

Biosourced Aromatic Derivatives in the Upcycling of Recycled PET: Mellophanic Dianhydride as a Chain Extender

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ABSTRACT: The synthesis of mellophanic dianhydride (MEDA) from biosourced 1,2,3,4-benzene tetracarboxylic derivatives and its use as a chain extender for mechanically recycled PET (R-PET) as an alternative to traditional oil-based pyromellitic dianhydride (PMDA) is reported. The rheological tests performed on the R-PET extruded with MEDA have shown similar results to those obtained with PMDA, and dynamic mechanical thermal analysis (DMTA) showed that, in the 90–110 °C range (i.e., the temperature range commonly used for blow molding of bottles), Young's modulus of R-PET containing MEDA is about 20% higher in comparison to that of pristine R-PET. The advantage of MEDA is that it can be prepared using building blocks obtained from agricultural waste *via* a sustainable protocol, whereas PMDA is a product of oil-based chemistry.

KEYWORDS: poly(ethylene terephthalate), R-PET, upcycling, biomass, chain extenders, plastic waste



INTRODUCTION

Poly(ethylene terephthalate) (PET), the most diffused thermoplastic polymer of the polyester family, in the last decades has aroused great interest due to its excellent chemical and physicommechanical properties, together with intrinsic easy processability.¹ Nowadays, PET finds many applications: in the packaging sector, it is by far the most used polymer for the production of stretch-blown beverage bottles, leading to global demand for PET of 27 million metric tons in 2020.² This large use of PET products results in its profound drawbacks at end-of-life, as these materials are overwhelmingly landfilled or leaked into the environment,³ as actually about 40% of plastics used for packaging is recycled and PET accounts for 12% of total solid waste,^{4,5} despite being easily recyclable via mechanical recycling.

The EU waste framework directive has outlined a hierarchical scale regarding waste, in which recycling is considered more important and impacting with regard to its use to recover energy.

As stated by Helen Jordan from the British Plastics Foundation, “we need to stop thinking of plastic as ‘waste’, but as a renewable resource that needs to be disposed of correctly”, as the recycling of plastics has the capability to save energy and to reduce resource consumption and waste.

Among the various methods for PET recycling,^{6–9} mechanical recycling is by far the preferred option on an industrial level: it consists of mechanically grinding the postconsumer PET that is then cleaned, dried, and extruded

again in the form of pellets, becoming the so-called recycled PET (R-PET).

It is known that postconsumer PET, coming mainly from bottles, has the tendency to degrade when processed at high temperatures due to partial hydrolysis, lowering its molecular weight and consequently downgrading its final properties, which, in turn, leads to also an economical downgrading of the R-PET itself. Chain extension and branching are known methods that enhance the rheological and mechanical properties of polymers, and in this context, many chemical substances have been used for promoting chain extension and branching of polyesters also during the mechanical recycling phase.¹⁰ In order to come back to the original molecular weight, “chain extenders” (CEs) are required, i.e., molecules that, during the melt extrusion process, can at least partially react with PET increasing its molecular weight. Currently, chain extenders for PET are mainly oligomers with a high quantity of epoxy groups (BASF Joncryl family) or anhydrides such as pyromellitic dianhydride (PMDA), and both these families of molecules are derived from fossil sources.²

