helped in promoting sustainability, and together with the use of renewable raw materials, it has become a widespread concept with positive effects on both the economy and ecology. Accordingly, the aim of this study was the synthesis of “green” plasticizers, marked as LA/PG/PET/EG/LA, formed from waste poly(ethylene terephthalate) (PET) and bio-based platform chemicals propylene glycol (PG) and levulinic acid (LA). The structure of the obtained plasticizers was complex, as confirmed by results from nuclear magnetic resonance (NMR) and Fourier-transform infrared spectroscopy (FTIR) analysis. The LA/PG/PET/EG/LA plasticizers and waste poly(vinyl chloride) (PVC) were used in an optimized technology for PVC re-granulate production. The hardness of the PVC-based material with “green” plasticizers, in comparison to commercial plasticizer dioctyl terephthalate (DOTP), increased by 11.3%, while migration decreased. An improved material homogeneity and wettability of the fibers by the matrix were observed using SEM analysis of the material’s fracture surface, with a higher efficiency of intermolecular interactions leading to better mechanical performances of the newly designed materials. Thus, LA/PG/PET/EG/LA are unique materials with good compounding and plasticizing potential for PVC, as revealed by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). In that manner, the use of bio-renewable resources and recycled polymers will contribute to diminishing waste polymer generation, contributing to a lower carbon footprint.

Keywords: PET glycolysis; green plasticizers; recycled PVC; mechanical property



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1. Introduction

Fossil-based polymers, due to their economic significance, are extensively used globally in diverse product forms and areas of application. The importance of recycling waste polymers is increasing, emphasizing the pronounced growth of polymer consumption. The projection for the year 2050 estimates that a staggering amount of over 12,000 million metric tons of plastic waste will accumulate in landfills or the environment, highlighting the urgency of resolving this issue [1]. Plastic waste, which is composed of non-biodegradable polymers and often contains different additives, mostly derived from petrochemical resources, presents a notable environmental threat when not appropriately managed. In response to increasing environmental pollution, efforts are being made to establish a circular economy, a concept that involves the implementation of sustainable practices to reduce and promote the recycling of waste materials [2]. This is prompted by growing environmental

and economic concerns, as well as the recognition of limited fossil resources [3]. Such a concept is based on the creation of a closed-loop system where materials are recycled, minimizing the environmental impact and fostering a more sustainable and responsible approach to waste and renewable resource management, leading to a lower dependence on petroleum-based components. Among commercial polymers, belonging to either thermoplastic or thermoset material, the most suitable thermoplastic is poly(vinyl chloride) (PVC), which can be used as the matrix for compounding with different additives to produce materials with improved properties.

PVC is an easily processed, versatile, and low-cost polymer widely used in different industries (e.g., building, food packaging, medical devices, textile, toy manufacturing). Therefore, the recycling of waste PVC, as a thermoplastic, is possible with the application of appropriate technology and additives for the setting, especially plasticizers that affect both the processing and mechanical properties of PVCs. It can be compounded with various additives to obtain a diverse range of properties. PVC requires the addition of cost-effective plasticizers, e.g., traditional phthalate plasticizers (di(2-ethylhexyl) phthalate–DOP) [4], to provide good flexibility and permanence for the PVC product, as well as to remain competitive in the polymer market. Although phthalates show a favorable effect on PVC processing, they migrate easily from the PVC matrix and exhibit a subsequent loss in material properties, and, in conjunction with their harmful effect, they pose significant risks to both human health and the natural environment, i.e., toxicological and ecotoxicological threats, respectively [4]. Therefore, the newest European regulatory prohibits the use of phthalate plasticizers in PVC products for human use [5]. This recognition of the adverse effects of phthalates underscores the urgent need for alternative solutions in the realm of plasticizers [6].

The use of phthalate-free and non-toxic plasticizers to replace phthalates containing them has become a research topic of great importance [7,8]. Choosing a plasticizer with optimal structure and low environmental impact improves the properties, health safety, and CO₂ footprint of the recycled PVC products. The global market of commercial bio-plasticizers is segmented into four main groups: epoxidized soybean oil, castor oil, citrates, and succinic acid [9–11]. Considering the fact that the bio-plasticizer market size is estimated at 446.29 kilotons in 2024, and is expected to reach 604.89 kilotons by 2029 [9], there are numerous opportunities to expand the assortment of green plasticizers. Mazitova et al. [10] conducted an ecological and economic assessment of the use of new adipate plasticizers in PVC composites. They confirmed the effectiveness of their use in accelerating biodegradation processes. The production and application of bio-plasticizers from renewable sources such as lactic acid, glycerol and succinate esters, and isosorbide are described in recent studies [11]. In the current study, we consider the potential use of the waste poly(ethylene terephthalate) (PET) as raw material for the synthesis of “green” phthalate-free plasticizers for processing the waste PVC.

As one of the widespread thermoplastic polymers, PET is largely used in the food industry and for the preservation of beverages [12,13], in the automotive industry, and in packaging due to its favorable mechanical properties; high transparency; chemical stability; and good oxygen, carbon dioxide, and water-vapor barrier properties. However, it represents a significant ecological problem [14]. These challenges are associated with the non-biodegradability and necessity of the development of proper PET recycling technologies, thus highlighting the complexity of the process and addressing financial aspects in key sectors of the economy [15–17]. The pursuit of effective polymer recycling remains challenging and crucial for achieving sustainability goals and reducing reliance on finite fossil-based resources. Waste PET is relatively well recycled compared to other plastics, as one of the most successfully recycled polymers [1,18,19]. Recycling processes include re-extrusion, mechanical, chemical, and energy recovery methods [20]. The chemical recycling of PET involves various processes such as hydrolysis, alcoholysis, glycolysis, and aminolysis, producing oligomeric/monomeric products with different functionalities [21]. The aim of chemical recycling is to convert the macromolecular structure of waste PET into

specialty added-value chemicals and materials, promoting effective and environmentally friendly technology [22]. Products resulting from PET glycolysis can serve as plasticizers and monomers in polymer synthesis (epoxy resins, unsaturated polyester, melamine formaldehyde and alkyd resins, polyurethane dispersions) [23,24]. The plasticizers play a crucial role in reducing the viscosity and in easing the melt processing of polymers [25].

Combining multiple plasticizers has proven to be more effective in optimizing the properties of polymers [6]. Creating novel plasticizers is a complex task that involves the consideration of various factors such as mechanical properties, low migration capability, simplicity of production, and cost-effectiveness. Recent studies indicate that high-molecular-weight plasticizers derived from renewable resources hold potential applications [26–28]. Also, to address these issues, the incorporation of low-migration plasticizers can be a viable solution [14], and the potential of using waste PET glycolysates, which leads to improved processing capabilities and mechanical properties, could be a promising alternative [23,29,30]. PET, when depolymerized by hydrazine monohydrate, exhibits potential as a secondary plasticizer [31]. Furthermore, studies have demonstrated that the use of diethylene glycol terephthalate modified with maleic anhydride results in a material with commendable mechanical properties [30]. Terephthalate-based plasticizers contribute to excellent product durability, flexibility at low temperatures, and enhanced electrical insulation capabilities [32]; thus, they hold promise as a viable and beneficial alternative. Therefore, if waste PET, a polyester-type thermoplastic polymer, and reactants of natural origin are used in plasticizer syntheses, an extraordinary situation is realized that includes the principles of green chemistry in technological processes. Moreover, this study provides a production process that unites two polymeric wastes, PET and PVC, in added-value materials, plasticizers and re-granulates, respectively.

The aim of this study was to test the applicability of a “green” plasticizer obtained by waste PET glycolysis (transesterification) using renewable reactive diol, i.e., propylene glycol (PG) terminated with bio-based levulinic acid (LA), as a substituent to commercial product DOTP. Accordingly, the main goals of the present study were related to the replacement of the commercial non-phthalate plasticizer DOTP in the production of PVC re-granulates with synthesized “green” LA/PG/PET/EG/LA surrogate. In order to analyze influences of structural characteristics of the plasticizer, we performed a comparative study of the mechanical properties of the PVC-based materials, including LA/PG/PET/EG/LA plasticizers and that obtained in an analogous manner using DEG, instead of PG, to produce LA/DEG/PET/EG/LA. As a commercial counterpart, a non-phthalate DOTP plasticizer and diisononyl phthalate (DINP) were used in order to examine the influences of *ortho*- versus *para*-substitution on the change in mechanical properties of the obtained materials. Additionally, the production of glycolysates and PET-based plasticizers was performed on a semi-industrial scale, followed by thorough plasticizer characterization. The developed optimal technology for PVC re-granulates production was applied, and further, derived PVC-based materials were comparatively tested in relation to their mechanical and physical properties, as well as their resistance to migration. The “green” LA/PG/PET/EG/LA plasticizers showed promising results that open the possibility for their application in the waste PVC recycling process in the production of commercially valuable re-granulates and derived products such as car mats, soles for slippers and shoes, floor covering, household equipment, agriculture auxiliary materials, and similar products.

2. Materials and Methods

2.1. Materials

To eliminate any trace of contaminants and residual adhesives, waste PET (Figure S1) was flaked into small pieces (approx. 0.5–0.5 cm) and washed with detergent and ethanol (Zorka, Šabac, Serbia). The diethylene glycol (DEG) (Figure S1) (Brenntag, Vienna, Austria) and Fascat 4100 (PMC Orgnaometallix, Hoofddorp, The Netherlands) were used as catalysts for the depolymerization of waste PET (glycolysis). Propylene glycol (PG) (Figure S1) was produced from glycerol using previously reported processes, as shown in Supplementary

Material S2.2.1 [33]. Levulinic acid (LA) (Figure S1) was synthesized from fructose using the method described by Pyo et al. [34] (Supplementary Information Section S2.2.2) [35], while the commercial one (Merck, Darmstadt, Germany) was used as a standard in the course of structural and physicochemical characterization.

Tetrabutyl titanate (TBT) and γ -alumina were provided by Sigma-Aldrich (Burghausen, Germany). All compounds were utilized with no further purification. Diisononyl phthalate (DINP) and Bis(2-ethylhexyl) terephthalate (DOTP) (structures given in Figure S2) are commercial raw materials provided by Brenntag, Austria. Ground waste PVC (structure given in Figure S3) material was provided by RKS Kompoziti, Čelarevo, Serbia (RKS Composites).

2.2. Synthesis of Plasticizers Based on Waste PET Glycolysates

Plasticizer syntheses were performed at laboratory level, in the first phase, in order to develop optimal production technology, and subsequently transferred to a greater-capacity reactor to provide the required quantity for semi-industrial manufacturing of PVC re-granulates.

2.2.1. Synthesis of Propylene Glycol (PG)

Propylene glycol (PG) was produced from glycerol using previously reported processes, as given in Supplementary Material (Section S2.2.1) [33].

2.2.2. Synthesis of Levulinic Acid (4-Oxopentanoic Acid, LA)

LA was synthesized from fructose using the method described by Pyo et al. [34] (Supplementary Material, Section S2.2.2) [35].

2.2.3. Synthesis of LA/PG/PET/EG/LA and LA/DEG/PET/EG/LA Plasticizers at the Laboratory Level: General Procedure

The glycolysis was carried out in a high-pressure Parr reactor (Figure 1a) in which 76 g of PG (1 mol) or 106 g of DEG (1 mol) (performed in two distinct runs, Table 1), and 194 g of PET (1 mol) and 0.3 wt.% Fascat 4100 catalyst were added. Glycolysis was carried out for 6 h at 230 °C, producing DEG/PET/EG and PG/PET/EG precursors (Table 1). The hot precursors (~100 °C), PG/PET/EG or DEG/PET/EG, were transferred to three-necked round-bottom flasks equipped with a thermometer, mechanical stirrer, and Dean Stark separator. Further, bio-based LA (232 g, 2 moles) was added drop-wise for 15 min, and the reaction took place until more than 85% of the stoichiometrically reacted water was separated. At this point, TBT (0.3 wt.%) was added to promote an increase in the plasticizer yield to reach more than 97% of the theoretically calculated water separation. Synthesized raw plasticizers LA/DEG/PET/EG/LA (Plast 1) or LA/PG/PET/EG/LA (Plast 2) were subjected to vacuum (max 120 °C/1500 Pa) to remove water and low-boiling compounds, and collected product was yellowish viscous liquid (yield > 93% with respect to either isolated water or product weight in relation to DEG/PG reactants). Products can be used as obtained or purified by washing with 5% solution of sodium hydroxide and water, drying, and solvent distillation. The results of product characterization, obtained from the use of physicochemical, FTIR, and NMR methods, showed negligible differences in products, and thus both alternatives can be used in a PVC production technology (Scheme 1).

Table 1. Amounts of reactants used for LA/DEG/PET/EG/LA (Plast 1) or LA/PG/PET/EG/LA (Plast 2) plasticizer syntheses.

Reactant	G	mol
PET	194	1
PG/DEG	76/106	1
Fascat 4100	0.9/0.81	
LA	232	2
TBT	2.07/1.95	
Σ	692.3/653.1	

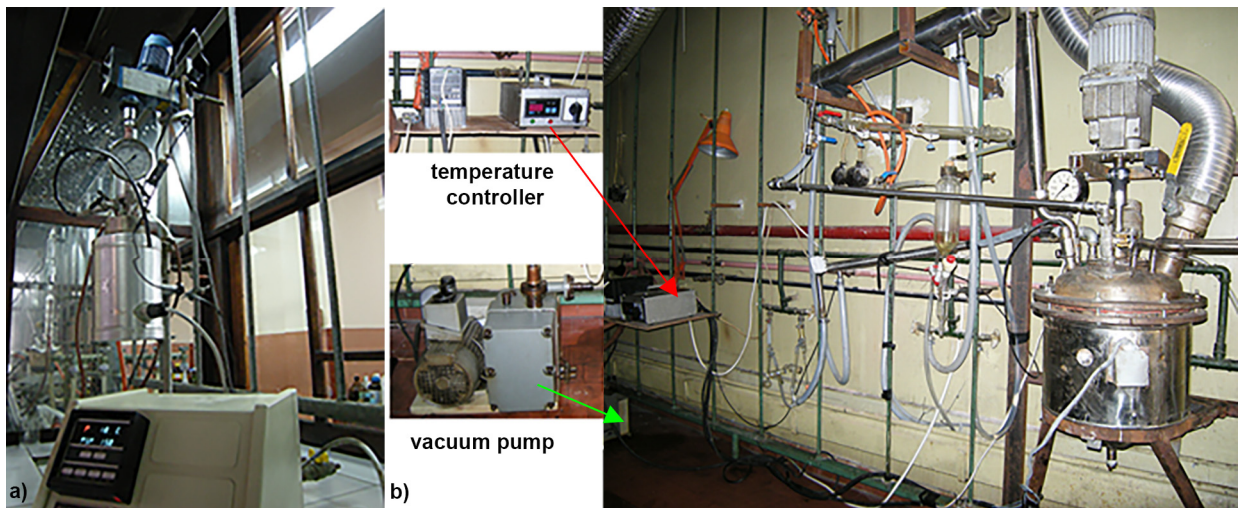
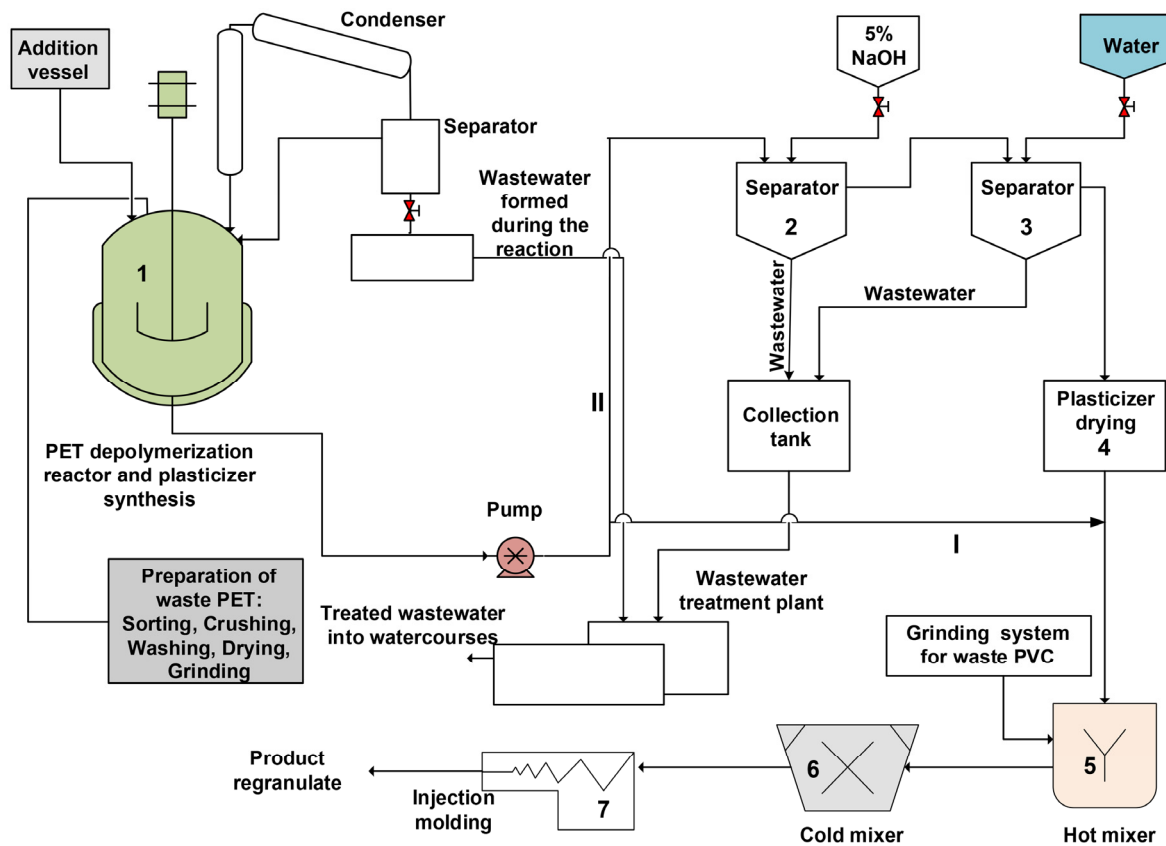


Figure 1. (a) Parr high-pressure reactor for plasticizer synthesis, (b) pilot reactor (10 L) used for plasticizer synthesis.



Scheme 1. Schematic representation of the plant for the production of PVC re-granulates and plasticizer for use in construction, industry, and general application.

Two alternative processes are defined with or without purification of plasticizer. From a techno-economical point of view, the process without plasticizer purification was used in the following study.

2.2.4. Synthesis of LA/PG/PET/EG/LA and LA/DEG/PET/EG/LA Plasticizers Using 10 L Home-Made Reactor

The transesterification of waste PET (glycolysis) (1.94 kg, 10 mol) was carried out using PG (0.76 kg, 10 mol) (PG/PET/EG) or DEG (1.06 kg, 10 mol) (DEG/PET/EG) at a molar ratio of either 1:1 PET: DEG or PET: PG in a 10 L home-made laboratory reactor (Figure 1b). The reactor was equipped with an inlet for reactants, a discharge pipe for the gaseous mixture, a short column filled with a stainless-steel spring packing (a distillation of the excess of ethylene glycol and water from the system), and a thermometer. The reaction was carried out at 220–225 °C for 6 h, adding 0.3 wt.% Fascat 4100 catalysts and one of the glycols (closed system). After the glycolysis process, adding 2.32 kg (20 mol) of LA was followed by heating at 180 °C. The reaction took place until more than 85% of the theoretically calculated water was separated. At this point, TBT (0.3 wt.%) was additionally charged to promote an increase in the plasticizer yield to reach more than 97% of the theoretically calculated water separation. Synthesized raw plasticizers LA/DEG/PET/EG/LA (Plast 1) or LA/PG/PET/EG/LA (Plast 2) were subjected to vacuum (max 150 °C/1500 Pa) to remove water and low-boiling compounds. The collected products were light brownish viscous liquids (yield > 94% with respect to either the isolated water or the product weight in relation to DEG/PG reactants). The full characterization was provided using physicochemical, FTIR, and NMR methods. Reactors used for synthesizing plasticizers at the laboratory and semi-industrial levels are presented in Figure 1b.

Both plasticizers LA/DEG/PET/EG/LA (Plast 1) and LA/PG/PET/EG/LA (Plast 2) were synthesized at a quantity ~8 kg (from two batches) and used in the production of PVC re-granulates.

2.3. Production of PVC Re-Granulates Using Commercial and “Green” Plasticizers: General Method

Waste PVC (ground PVC material provided by RKS Kompoziti, Čelarevo, Serbia) was used at both laboratory and semi-industrial levels of PVC re-granulate production (Scheme 1). In the first instance, waste PET depolymerization provides glycolysates that can be used with purification (flow II) or directly in compounding with ground waste PVC (flow I) (Scheme 1). The process of compounding ground waste PVC with plasticizer and additives in hot and cold mixers followed by re-granulation was first optimized in a laboratory-level grinding mill (6 L) (Figure 2).



Figure 2. Laboratory hot mixer.

The ground waste PVC material (2.4 kg) was placed in a laboratory mixer with a system for either water heating or cooling to set the process temperature.

When the temperature was 35 °C, the plasticizer, at quantities of 10, 12.5, 15, 17, and 17.5 wt.% with respect to PVC, was added and mixed for 5 min at a specified speed (~2500 rpm). Also, the thermal stabilizer, antioxidant, carbon black, stearic acid, and acrylic process aid was charged (in total 5.5 wt.%). After, the mixture was gradually heated due to material friction and externally heated using hot water to attain a temperature increase of ~3 °C/min. When the temperature reached 115–120 °C, material was additionally homogenized for 10 min at 120 °C and then discharged into a cold mixer, where the pasty product was cooled to 45 °C and ground to obtain a granular product. Tensile strength was used as a meritorious parameter for the definition of optimal plasticizer content, and it was found that 20 wt.% was optimal (example tensile strength of PVC material with 20 wt.% of LA/PG/PET/EG/LA was 34 MPa), where variation around this median value, e.g., for the 0.5 wt.% step of plasticizer addition, causes small variations in the tensile strength value. Thus, final specimens produced at 20 wt.% plasticizer addition were used for physical and mechanical characterization, as well as plasticizer migration testing. Analogous procedure was also carried out using commercial DOTP and synthesized LA/DEG/PET/EG/LA plasticizers.