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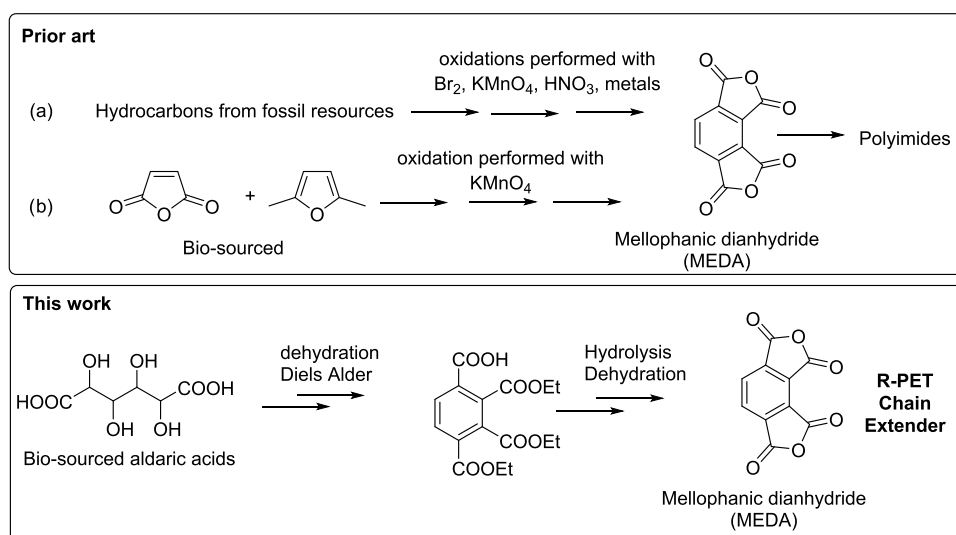


Figure 1. Prior art and this work.

Despite being used in relatively small quantities in the material (usually between 0.2 and 1.0% w/w), the huge market and potential market of R-PET make the overall quantity of oil-derived CE used for this application significant.

On the other hand, as well known, agriculture waste represents a biomass that can be used as a source of many building blocks,^{11–13} and it is estimated that the agricultural dry biomass is about 25 Gton/year and 20 of them become waste.

In particular, aldaric acids, derived from the oxidation of carbohydrates, are largely used as platform molecules.¹⁴ Galactaric acid, also known as mucic acid, can be obtained from pectins,¹⁵ and it is a precursor of valuable chemicals such as pyrones, functionalized aromatic derivatives, and adipic acid.^{16–23}

Mellophanic dianhydride (MEDA) is currently synthesized starting from fossil sources (Figure 1a).^{24–28} Recently, a synthesis from bio-based dimethylfuran and maleic anhydride has been proposed (Figure 1b), and the process includes an oxidation step performed with potassium permanganate.²⁹ To the best of our knowledge, MEDA is actually used only in the preparation of polyimides.^{24,29}

We now propose the use of MEDA as a bio-based chain extender for R-PET as an alternative to PMDA. The sustainable synthesis of MEDA starting from tetracarboxylic acid derivatives, obtained from aldaric acids and diethyl fumarate (Figure 1, this work),^{18,19} proceeds efficiently without the need for oxidation steps and the use of high valence transition metals as a catalyst, preserving all of the six carbon atoms in the aldaric acid precursor.

The intent is therefore to use a building block that can be obtained from agricultural waste in the recycling of PET as a bioalternative to oil-based PMDA (Figure 2).

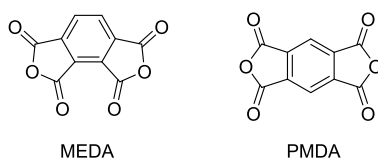


Figure 2. MEDA and PMDA.

EXPERIMENTAL SECTION

A Bruker AV 400 MHz instrument equipped with a 5 mm multinuclear probe with reverse detection was used to record ¹H NMR spectra (400 MHz); ¹H chemical shifts (δ) are given in ppm relative to the residual proton of the solvent. MEDA was analyzed in anhydrous DMSO-*d*₆.

All reagents and solvents were purchased from Merck and used without any further purification.

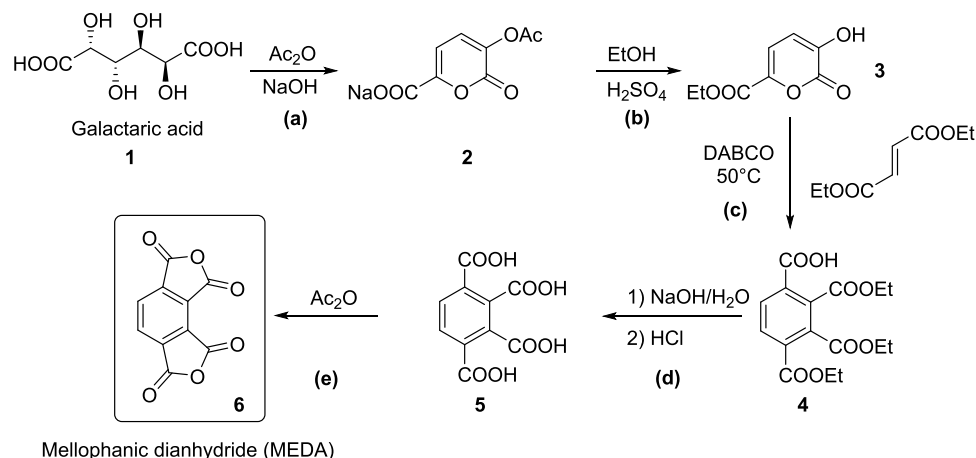
Recycled PET (R-PET) powder was provided by Montello SPA (Montello, BG, Italy).

A Thermo Scientific Process 11 extruder corotating twin screw extruder with a screw diameter of 11 mm, screw temperatures of 245 °C (feed), 260 °C (central), and 225 °C (die) with screw speeds of 210 rpm and feeder speed 7 rpm was used for extruded R-PET samples. A rheometer Anton Paar MCR302 was used for frequency sweep and time vs viscosity rheological testing with a plate–plate system of 25 mm and a 1 mm gap. The frequency sweep was performed from 100 to 0.1 Hz with 30 points with the logarithmic progression of the points and 5% deformation at 280 °C. To better show the effects of shear rate over melt viscosity, in all figures showing frequency sweep experiments, experimental data obtained as complex viscosity vs angular frequency are here presented as standard shear viscosity vs shear rate thanks to the Cox–Merz rule. The time vs viscosity curves were obtained over a 30 min time, taking a total of 180 points, one every 10 s, at 280 °C and a frequency of 10 Hz. All of the analyses were performed under a nitrogen atmosphere. Dynamic mechanical analysis tests were conducted on an ISO 527-5A specimen using the Anton Paar MCR302 Rheometer, and the module used was SRF12, with a frequency of 1 Hz, temperature from 30 to 150 °C with an increment of 1 °C/min and 121 points total. The specimen molding was conducted using a Babyplast press at 265 °C, 37 bar, and a mold temperature of 60 °C.

Synthesis of 3-Acetoxy-2-oxo-2H-pyran-6-carboxylic Acid (2).¹⁸ To a suspension of galactaric acid (1) (20.0 g, 95.2 mmol) in 120 mL of acetic anhydride heated and stirred at 90 °C, sodium hydroxide was slowly added (4.1 g, 95.2 mmol), keeping the temperature lower than 95 °C. The resulting mixture was kept at 90 °C for 4 h. Then, the mixture was cooled at room temperature and left at this temperature overnight. The formed solid was filtered, the mother liquid was separated, and then the solid was washed with 70 mL of ethyl acetate and dried, obtaining 15.6 g of 2-nAcOH as a solid (purity of 2, 69% based on internal standard, yield 52%). ¹H NMR analysis (Supporting information Figure S1) was consistent with the data reported in the literature.¹⁸

Synthesis of Ethyl 3-Hydroxy-2-oxo-2H-pyran-6-carboxylate (3). To a suspension of 3-acetoxy-2-oxo-2H-pyran-6-carboxylic

Scheme 1. Synthesis of Mellophanic Dianhydride (6)



acid (2) (6.0 g of 2-nAcOH, 69% of 2, 4.14 g, 18.8 mmol of 2) in 100 mL of ethanol, sulfuric acid (1.85 g, 18.8 mmol) was added, and the resulting mixture was refluxed under stirring for 24 h. After this time, the major part of ethanol containing the formed ethyl acetate (tot. 83 mL, 3% of ethyl acetate) was removed under reduced pressure and recovered (Supporting information Figure S3); then, 100 mL of distilled water was added, and the mixture was extracted with 3 × 40 mL of dichloromethane. The organic layer was washed with 2 × 40 mL of water, dried over Na_2SO_4 , and the solvent was removed under reduced pressure, obtaining 3.05 g of 3 as a white solid (16.6 mmol, 88%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 7.17 (d, J = 7.5 Hz, 1H), 6.69 (d, J = 7.5 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H) ppm.¹⁹