In the second step, optimized technology was transferred to the semi-industrial level (performed using equipment owned by RKS Kompoziti Ltd., Čelarevo, Serbia). Briefly, ground PVC waste (20 kg) was processed at a semi-industrial level (Figure 3) using 4.25 kg of plasticizers (commercial or manufactured) according to optimized technology. The temperature of the processed material was adjusted using a boiler (Figure 3a) connected to a duplicator as an integral part of the hot mixer (Figure 3b). The obtained materials were further used for re-granulate production using a tween-screw extruder (Figure 4), and the obtained products are given in Figure 5.



Figure 3. Boiler for controlled heating of hot mixture (a), and hot mixer (b) (PVC high-speed mixer; 50 L) for blending of PVC with plasticizers and additives.



Figure 4. Extruder used for PVC re-granulate processing.

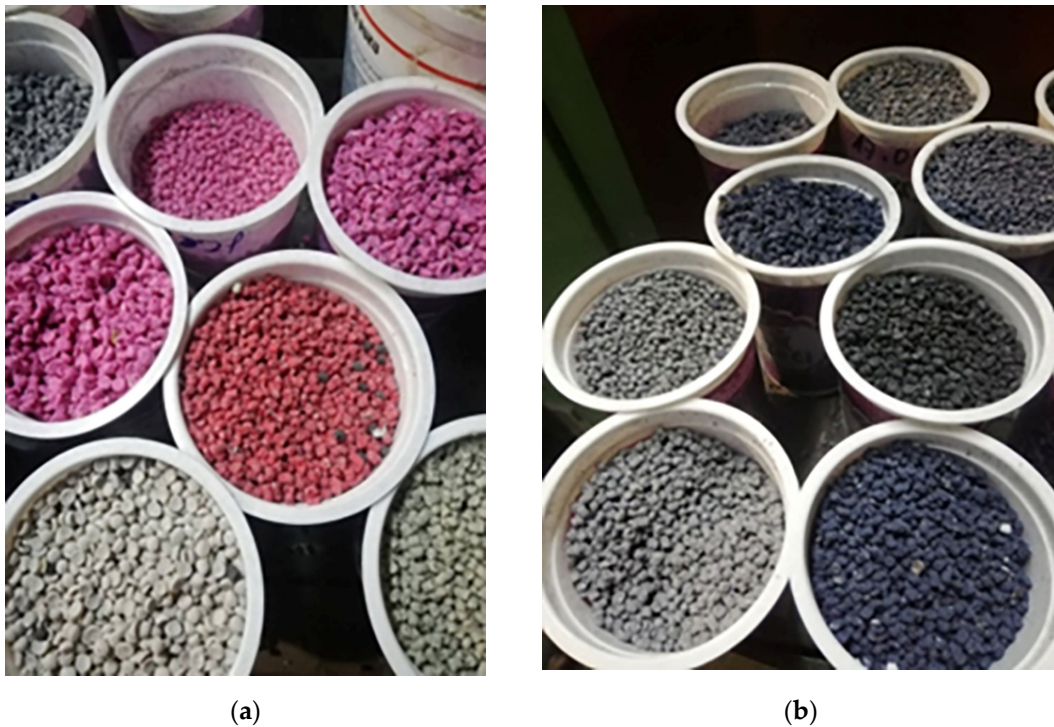


Figure 5. (a,b) Assortment of PVC re-granulates.

The final PVC product manufacturing process was carried out in the twin-screw extruder (Figure 4) regime:

- The first zone—hold time 20 s; temperature 140 °C.
- The second zone—30 s; temperature 180 °C.
- The third zone—retention time 15 s; temperature 145 °C.

There was no waste generated throughout the applied procedures, and the resulting product had no harmful product features and was ready for further use and ultimate product manufacture. Figure 5 depicts some colorful re-granulates obtained using the commercial master batch and current technology.

Additionally, the production of material based on PVC K70 and DOTP was performed in an analogous manner, and the results of mechanical testing are given in Table 2.

Table 2. Results of HV and AV values, and elemental analysis of the synthesized glycolysates and plasticizers.

Exp.	HV mg KOH/g	AV mg KOH/g		%C	%H	%O ¹
DEG/PET/EG	162	2.4	Exp.	56.10	6.22	37.68
			Calc.	56.37	6.08	37.54
PG/PET/EG	172	1.9	Exp.	58.02	6.21	35.77
			Calc.	58.20	6.01	35.78
Plast 1	15	3.3	Exp.	58.04	6.25	35.71
			Calc.	58.29	6.12	35.59
Plast 2	14	4.1	Exp.	59.66	5.98	34.46
			Calc.	59.48	6.08	34.45

¹ Oxygen percent was calculated as residual value of carbon and hydrogen to 100%.

2.4. Characterization Methods

Details on used characterization methods are given in Supplementary Material S2.4.

3. Results and Discussion

The success of the stepwise process of the catalytic depolymerization of waste PET was confirmed using FTIR analysis, and the functionality determination of PET glycolysates and the subsequent esterification of glycolysates with LA were performed using FTIR and NMR techniques. The LA/DEG/PET/EG/LA analog with DEG was comparatively used to distinguish structural effects, i.e., the contribution of the ether linkage to mechanical property changes in PVC-based material.

3.1. Results of the Functionality and Elemental Analysis

The results of hydroxyl value (HV), acid value (AV), and elemental analysis for synthesized glycolysates and plasticizers are given in Table 2.

The elemental analysis and HV results validated the proposed structures of both glycosylates and Plast 1 and Plast 2 (Figures 6 and 7). The presented results undoubtedly confirmed the success of PET depolymerization, considering a theoretically calculated hydroxyl value close to one and the results of NMR analysis.

3.2. ¹H and ¹³C NMR Results

3.2.1. Results of ¹H and ¹³C NMR Characterization of Plast 1—LA/DEG/PET/EG/LA

The results of the ¹H and ¹³C NMR analysis (the most convenient structure with atom numbering is given in Figure 6) of the plasticizers based on the product of PET glycolysis with DEG esterified with LA (Plast 1) are as follows:

¹H NMR (500 MHz, CDCl₃, δ ppm): 2.02–2.19 (m, 6H, C(14)H₃ and C(24)H₃), 2.58–2.63 (m, 4H, C(11)H₂ and C(21)H₂), 2.74–2.80 (m, 4H, C(12)H₂ and C(22)H₂), 3.60–4.00 (m, 4H, C(17)H₂ and C(18)H₂), 4.22–4.71 (m, 8H, C(8)H₂, C(9)H₂, C(16)H₂, and C(19)H₂), 8.02–8.14 (m, 4H, C(2)H, C(3)H, C(5)H and C(6)H).

¹³C NMR (125 MHz, CDCl₃, δ ppm): 27.57–28.04 (2C, C(11) and C(21)), 29.89 (2C, C(14) and C(24)), 37.86–38.13 (2C, C(12) and C(22)), 61.16–62.30 (1C, C(8)), 63.09–63.72 (1C, C(9)), 64.37–64.85 (1C, C(16)), 66.33–67.16 (1C, C(19)), 69.09–72.50 (2C, C(17) and C(18)), 129.68–130.46 (4C, C(2), C(3), C(5) and C(6)), 133.63–134.04 (2C, C(1) and C(4)), 165.60–166.11 (2C, C(7) and C(15)), 172.64–176.11 (2C, C(10) and C(20)), 206.55–207.13 (2C, C(13) and C(23)).

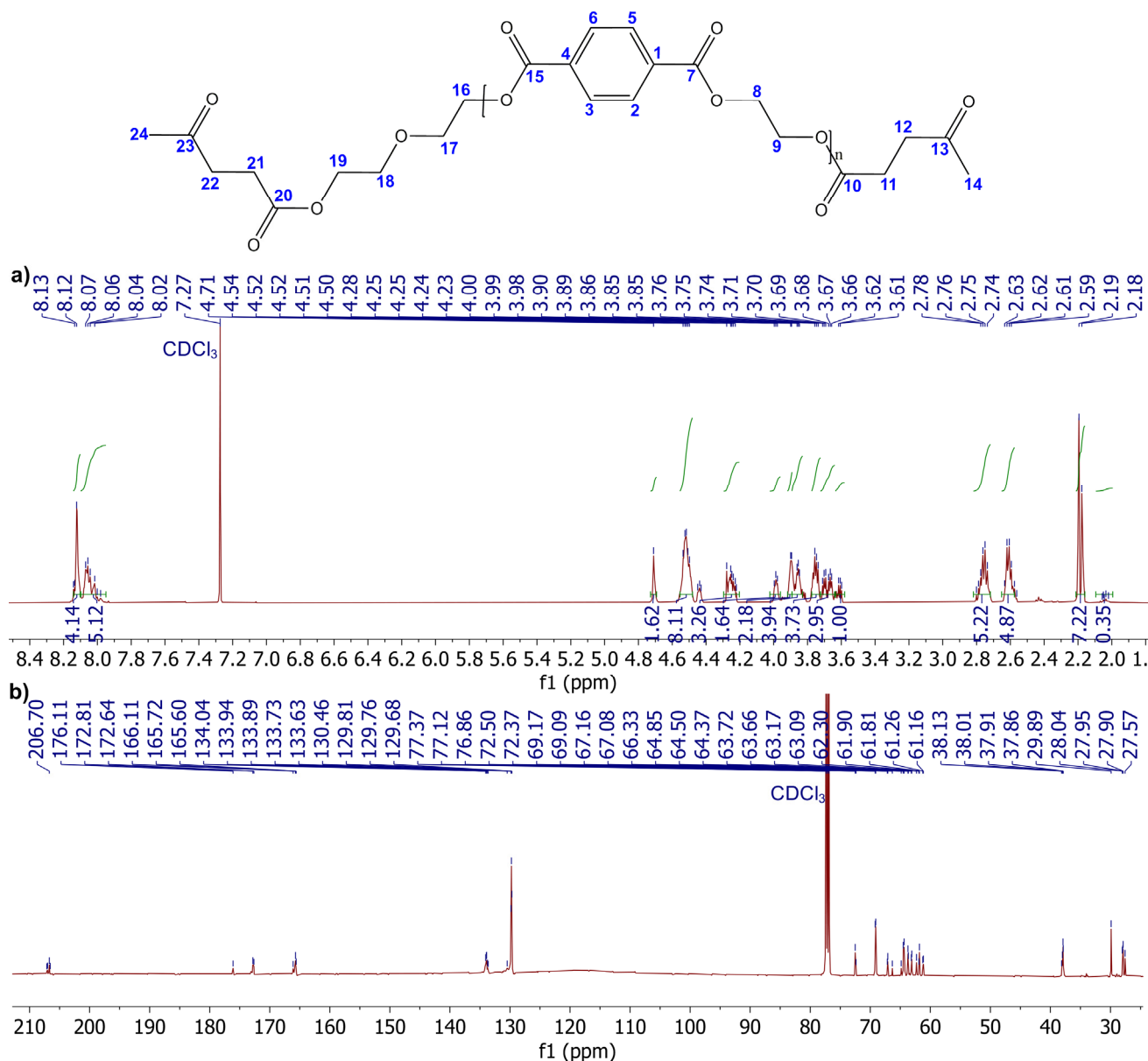


Figure 6. ¹H NMR (a) and ¹³C NMR (b) spectra of LA/DEG/PET/EG/LA (Plast 1).

The value of the integral related to C(11)H₂ and C(21)H₂ protons (at 4.87) and C(12)H₂ and C(22)H₂ (at 5.22) with respect to C(2)H, C(3)H, C(5)H, and C(6)H protons (at 8.04–8.13) indicate the presence of the main component of 2-((4-((2-((4-oxopentanoyl)oxy)ethoxy)carbonyl)benzoyl)oxy)ethyl (2-(2-((4-oxopentanoyl)oxy)ethoxy)ethyl) terephthalate or an analogous structure which contains $n = 3$ and 4 terephthalate moieties (Figure 6). Also, these structures are confirmed by the appearance of signals in the region of 3.60–4.71, associated with respect to C(2)H, C(3)H, C(5)H, and C(6)H protons at 7.98–8.14, as well as C(11)H₂ and C(21)H₂ protons in the δ range of 2.58–2.63, and C(12)H₂ and C(22)H₂ in the δ range of 2.74–2.80 (Figure 6). The most convenient structure of the synthesized LA/DEG/PET/EG/LA (Plast 1) plasticizer is given in Figure S6.

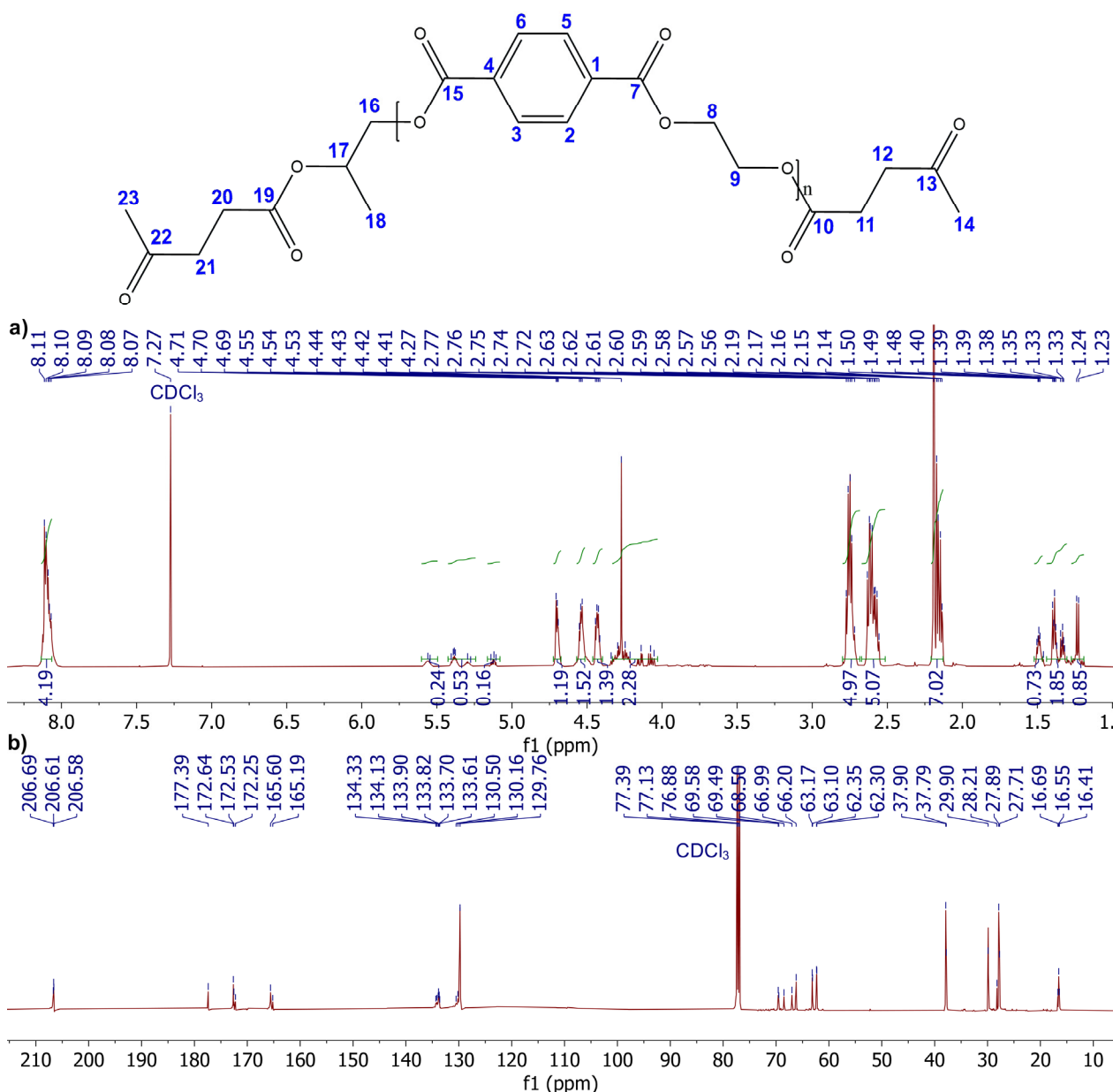


Figure 7. ^1H NMR (a) and ^{13}C NMR (b) spectra of LA/PG/PET/EG/LA (Plast 2).

3.2.2. Results of ^1H and ^{13}C NMR Characterization of Plast 2—LA/PG/PET/EG/LA

The results of the ^1H and ^{13}C NMR analysis of the plasticizers based on the PET glycolysis product with PG esterified with levulinic acid (LA) (the most convenient structure with atom numbering is given in Figure 7) are as follows:

^1H NMR (500 MHz, CDCl_3 , δ ppm): 1.23–1.50 (m, 3H, C(18) H_3), 2.13–2.19 (m, 6H, C(14) H_3 and C(23) H_3), 2.56–2.63 (m, 4H, C(11) H_2 and C(20) H_2), 2.72–2.77 (m, 4H, C(12) H_2 and C(21) H_2), 4.05–4.71 (m, 6H, C(8) H_2 , C(9) H_2 and C(16) H_2), 5.11–5.58 (m, 1H, C(17)H), 8.07–8.11 (m, 4H, C(2)H, C(3)H, C(5)H and C(6)H).

^{13}C NMR (125 MHz, CDCl_3 , δ ppm): 16.41–16.69 (1C, C(18)), 27.71–28.21 (2C, C(11) and C(20)), 29.90 (2C, C(14) and C(23)), 37.79–37.90 (2C, C(12) and C(21)), 62.30–62.35 (1C, C(8)), 63.10–63.17 (1C, C(9)), 66.20–66.99 (1C, C(16)), 68.50–69.58 (1C, C(17)), 129.76–130.50 (4C, C(2), C(3), C(5) and C(6)), 133.61–134.33 (2C, C(1) and C(4)), 165.19–165.60 (2C, C(7) and C(15)), 172.25–177.39 (2C, C(10) and C(19)), 206.58–206.69 (2C, C(13) and C(22)).

The value of the integral related to C(11) H_2 and C(20) H_2 protons in the δ range of 2.56–2.63 (at integral of 5.07) and C(22)H and C(21) H_2 in the δ range of 2.72–2.77 (at integral

of 4.97) (Figure 7), with respect to C(2)H, C(3)H, C(5)H, and C(6)H protons in the δ range of 8.07–8.11 (at signal of 4.19), indicate the presence of a small amount of propane-1,2-diyl bis(4-oxopentanoate) plasticizers (1,2-propanediol dilevulinate). Overall, the main component of the product obtained is 2-((4-((2-((4-oxopentanoyl)oxy)ethoxy)carbonyl)benzoyl)oxy)ethyl (2-((4-oxopentanoyl)oxy)propyl) terephthalate or higher-condensed analogs with $n = 3$ and 4 terephthaloyl units (Figure 7) [36]. The most convenient structure of the synthesized LA/PG/PET/EG/LA (Plast 2) plasticizer is given in Figure S7.

3.3. FTIR Spectroscopy Results

3.3.1. FTIR Analysis of DEG/PET/EG and PG/PET/EG Glycolysates

Infrared absorption spectra of the PET glycolysis products are shown in Figure 8. Absorption bands associated with hydroxyl groups are observed in the 3399–3441 cm^{-1} region. The C-H stretching frequencies in the 2957–2875 cm^{-1} and 2975–2875 cm^{-1} ranges are assigned to asymmetric and symmetric methylene and methyl functional groups in DEG/PET/EG and PG/PET/EG, respectively.

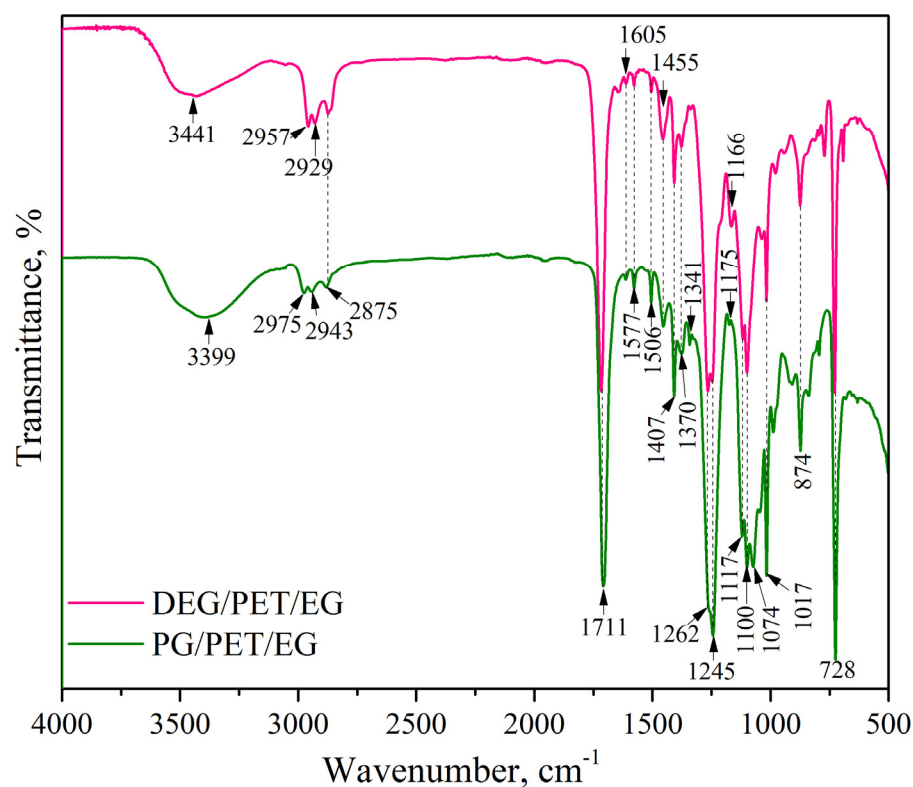


Figure 8. FTIR spectra of the synthesized DEG/PET/EG and PG/PET/EG.