2,3,4-Tris(ethoxycarbonyl)benzoic Acid (4).¹⁹ A solution of pyrone 3 (7.55 g, 41.0 mmol), DABCO (9.18 g, 81.8 mmol), and diethyl fumarate (13.36 g, 77.6 mmol) in 65 mL of acetonitrile was stirred at 50 °C for 24 h. After this time, the reaction mixture was concentrated under reduced pressure, and 300 mL of distilled water was added. The resulting suspension was extracted with 2 × 100 mL of ethyl acetate, the organic layer was dried over Na_2SO_4 , filtered, and the solvent was removed under vacuum, obtaining 6.56 g of recovered diethyl fumarate (38.1 mmol, 49%). The ^1H NMR analysis (Supporting information, Figure S4) showed the presence of traces (<0.5%) of triester 4. The aqueous layer was then acidified (pH ~ 2) with concentrated HCl (~12.5 mL) and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over Na_2SO_4 , filtered, and the solvent was removed under vacuum and recovered (Supporting information, Figure S5), obtaining 12.5 g of 4 as a light brown solid (90% yield). ^1H NMR (400 MHz, CDCl_3) δ = 8.11 (d, J = 8.2 Hz, 1H), 8.02 (d, J = 8.1 Hz, 1H), 4.42–4.33 (m, 6H), 1.39–1.33 (m, 9H) ppm.

Benzene-1,2,3,4-tetracarboxylic Acid (5). 2,3,4-Tris(ethoxycarbonyl)benzoic acid (4) (12.5 g, 37 mmol) was dispersed in 220 mL of distilled water; then, sodium hydroxide (10.8 g, 270 mmol) was added, and the resulting solution was refluxed under stirring for 24 h. After this time, the mixture was cooled at room temperature and acidified with concentrated hydrochloric acid (pH ~ 1, ~24 mL). The water was evaporated under vacuum, and to the light-yellow solid, 120 mL of THF was added. The suspension was vigorously stirred for 15 min and then filtered. The solvent was removed under vacuum and recovered (Supporting information, Figure S8), obtaining 7.7 g (purity 95%, 28.9 mmol) of 5 (78% yield). ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ = 7.90 (s, 2H) ppm;³⁰ ^{13}C NMR (100.6 MHz, $\text{DMSO}-d_6$) δ = 167.7, 166.8, 134.0, 133.2, 129.9 ppm.

Synthesis of Mellophanic Dianhydride (MEDA, 6). Benzene-1,2,3,4-tetracarboxylic acid (5) (9.7 g, purity 95%, 36.3 mmol) was dispersed in 80 mL of acetic anhydride, and the resulting solution was refluxed for 48 h. After this time, the solvent mixture, containing the formed acetic acid, was completely removed under vacuum and recovered (Supporting information, Figure S11), obtaining 7.1 g of 6

as a brown solid (90% yield). A small part was then sublimated for analysis (Supporting information, Figure S10). ^1H NMR ($\text{DMSO}-d_6$) δ = 8.57 (s, 2H) ppm.³⁰

Synthesis of Mellophanic Dianhydride (MEDA, 6) by Thermal Dehydration of 5. Two identical samples of benzene-1,2,3,4-tetracarboxylic acid (5) (50 mg) were placed in a test tube and heated at 200 °C, respectively, for 2 and 24 h. After these times, the crude was cooled at room temperature under a nitrogen atmosphere, dissolved in $\text{DMSO}-d_6$, and analyzed by ^1H NMR. In these two experiments, all of the solids present in the test tubes were dissolved.

In a similar experiment performed by heating for 24 h, the white crystals obtained as a result of sublimation were separately analyzed.