The C-H bending frequencies of methylene groups are observed at 1407–1370 cm^{-1} (Figure 8) in both spectra, and the frequency of methyl groups from propylene glycol in the PG/PET/EG spectrum is observed at 1341 cm^{-1} (Figure S5). The strong band at 1711 cm^{-1} belongs to C=O stretching vibrations in the carboxyl group overlapped with the ester group, confirming the success of the transesterification reaction [37]. The bands between 1605 and 1506 cm^{-1} and the peak at 1455 cm^{-1} are attributed to skeletal C=C stretching and bending vibrations of aromatic ring terephthalic units, respectively. The absorption bands in the region of 1262–1017 cm^{-1} are attributed to the -C-O-H stretching of glycols, the -C-O-C- asymmetric/symmetric stretching of ether, and the -(C=O)-O-CH₂- stretching of ester groups [38]. The out-of-plane bending vibrations of terephthalic units are shown by strong bands at 900–728 cm^{-1} [39].

3.3.2. FTIR Analysis of Plast 1 (LA/DEG/PET/EG/LA) and Plast 2 (LA/PG/PET/EG/LA)

The FTIR spectra of Plast 1 and Plast 2 plasticizers are shown in Figure 9.

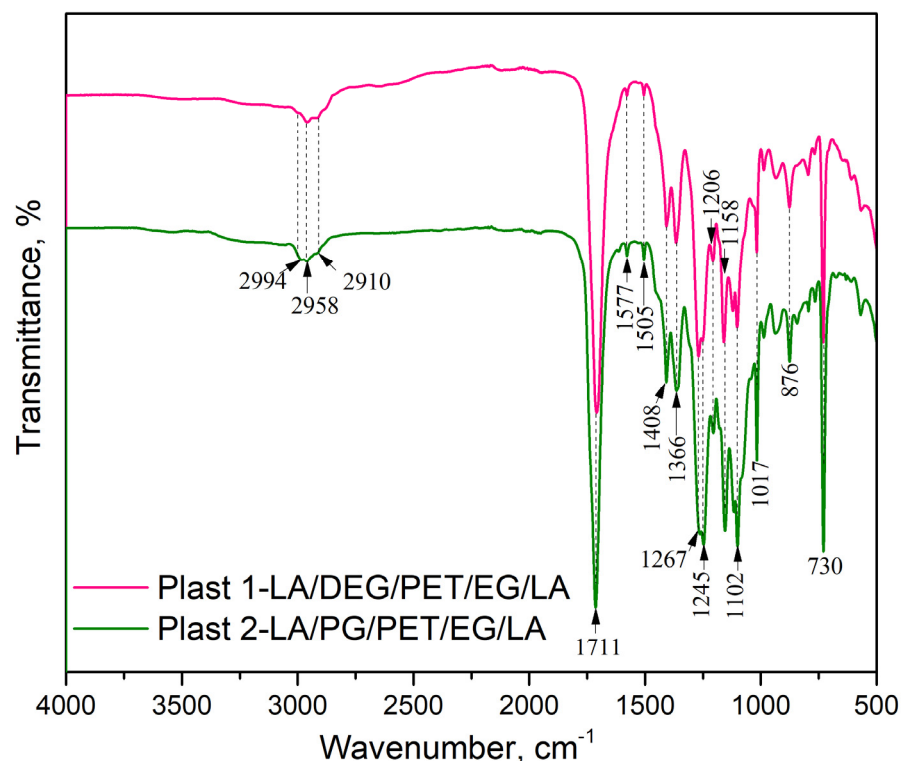


Figure 9. FTIR spectra of the synthesized waste PET-based plasticizers.

Bands from the inherent glycolysate structure and new ones from the LA modification were observed. Thus, a small shift in the position of vibrational methylene/methyl groups to higher wavenumbers was observed, and a slight decrease in intensity was also noticed. Further, the absence of stretching vibrations of hydroxyl groups, the presence of a doublet at 1408 cm^{-1} and 1366 cm^{-1} corresponding to C–H bending vibrations of methylene/methyl groups from LA (Figure S5), and the increased absorption of C=O groups indicate the successful reaction esterification between LA and glycolysates. In addition, in both spectra, two peaks at 1166 cm^{-1} and 1175 cm^{-1} of ether groups in the spectra of DEG/PET/EG and PG/PET/EG glycolysates, respectively (Figure 8), are increased and shifted to 1158 cm^{-1} (Figure 9) after esterification with LA (Figure S5). This suggested an involvement of hydroxyl groups in the synthesis of Plast 1 and Plast 2. Also, the FTIR spectra reveal a small decrease in bands associated with out-of-plane C=C stretching and C-H bending of the aromatic ring of terephthalic units.

3.4. FESEM Analysis

The FESEM technique was used to investigate the morphology of the fracture surfaces in order to determine the homogeneity and material compactness of the re-granulated sample as influential parameters for the deterioration/improvement in the mechanical properties. The fracture structure of the PVC re-granulates with commercial plasticizers is not homogeneous, as illustrated in Figure 10a, which indicates material inhomogeneity with the presence of holes as a potential weakening point that can lead to fracture and poor mechanical performance. The fibers emerge as almost free-standing particles at the cross-sectional surface with contributions to material discontinuity. The presence of any impurity could act as a stress concentrator and be the initial point of material cracking. The low wetting of fibers means that during the application of force and breaking of

the material, it helps in cracking dissipation with significant deformation of the material structure. The number and structure of these material irregularities, as can be observed in diverse shapes such as particles or fibers [40] and holes, are higher in the PVC material obtained using commercial plasticizer DOTP. It seems that cleavage fracture dominates with a significant micro-void coalescence causing the formation of larger holes due to higher material ductility (Figure 10a). These processes are of lower significance in PVC with Plast 1 showing an area with elements of brittle fracture surfaces (Figure 10b). On the other hand, the PVC-based material with the LA/PG/PET/EG/LA plasticizer (Plast 2) showed the highest material homogeneity due to effective fiber wetting, and, thus, local stress concentration is prevented (Figure 10c).

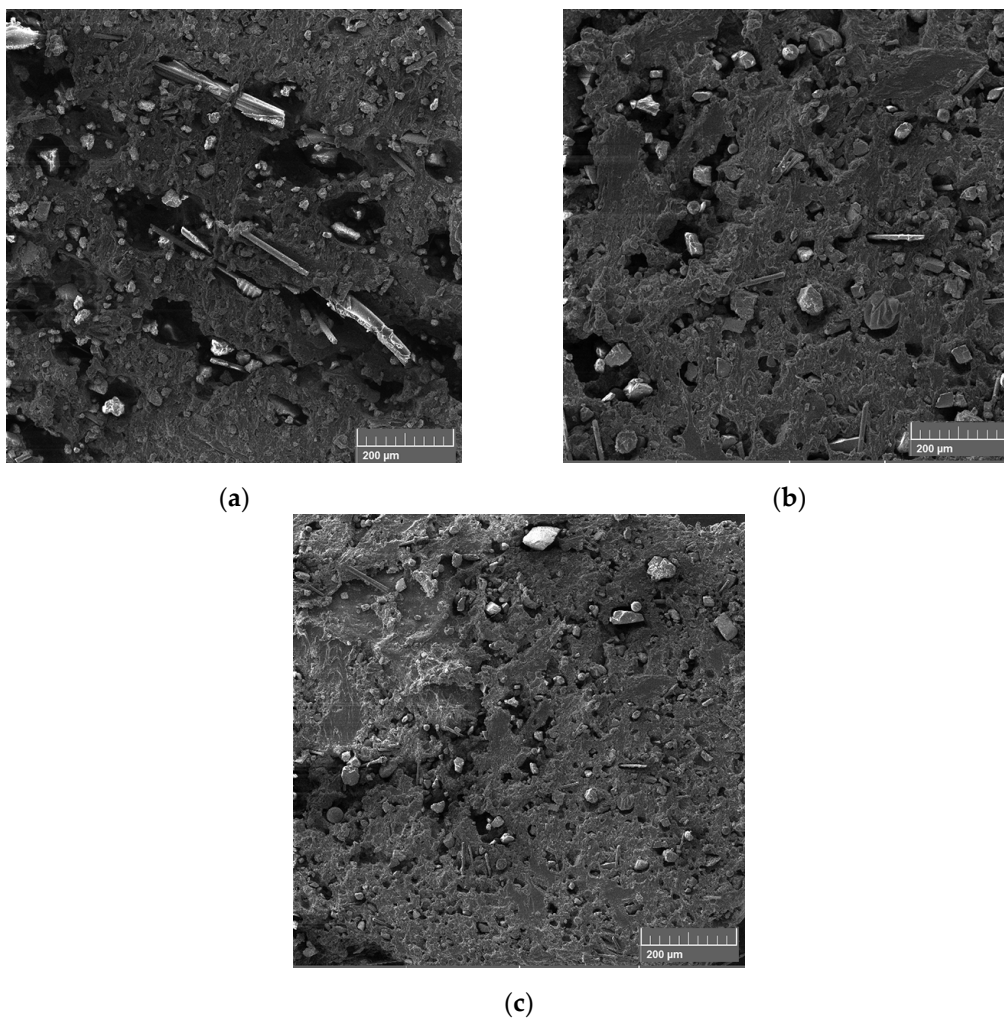


Figure 10. The morphology of a cross-section of the obtained re-granulates with (a) commercial plasticizer DOTP and (b) synthesized Plast 1 and (c) Plast 2.

The results from FESEM analysis confirmed that Plast 2 is the most convenient for real application as it contributes to better material processability and homogeneity, and its compatibility influences the improvement in the mechanical properties (Table 3).

Table 3. Mechanical and physical properties of the obtained PVC re-granulate.

	PVC#1	PVC#2	PVC#3	PVC/DOTP ¹
Tensile strength (MPa)	26.2 ± 1.73	30.4 ± 1.97	34.7 ± 2.05	39.7 ± 1.92
Elongation (%)	268 ± 13.2	252 ± 10.2	240 ± 9.2	298 ± 9.2
Modulus of elasticity (MPa)	123 ± 6.15	130 ± 7.80	141 ± 6.34	252 ± 12.8
Bending strength (MPa)	54.5 ± 5.82	55.6 ± 6.13	56.9 ± 6.44	67.4 ± 5.91
Compressive strength (MPa)	51.7 ± 4.63	52.2 ± 5.02	53.4 ± 5.61	58.5 ± 5.95
Shore A hardness	62 ± 3.3	66 ± 2.9	69 ± 3.4	78 ± 4.6
Impact strength (kJ m ⁻²)	2.91 ± 0.27	3.23 ± 0.31	3.54 ± 0.23	4.57 ± 0.42
Physical properties				
Density (g cm ⁻³)	1.33	1.36	1.35	1.30
Flammability	SE ²	SE	SE	SE

¹ material obtained from commercial PVC K70 and DOTP; ² SE—self-extinguishing.

3.5. Mechanical Properties of PVC Product Obtained from Re-Granulates

The results of the influence of the structural characteristics and plasticizer content on the mechanical and physical properties of PVC materials are given in Table 3. Three materials, i.e., PVC re-granulates with the DOTP plasticizer (PVC#1), Plast 1 (PVC#2), and Plast 2 (PVC#3), were used for test specimen production. The added plasticizer in the course of PVC re-granulate production was 17.5 wt.%. The results of mechanical and physical property determination are given in Table 3.

All of the PVC materials developed have good mechanical properties, indicating that the use of waste PET and commercial and synthesized plasticizers in the production of PVC materials did not impair their mechanical performances or chemical stability.

Shore hardness testing was used to compare the indentation resistance of the tested specimens. Usually, results from hardness testing can be used for predicting polymer qualities as well; however, it is most typically employed to forecast mechanical performance [41]. Because the PVC employed in this investigation falls within the category of softer materials, a Shore A scale was used. The hardness of samples PVC#2 and PVC#3 with plasticizers (Plast 1 and Plast 2) increased by 7.4% to 11.8%, respectively, with respect to the material with DOTP (PVC#1).

Additionally, the addition of Plast 1 and Plast 2 resulted in a transition from low medium-hard values to high medium-hard values (70–85), as well as an increase in tensile strength due to the higher carbonyl content compared to DOTP, resulting in stronger dipole–dipole interactions with the PVC chain [28,42,43]. Furthermore, when compared to *ortho*-ester, i.e., a material with the DINP plasticizer ($\sigma = 24.7$ MPa), the structure with a *para*-substituted benzene ring in terephthalate diester moieties, i.e., DOTP, contributes to improved strength of the PVC re-granulate derived materials [44]. These findings are consistent with the structures of plasticizers proposed by NMR and FTIR investigations. The addition of the PET plasticizer causes a negligible increase in the specific density of the re-granulates investigated.

The impact strength test was performed using the standard ASTM method for toughness determination (Charpy Method). It denotes the ability of the material to absorb energy during plastic deformation. Strong materials have high impact resistance, and their strength is the result of a combination of strength and ductility. The Charpy toughness of PVC#2 and PVC#3 increased by 10.3% to 20.7% with the addition of PET plasticizer. Higher elongation values in PVC re-granulates with Plast 1 and Plast 2 are generated by hydrogen bonding between ester carbonyl groups in plasticizers and the PVC backbone, which reduces polymer intermolecular interactions, resulting in enhanced chain segment mobility [44].

The mechanical properties of the material obtained from PVC re-granulates, which contain synthesized plasticizer LA/PG/PET/EFG/LA, are slightly lower than those of virgin PVC with commercial plasticizers. Specifically, for virgin PVC incorporated with 25%

of the commercial DOTP plasticizer, the tensile strength measures 39 MPa, the modulus of elasticity is 252 MPa, the bending strength reaches 67.4 MPa, the Shore A hardness stands at approximately 78.2, and the impact strength records 4.57 kJ/m² (Table 3).

3.6. Migration Test

Plasticizer migration from the produced PVC materials was performed according to the International Standard Criteria (ISC) and compared to the reference sample under the hypothesis that the liquid commercial plasticizer, DOTP, is a migratory species. Table 4 shows the migration test results for the flexible PVC compounds.

Table 4. The results of migration tests of produced PVC materials.

Samples	Weight Loss (%)
PVC#1	1.22 ± 0.06
PVC#2	0.92 ± 0.05
PVC#3	0.78 ± 0.03

Because of the lower molecular size, the PVC samples containing Plast 1 and Plast 2 samples demonstrated reduced weight loss due to the greater carbonyl cohesive block moiety compared to DOTP [4]. Due to the beneficial properties of the PVC#3 material, DSC and DMTA analysis were used for PVC#1 and PVC#3 materials.

3.7. Differential Scanning Calorimetry

During processing, gelation of PVC occurs, which strongly affects the physical properties of the final product [45]. As the material is heated, the smaller “grains” (crystallites) melt first [46]. While melting occurs, the grains combine to create a state of partial gelation. The extent of gelation is influenced by the processing temperature, with elevated temperatures resulting in a greater degree of gelation. Since Gilbert and Vyvoda [47] identified two endothermic peaks on DSC curves of processed PVC, and Potente [48] proposed Equation (1) to calculate the degree of gelation (G) using the melting enthalpies of primary (H_A) and secondary (H_B) crystallites, analysis of PVC gelation using DSC gained acceptance as a standard approach for examining processed PVC.

$$G = \frac{H_A}{H_A + H_B} \times 100, \quad (1)$$

As shown in Figure 11, sample PVC#1 has one large and broad endothermic peak, while sample PVC#3 has two endothermic peaks, i.e., the PVC#1 sample is completely gelled, and PVC#3 has some portion of PVC that is not yet gelled. The interpeak temperature related to processing temperature is found at the onset of the second endothermic peak and has a value of 184 °C. The degree of gelation of sample PVC#3 determined according to Equation (1) is 98.4%. Furthermore, it is obvious that curves differ very much in shape and area; the melting enthalpy of sample PVC#1 is twice as large as the melting enthalpy of sample PVC#3. This indicates that between samples, there are large differences in morphological features, crystallite structures, and networks of forces. The strength of this network is recognized as a significant factor influencing the mechanical properties of PVC-based materials [45].

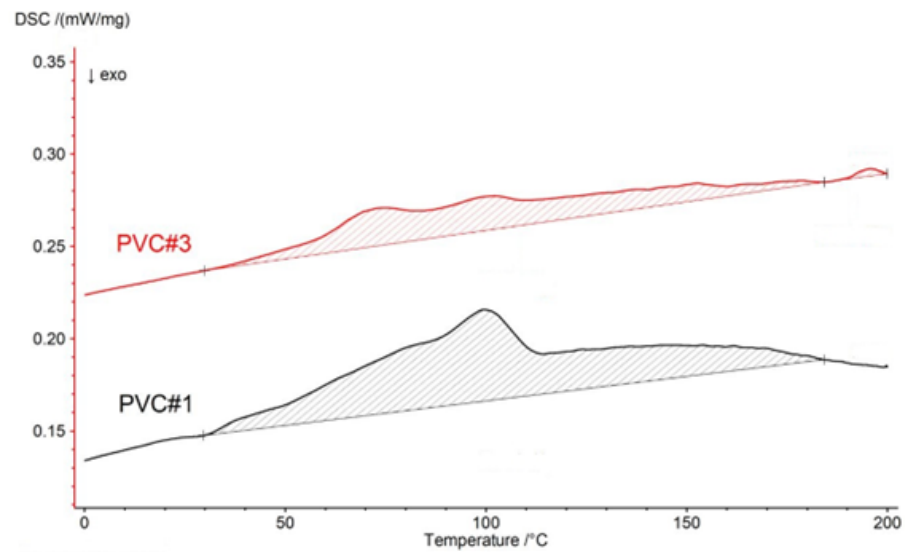


Figure 11. DSC curves of sample PVC#1 (black curve) and PVC#3 (red curve).

3.8. Dynamic Mechanical Thermal Analysis

The DMTA results are illustrated in Figures 12 and 13. Below $-50\text{ }^{\circ}\text{C}$, in a glassy state, free volume is not enough for the motion of chain segments. The storage moduli of samples are high and almost identical; failures during application in this temperature range are possible because the samples may be too rigid and brittle. With increasing temperature, the free volume and mobility of segments increase, friction between the chains causes the loss of more energy, and the loss modulus passes through the maximum [49–52]. The maximum loss modulus corresponds to the glass transition temperature T_g , and it was found that the T_g of sample PVC#1 is $-45\text{ }^{\circ}\text{C}$, and the T_g of sample PVC#3 is $-48\text{ }^{\circ}\text{C}$. These results are in accordance with the T_g values which Langer et al. [30] obtained for PVC plasticized with 32 wt.% of different oligoester plasticizers. Above T_g , in the transition range, the moduli of PVC#1 sample fall abruptly for two orders of magnitude, while the moduli of the PVC#3 sample fall moderately, i.e., sample PVC#3 has a wide transition range that extends over $70\text{ }^{\circ}\text{C}$.

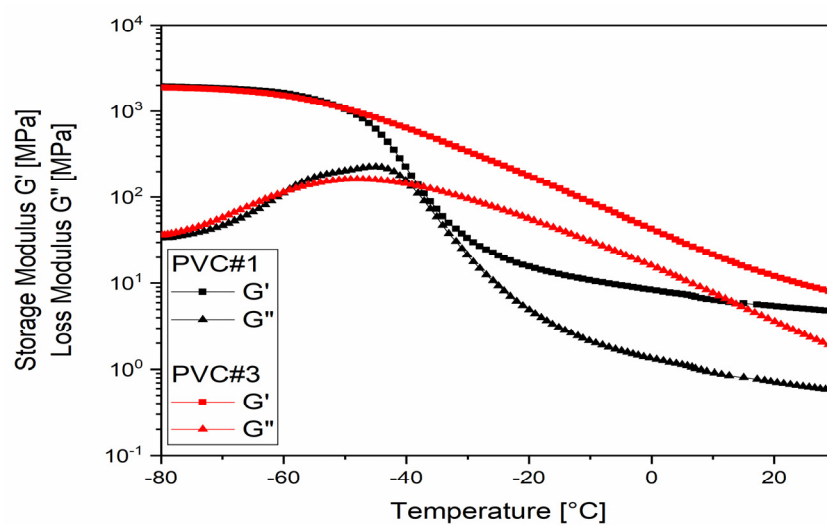


Figure 12. Storage modulus G' and loss modulus G'' of sample PVC#1 (black curves) and PVC#3 (red curves) as a function of temperature.

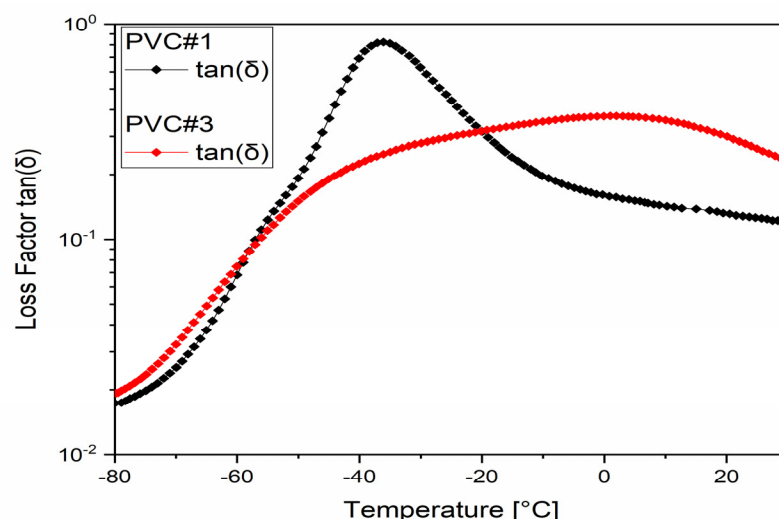


Figure 13. The loss factor $\tan(\delta)$ of sample PVC#1 (black curve) and PVC#3 (red curve) as a function of temperature.