RESULTS AND DISCUSSION

Mellophanic dianhydride was prepared through a multistep protocol, starting from galactaric acid (Scheme 1). Galactaric acid 1 was converted (step a) into pyrone 2,¹⁸ which was directly transformed into pyrone 3 (step b) with ethanol in the presence of sulfuric acid by a single-step reaction. The best yield was achieved by using the acid in slight excess with respect to intermediate 2. Using a lower amount of sulfuric acid, the reaction resulted to be incomplete as the formation of decarboxylated byproducts was observed (Supporting information, Figure S2). The Diels–Alder cycloaddition of pyrone 3 with diethyl fumarate (step c) afforded the corresponding aromatic triester 4 according to the procedure reported in the literature.¹⁹ As step (c) requires an excess of fumarate to occur efficiently, the possibility to recycle the extra stoichiometric amount was explored. The fumarate was efficiently recovered from the crude by extraction and used as a reagent without the need for further purification (Supporting information, Figure S4). The experiments performed with this latter gave product 4 in the same yields. Triester 4 was then hydrolyzed (step d) in aqueous NaOH, obtaining after acidic workup, benzene-1,2,3,4-tetracarboxylic acid (5) in a 90% yield. Finally, 5 was converted in quantitative yield to the target dianhydride 6 (step e) by refluxing the tetracid in acetic anhydride.

In order to assess the potential environmental impact of the synthetic pathway that was developed, process mass intensity (PMI) metric was used. PMI is considered one of the most complete green metrics because it takes into account the whole mass of the material used in the process including the solvents used in the purification.³¹ The PMI of our overall protocol, starting from galactaric acid, has been calculated, resulting in a value of 446. This value is higher than the one calculated on the basis of the data reported in the literature (312) for the

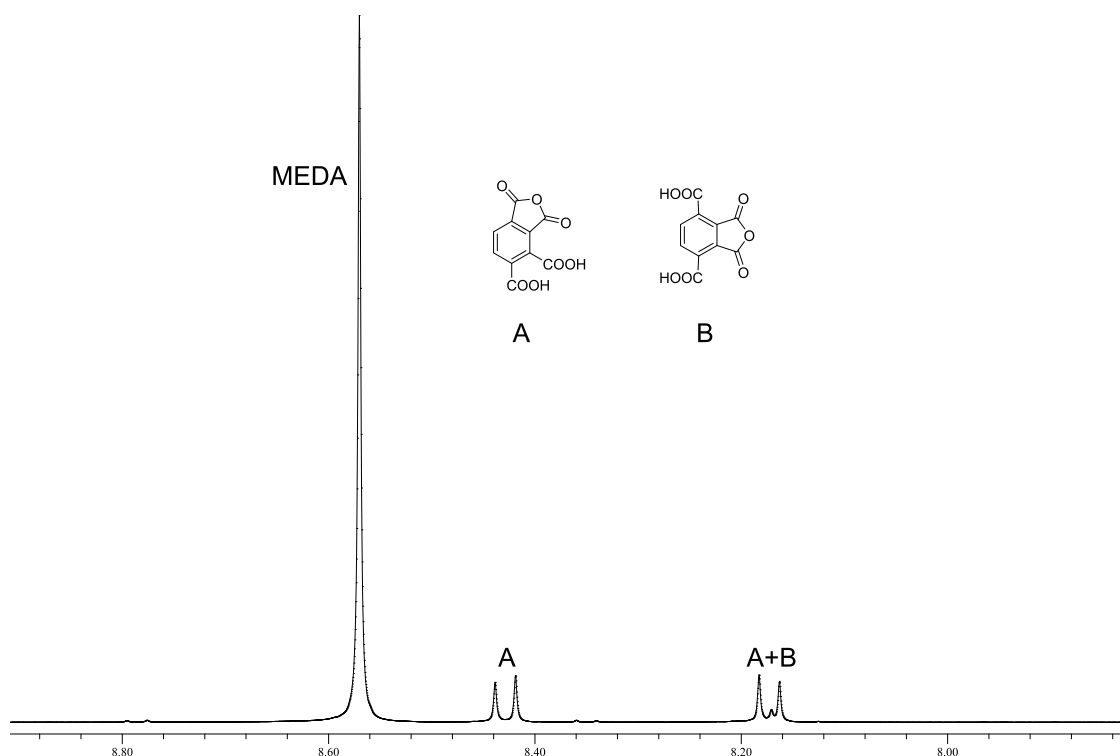


Figure 3. ^1H NMR spectra of the thermal dehydration of tetracid 5.