The rubber-elastic plateau of PVC#1 begins at a temperature of approximately $-20\text{ }^{\circ}\text{C}$, and for PVC#3, it cannot be clearly distinguished from the transition range. Nevertheless, in this temperature range, motions of whole polymer chains are prevented by entanglements and physical interactions, which act as temporary networks between the macromolecules. Due to the stronger physical interactions in the PVC#3 sample, it has significantly better mechanical properties than PVC#1.

Although above T_g , the PVC#3 sample has higher modulus values than the PVC#1 sample, Figure 13 shows that the PVC#3 loss factor has higher values than PVC#1 in the rubber elastic region. The higher loss factor of PVC#3 indicates that its ability to dissipate the applied energy is better compared to PVC#1, i.e., its damping characteristics are superior. The larger area under the loss factor curve signifies the extent of polymer chain mobility and, consequently, its impact resistance. Figure 13 also reveals that the curves exhibit a single peak, indicating favorable compatibility between the plasticizers and PVC, resulting in homogeneous compounds [53].

3.9. Evaluation of the Successfulness of Sustainable Concept

An acceptable and simple method for evaluating the environmental acceptability of the developed technology is the calculation of the E factor (Supplementary Material S3.9) [54–56]. In order to simplify the calculation, the complex technology was divided into three phases: the E -factor for the first phase was found to be 0.84, that for the second was 4.37, and that for the third was 0.074, which indicated the acceptability of the proposed technology in relation to environmental impact. The last step, i.e., PVC re-granulate production, does not generate wastewater or waste material, which can also be quantified with an E factor of 0. Improvement in the environmental impact, i.e., E factor decrease, can be achieved by designing the appropriate technology for wastewater treatment from LA, PG, and plasticizer production that would eliminate the negative influence on the environment.

On the other hand, the Life Cycle Assessment (LCA) concept can be considered. Raw material production is the first step in life cycle assessments (LCAs), which cover manufacturing, production, recycling, and end-of-life exhausted material disposal. To ascertain the environmental impact of PET bottle goods in terms of energy consumption and waste generation, Ncube and Borodin [57] conducted a life cycle assessment (LCA) on PET bottles. According to their investigation, Table S1 displays the environmental profile of a 1 kg PET bottle. Table S2 presents the equivalent categories for the years of 2011 and 2018, based on the production of 1000 kg of PET resin, along with the percentage change

from the initial results for each category [58]. The presented data indicate the necessity of the development of the technology for the efficient use of waste PET and transformation into new product.

The commercial solution in [59] is a proprietary economic and efficient technology for DOTP production from terephthalic acid (detail given in Supplementary Material) [59]. No reaction time was offered, but according to other patent literature [60], eight hours was necessary to finish the esterification reaction. A higher energy consumption was realized by the application of current technology, but due to the use of waste PET as raw material, a two-fold-lower cost in relation to commercial terephthalic acid (PTA), and the use of 2-ethyl hexanol (2EH) as commercial raw materials in commercial technology justify the possible implementation of the technology developed in this work.

Overall, based on the reproducible results from the laboratory level of production of synthesized plasticizer LA/PG/PET/EG/LA (based on bio- and recycled sources) and related PVC re-granulates based on waste PVC at the semi-industrial level of production, they have good physical and mechanical properties, but these are lower in comparison to the material obtained from virgin PVC K70 and DOTP. These results indicate that the use of synthesized plasticizers in the production of PVC materials acts as plasticizers and reinforcing agents due to their oligomeric nature and wealth of present functional groups.

4. Conclusions

Waste-PET-based glycolysates were esterified using levulinic acid in order to produce a plasticizer for PVC re-granulate production using synthesized “green” PET-based plasticizers and waste PVC. NMR and FTIR techniques, as well as physicochemical methods, were used for the characterization of waste PET-based plasticizers. Manufactured-waste-PVC-based materials showed increased hardness, tensile strength, and elongation at break, which are consistent with the characterization results that indicate the significance of ester and keto carbonyl groups in the plasticizers, the ortho- versus para-position, and the intensities of dipole–dipole interactions of the PVC backbone (C–Cl dipole) and carbonyl group present in plasticizer. The lower migration in PVC compared to DOTP was also consistent with these findings, due to the higher number of terephthaloyl moieties. DSC analysis showed gelation with DOTP and LA/PG/PET/EG/LA plasticizer, at 98.4%, with morphological features, crystallite structures, and networks of forces. DMTA confirmed the better compatibility between the “green” plasticizer and PVC, resulting in a homogeneous structure of produced PVC re-granulates.

The results of the research presented revealed the potential of “green” plasticizer production, obtained by combining polymer recycling technology with the raw materials derived from bio-renewable resources, which would contribute to a reduction in carbon footprint as well as the reliance on fossil-based materials. Efforts towards sustainable waste management are essential to mitigate the environmental impact of plastic waste and move towards a more sustainable future.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/pr12030520/s1>. Figure S1: Two-dimensional and 3D structure of reactant included in synthesis of plasticizers; Figure S2: Two-dimensional and 3D structure of commercial DINP and DOTP plasticizer; Figure S3: Two-dimensional and 3D structure of PVC; Figure S4: DOTP plasticizer extracted from waste PVC material; Figure S5: FTIR spectrum of PG and LA; Figure S6: Two-dimensional and 3D structure of the most convenient structure of synthesized LA/DEG/PET/EG/LA (Plast 1) plasticizer; Figure S7: Two-dimensional and 3D structure of the most convenient structure of synthesized LA/PG/PET/EG/LA (Plast 2) plasticizer; Figure S8: Test specimen for tensile and flexural strength determination. Table S1. Environmental profile for 1 kg of PET bottle [57]; Table S2. LCA analysis comparison for 1000 kg PET in 2011 and 2018 [58]. Refs. [30,33,34,36,49–52,54,55,57–59] are cited in Supplementary Materials.

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writing—original draft preparation, M.M.V. and A.M.; writing—review and editing, M.M.V. and A.M.; visualization, J.G.; supervision, M.M. (Milutin Milosavljević) and A.M.; project administration, A.M. All authors have read and agreed to the published version of the manuscript.

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References

1. Smith, R.L.; Takkellapati, S.; Riegerix, R.C. Recycling of Plastics in the United States: Plastic Material Flows and Polyethylene Terephthalate (PET) Recycling Processes. *ACS Sustain. Chem. Eng.* **2022**, *10*, 2084–2096. [CrossRef] [PubMed]
2. Allaf, R.M.; Albarahmeh, E.; Futian, M. Preparation of Sawdust-Filled Recycled-PET Composites via Solid-State Compounding. *Processes* **2020**, *8*, 100. [CrossRef]
3. Bozell, J.J.; Petersen, G.R. Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates—The US Department of Energy’s “Top 10” Revisited. *Green Chem.* **2010**, *12*, 539. [CrossRef]
4. Ledniowska, K.; Nosal-Kovalenko, H.; Janik, W.; Krasuska, A.; Stańczyk, D.; Sabura, E.; Bartoszewicz, M.; Rybak, A. Effective, Environmentally Friendly PVC Plasticizers Based on Succinic Acid. *Polymers* **2022**, *14*, 1295. [CrossRef] [PubMed]
5. Available online: <https://echa.europa.eu/hot-topics/phthalates> (accessed on 1 February 2024).
6. Chaudhary, B.I.; Liotta, C.L.; Cogen, J.M.; Gilbert, M. Plasticized PVC. In *Reference Module in Materials Science and Materials Engineering*; Elsevier: Amsterdam, The Netherlands, 2016.
7. Tumu, K.; Vorst, K.; Curtzwiler, G. Endocrine Modulating Chemicals in Food Packaging: A Review of Phthalates and Bisphenols. *Compr. Rev. Food Sci. Food Saf.* **2023**, *22*, 1337–1359. [CrossRef]
8. Nagorka, R.; Birmili, W.; Schulze, J.; Koschorreck, J. Diverging Trends of Plasticizers (Phthalates and Non-Phthalates) in Indoor and Freshwater Environments—Why? *Environ. Sci. Eur.* **2022**, *34*, 46. [CrossRef]
9. Bio Plasticizers Market Size & Share Analysis—Growth Trends & Forecasts (2024–2029). Available online: <https://www.mordorintelligence.com/industry-reports/bio-plasticizers-market> (accessed on 25 February 2024).
10. Mazitova, A.K.; Aminova, G.K.; Vikhareva, I.N. Designing of Green Plasticizers and Assessment of the Effectiveness of Their Use. *Polymers* **2021**, *13*, 1761. [CrossRef] [PubMed]
11. Kumar, S. Recent Developments of Biobased Plasticizers and Their Effect on Mechanical and Thermal Properties of Poly(Vinyl Chloride): A Review. *Ind. Eng. Chem. Res.* **2019**, *58*, 11659–11672. [CrossRef]
12. Baghaee Moghaddam, T.; Soltani, M.; Karim, M.R. Evaluation of Permanent Deformation Characteristics of Unmodified and Polyethylene Terephthalate Modified Asphalt Mixtures Using Dynamic Creep Test. *Mater. Des.* **2014**, *53*, 317–324. [CrossRef]
13. Akato, K.M.; Nguyen, N.A.; Bonnesen, P.V.; Harper, D.P.; Naskar, A.K. Recycling Waste Polyester via Modification with a Renewable Fatty Acid for Enhanced Processability. *ACS Omega* **2018**, *3*, 10709–10715. [CrossRef]
14. Kiliç, S.; İyim, T.B.; Emik, S.; Özgümüş, S. Recycling of Waste PET: Usage as Secondary Plasticizer for PVC. *Polym. Plast. Technol. Eng.* **2005**, *44*, 1379–1388. [CrossRef]
15. Bäckström, E.; Odelius, K.; Hakkarainen, M. Ultrafast Microwave Assisted Recycling of PET to a Family of Functional Precursors and Materials. *Eur. Polym. J.* **2021**, *151*, 110441. [CrossRef]
16. Nayak, S.; Khuntia, S. kumar Development and Study of Properties of Moringa Oleifera Fruit Fibers/ Polyethylene Terephthalate Composites for Packaging Applications. *Compos. Commun.* **2019**, *15*, 113–119. [CrossRef]
17. Zeng, J.-J.; Ye, Y.-Y.; Gao, W.-Y.; Smith, S.T.; Guo, Y.-C. Stress-Strain Behavior of Polyethylene Terephthalate Fiber-Reinforced Polymer-Confined Normal-, High- and Ultra High-Strength Concrete. *J. Build. Eng.* **2020**, *30*, 101243. [CrossRef]
18. Sinha, V.; Patel, M.R.; Patel, J.V. Pet Waste Management by Chemical Recycling: A Review. *J. Polym. Environ.* **2010**, *18*, 8–25. [CrossRef]
19. Schyns, Z.O.G.; Shaver, M.P. Mechanical Recycling of Packaging Plastics: A Review. *Macromol. Rapid Commun.* **2021**, *42*, 2000415. [CrossRef]
20. Benyathiar, P.; Kumar, P.; Carpenter, G.; Brace, J.; Mishra, D.K. Polyethylene Terephthalate (PET) Bottle-to-Bottle Recycling for the Beverage Industry: A Review. *Polymers* **2022**, *14*, 2366. [CrossRef]
21. Karayannidis, G.P.; Achilias, D.S. Chemical Recycling of Poly(Ethylene Terephthalate). *Macromol. Mater. Eng.* **2007**, *292*, 128–146. [CrossRef]
22. Ghosal, K.; Nayak, C. Recent Advances in Chemical Recycling of Polyethylene Terephthalate Waste into Value Added Products for Sustainable Coating Solutions—Hope vs. Hype. *Mater. Adv.* **2022**, *3*, 1974–1992. [CrossRef]
23. More, A.P.; Kute, R.A.; Mhaske, S.T. Chemical Conversion of PET Waste Using Ethanamine to Bis(2-Hydroxyethyl) Terephthalamide (BHETA) through Aminolysis and a Novel Plasticizer for PVC. *Iran. Polym. J.* **2014**, *23*, 59–67. [CrossRef]
24. Cakić, S.M.; Ristić, I.S.; M-Cincović, M.; Nikolić, N.Č.; Ilić, O.Z.; Stojilković, D.T.; B-Simendić, J.K. Glycolized Products from PET Waste and Their Application in Synthesis of Polyurethane Dispersions. *Prog. Org. Coat.* **2012**, *74*, 115–124. [CrossRef]