fully bio-based synthesis of **6** starting from maleic anhydride and dimethylfuran.²⁹ However, the PMI calculated based on the synthesis reported in the literature is underestimated, as not all of the data regarding the purifications are reported. Moreover, the reactions to obtain the two precursors from natural sources were not considered (details about calculations are reported in the Supporting information).

Even if the PMI value appears relatively high, it has to be considered that the excess of diethyl fumarate as discussed above, and most of the solvents used, can be recovered in good quantity and purity (the ^1H NMR spectra of the solvents recovered are reported in the Supporting information, Figures S3, S5, S8, and S11). Furthermore, an experiment was performed using the recovered mixture containing acetyl anhydride and acetic acid (ratio 3:1) for the synthesis of **6**. The ^1H NMR analysis of the crude product (Supporting information, Figure S12) showed substantially a complete conversion of tetracid **5** to the desired dianhydride **6**.

Thus, in our opinion, the proposed protocol, even if not optimized, could represent a promising alternative for the bio-based synthesis of mellophanic dianhydride.

The TGA–DTA analysis was performed to test the thermal stability of **5** (Supporting information, Figure S13). In order to perform the reaction in a more sustainable way and to decrease the PMI, the thermal dehydration of **5** under neat condition, i.e., avoiding the use of acetic anhydride, was also performed and monitored by ^1H NMR analysis. The experiment carried out at 200 °C in a test tube after 2 h gave complete conversion with an 80% selectivity toward the desired MEDA (Figure 3), showing the presence of possible intermediates A and B compatible with 1,2- and 2,3-monoanhydrides. After 24 h, only a 5% of increase in selectivity was observed, and a product was collected as white crystals. Their ^1H NMR analysis showed a composition of 89% in the desired MEDA.

The MEDA (**6**) was then tested as a chain extender in R-PET powder and compared with the already used pyromellitic dianhydride (PMDA).³²

Triester **4** was also tested as a potential chain extender. However, the rheology test showed only a low improvement in the complex viscosity of the extrudate at low shear rate when compared with that of the extruded pristine R-PET powder (Supporting information, Figure S14), and this could be related to a lower reactivity of esters with respect to anhydride moiety.

Rheological Analyses on R-PET with PMDA and MEDA. As a preliminary test, mixtures between the R-PET powder with MEDA or PMDA in the same ratio (0.5% w/w) were prepared via dry blending and studied through frequency sweep experiments using a rotational rheometer (Figure 4).

As shown in Figure 4, R-PET + MEDA has a shear sensitivity lower than R-PET + PMDA but far higher than pristine R-PET. This finding suggests that the molecular mass and/or the degree of branching due to MEDA are slightly lower than the one that can be obtained using PMDA but it is, however, promising in view of the stretch-blown process. At the same time, R-PET + MEDA melt viscosity at higher shear rates gets slightly higher than the one of R-PET + PMDA and this feature indicates that also the complex modulus gets higher: usually, when comparing homologous materials, a higher complex modulus reflects better mechanical properties.

Since frequency sweep experiments are relatively fast (between 6 and 8 min) and used to assess the dependence of viscosity over shear rate, melt viscosities were also measured with constant oscillation speed over a 30 min time span to understand if MEDA might further react with PET over time (Figure 5). As for frequency sweep experiments, MEDA was compared with PMDA and with pristine R-PET. The complex viscosity of R-PET + MEDA was observed to increase with time and, at long times, was very similar to that of R-PET +