25. Lim, H.; Hoag, S.W. Plasticizer Effects on Physical–Mechanical Properties of Solvent Cast Soluplus® Films. *AAPS PharmSciTech* **2013**, *14*, 903–910. [[CrossRef](#)] [[PubMed](#)]
26. Czogała, J.; Pankalla, E.; Turczyn, R. Recent Attempts in the Design of Efficient PVC Plasticizers with Reduced Migration. *Materials* **2021**, *14*, 844. [[CrossRef](#)] [[PubMed](#)]
27. Jia, P.-Y.; Bo, C.-Y.; Zhang, L.-Q.; Hu, L.-H.; Zhang, M.; Zhou, Y.-H. Synthesis of Castor Oil Based Plasticizers Containing Flame Retarded Group and Their Application in Poly (Vinyl Chloride) as Secondary Plasticizer. *J. Ind. Eng. Chem.* **2015**, *28*, 217–224. [[CrossRef](#)]
28. Bocqué, M.; Voirin, C.; Lapinte, V.; Caillol, S.; Robin, J.-J. Petro-Based and Bio-Based Plasticizers: Chemical Structures to Plasticizing Properties. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54*, 11–33. [[CrossRef](#)]
29. Dutt, K.; Soni, R.K. Synthesis and Characterization of Polymeric Plasticizer from PET Waste and Its Applications in Nitrile Rubber and Nitrile–PVC Blend. *Iran. Polym. J.* **2013**, *22*, 481–491. [[CrossRef](#)]
30. Langer, E.; Waśkiewicz, S.; Bortel, K.; Lenartowicz-Klik, M.; Jurczyk, S. Application of New Oligomeric Plasticizers Based on Waste Poly(Ethylene Terephthalate) for Poly(Vinyl Chloride) Compositions. *Iran. Polym. J.* **2017**, *26*, 115–123. [[CrossRef](#)]
31. Soni, R.K.; Dutt, K.; Jain, A.; Soam, S.; Singh, S. A Novel Route of Synthesis, Characterization of Terephthalic Dihydrazide from Polyethylene Terephthalate Waste and It's Application in PVC Compounding as Plasticizer. *J. Appl. Polym. Sci.* **2009**, *113*, 1090–1096. [[CrossRef](#)]
32. Rusmirovic, J.; Milosevic, D.; Velicic, Z.; Karanac, M.; Kalifa, M.; Nikolic, J.; Marinkovic, A. Production of Rubber Plasticizers Based on Waste PET: Techno-Economical Aspect. *Zast. Mater.* **2017**, *58*, 189–197. [[CrossRef](#)]
33. Hirunsit, P.; Luadthong, C.; Faungnawakij, K. Effect of Alumina Hydroxylation on Glycerol Hydrogenolysis to 1,2-Propanediol over Cu/Al₂O₃: Combined Experiment and DFT Investigation. *RSC Adv.* **2015**, *5*, 11188–11197. [[CrossRef](#)]
34. Salih, R.; Veličković, Z.; Milošević, M.; Pavlović, V.P.; Cvijetić, I.; Sofrenić, I.V.; Gržetić, J.D.; Marinković, A. Lignin Based Microspheres for Effective Dyes Removal: Design, Synthesis and Adsorption Mechanism Supported with Theoretical Study. *J. Environ. Manag.* **2023**, *326*, 116838. [[CrossRef](#)] [[PubMed](#)]
35. Pyo, S.-H.; Glaser, S.J.; Rehnberg, N.; Hatti-Kaul, R. Clean Production of Levulinic Acid from Fructose and Glucose in Salt Water by Heterogeneous Catalytic Dehydration. *ACS Omega* **2020**, *5*, 14275–14282. [[CrossRef](#)] [[PubMed](#)]
36. Milentijević, G.; Milošević, M.; Milojević, S.; Marković, S.; Rančić, M.; Marinković, A.; Milosavljević, M. One-Pot Syntheses of PET-Based Plasticizer and Tetramethyl Thiuram Monosulfide (TMTS) as Vulcanization Accelerator for Rubber Production. *Processes* **2023**, *11*, 1033. [[CrossRef](#)]
37. Ahmed, D.; El-Hiti, G.; Hameed, A.; Yousif, E.; Ahmed, A. New Tetra-Schiff Bases as Efficient Photostabilizers for Poly(Vinyl Chloride). *Molecules* **2017**, *22*, 1506. [[CrossRef](#)] [[PubMed](#)]
38. Rusmirovic, J.D.; Trifkovic, K.T.; Bugarski, B.; Pavlovic, V.B.; Dzunuzovic, J.; Tomic, M.; Marinkovic, A.D. High Performances Unsaturated Polyester Based Nanocomposites: Effect of Vinyl Modified Nanosilica on Mechanical Properties. *Express Polym. Lett.* **2016**, *10*, 139–159. [[CrossRef](#)]
39. Spasojević, P.M.; Panić, V.V.; Džunuzović, J.V.; Marinković, A.D.; Woortman, A.J.J.; Loos, K.; Popović, I.G. High Performance Alkyd Resins Synthesized from Postconsumer PET Bottles. *RSC Adv.* **2015**, *5*, 62273–62283. [[CrossRef](#)]
40. Garcia, D.; Balart, R.; Crespo, J.E.; Lopez, J. Mechanical Properties of Recycled PVC Blends with Styrenic Polymers. *J. Appl. Polym. Sci.* **2006**, *101*, 2464–2471. [[CrossRef](#)]
41. Coltro, L.; Pitta, J.B.; Madaleno, E. Performance Evaluation of New Plasticizers for Stretch PVC Films. *Polym. Test.* **2013**, *32*, 272–278. [[CrossRef](#)]
42. Machacek, E.; Richter, J.L.; Habib, K.; Klossek, P. Recycling of Rare Earths from Fluorescent Lamps: Value Analysis of Closing-the-Loop under Demand and Supply Uncertainties. *Resour. Conserv. Recycl.* **2015**, *104*, 76–93. [[CrossRef](#)]
43. Patil, S.S.; Jena, H.M. Performance Assessment of Polyvinyl Chloride Films Plasticized with Citrullus Lanatus Seed Oil Based Novel Plasticizer. *Polym. Test.* **2021**, *101*, 107271. [[CrossRef](#)]
44. Zhang, H.; Zhu, F.; Fu, Q.; Zhang, X.; Zhu, X. Mechanical Properties of Renewable Plasticizer Based on Ricinoleic Acid for PVC. *Polym. Test.* **2019**, *76*, 199–206. [[CrossRef](#)]
45. Fillot, L.; Hajji, P.; Gauthier, C.; Masenelli-Varlot, K. U-PVC Gelation Level Assessment, Part 1: Comparison of Different Techniques. *J. Vinyl Addit. Technol.* **2006**, *12*, 98–107. [[CrossRef](#)]
46. Gramann, P.; Cruz, J.R.B. Using Differential Scanning Calorimetry to Determine the Quality of a PVC Part. *Eng. Mater. Sci.* **2010**.
47. Gilbert, M.; Vyvoda, J.C. Thermal Analysis Technique for Investigating Gelation of Rigid PVC Compounds. *Polymer* **1981**, *22*, 1134–1136. [[CrossRef](#)]
48. Potente, H.; Schultheis, S.M. Bestimmung Des Geliertgrads von PVC Mit Der DSC. *Kunststoffe* **1987**, *77*, 401–404.
49. Bair, H.E.; Warren, P.C. Morphology of Lightly Plasticized PVC. *J. Macromol. Sci. Part B* **1981**, *20*, 381–402. [[CrossRef](#)]
50. Tupý, M.; Čisáň, J.; Mokrejš, P.; Měřínská, D.; Tesaříková-Svobodová, A. Comparison of Processing Conditions for Plasticized PVC and PVB. *Int. Sch. Sci. Res. Innov.* **2015**, *9*, 617–621.
51. Available online: <https://www.anton-paar.com/corp-en/services-support/document-finder/application-reports/mechanical-thermal-behavior-of-pvc-based-strip-doors/> (accessed on 1 February 2024).
52. Characterization of Polyvinyl Chloride (PVC) by DMA, TAI Application Report TS-40. Available online: <https://www.tainstruments.com/pdf/literature/TS40.pdf> (accessed on 1 February 2024).

53. Chen, J.; Liu, Z.; Wang, K.; Huang, J.; Li, K.; Nie, X.; Jiang, J. Epoxidized Castor Oil-based Diglycidyl-phthalate Plasticizer: Synthesis and Thermal Stabilizing Effects on Poly(Vinyl Chloride). *J. Appl. Polym. Sci.* **2019**, *136*, 47142. [[CrossRef](#)]
54. Sheldon, R.A. The E Factor: Fifteen Years On. *Green Chem.* **2007**, *9*, 1273. [[CrossRef](#)]
55. Manahan, S.E. The E-Factor in Green Chemistry. In *Green Chemistry and the Ten Commandments of Sustainability*; ChemChar Research: Columbia, SC, USA, 2011; pp. 322–323.
56. Thomas, J.; Patil, R.S.; Patil, M.; John, J. Addressing the Sustainability Conundrums and Challenges within the Polymer Value Chain. *Sustainability* **2023**, *15*, 15758. [[CrossRef](#)]
57. Ncube, A.; Borodin, Y. Life Cycle Assessment of Polyethylene Terephthalate Bottle. In Proceedings of the 2012 7th International Forum on Strategic Technology (IFOST), Tomsk, Russia, 18–21 September 2012; IEEE: Piscataway, NJ, USA, 2012; pp. 1–6.
58. Sarda, P.; Hanan, J.C.; Lawrence, J.G.; Allahkarami, M. Sustainability Performance of Polyethylene Terephthalate, Clarifying Challenges and Opportunities. *J. Polym. Sci.* **2022**, *60*, 7–31. [[CrossRef](#)]
59. Available online: https://ceykimya.com/en/services-k36-dotp_plant-s53 (accessed on 25 February 2024).
60. Anhui Xiangfeng New Materials Co., Ltd. Production Method of Dioctyl Terephthalate. CN102701984A, 3 October 2012.

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