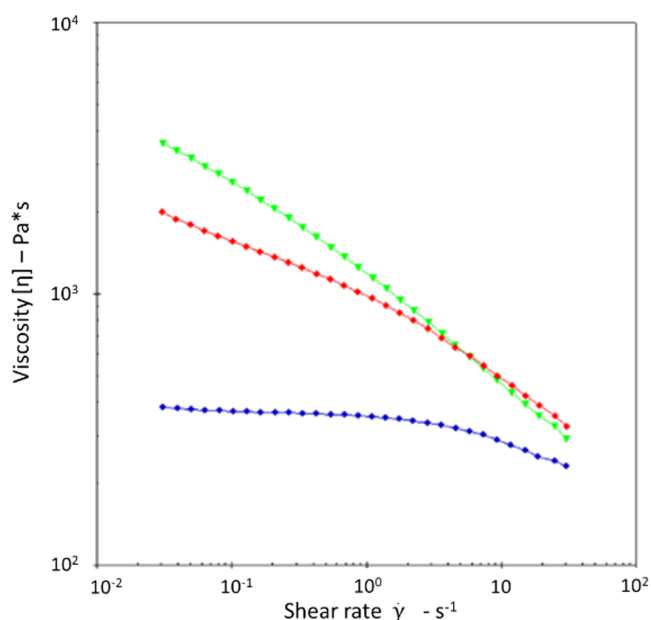


Figure 4. Frequency sweep viscosity curves of pristine R-PET (blue), R-PET + PMDA (green), and R-PET + MEDA (red).

PMDA, which, in turn, reveals a slight decrease after more than 10 min of test (Figure 5). The increase, observed, albeit to a low extent, also in the case of pristine R-PET could be attributed to a partial polycondensation of the polymer, which occurs at high temperatures under a nitrogen atmosphere: when MEDA is present, it probably continues promoting the reaction with R-PET over time, thus increasing the overall complex viscosity of the polymer.

These results suggested that MEDA could be a promising chain extender for PET. Hence, MEDA was tested with R-PET in a twin screw extruder.

Extrusion of R-PET with MEDA. A dry blend between MEDA (0.5% w/w) and R-PET (99.5% w/w) was prepared and extruded using a twin screw extruder, as described in the experimental part. The resulting compound was pelletized and

analyzed via frequency sweep experiments in comparison with R-PET, extruded in the same experimental conditions without the addition of any additive.

As shown in the graph in Figure 6, the melt viscosity of extruded R-PET + MEDA is far higher than that of pristine R-PET, which, in turn, is lower than the melt viscosity of the R-PET powder (as shown in Figure 4), as it could be expected in consideration of the hydrolysis caused by processing. It is indeed well known that, due to environmental moisture, melt extrusion and processing usually lead to a remarkable reduction of the molecular weight and hence of the melt viscosity of polyesters.³³ Extruded R-PET + MEDA shows a viscosity that is also higher than that of R-PET, confirming that the molecular weight of the sample is probably higher than that of the powder itself. It is also worth noting that the shear sensitivity of R-PET + MEDA is much lower than that of the R-PET + MEDA powder (see the graph in Figure 4). This phenomenon could be ascribed to the partial hydrolysis caused by melt extrusion. These results confirm that MEDA is a suitable chain extender for PET also when industrial processing technologies are taken into consideration.

Dynamic Mechanical Thermal Analysis. Injection-molded ISO 527-5A specimens were obtained using a Babyplast injection molding machine (Figure 7). Dynamic mechanical thermal analysis (DMTA) was performed on the specimens: analyses were performed on 5 specimens, and mean values, shown in Table 1, were obtained on 3 specimens for each sample, discarding the worst and the best specimens. Results obtained on all of the samples are shown in the Supporting information in Figures S15 and S16. A representative analysis of one specimen of R-PET and one of R-PET + MEDA is shown in Figures 7 and 8. At low temperatures, the modulus of pristine R-PET is almost identical, i.e., about 2.5% higher, than that of R-PET + MEDA but in the range of temperature usually used in the PET blow molding; i.e., from 90 °C to about 110 °C, the modulus of R-PET + MEDA is about 20% higher than that of R-PET, thus confirming the potential effect of MEDA as a chain extender. A higher modulus at blow molding can indeed

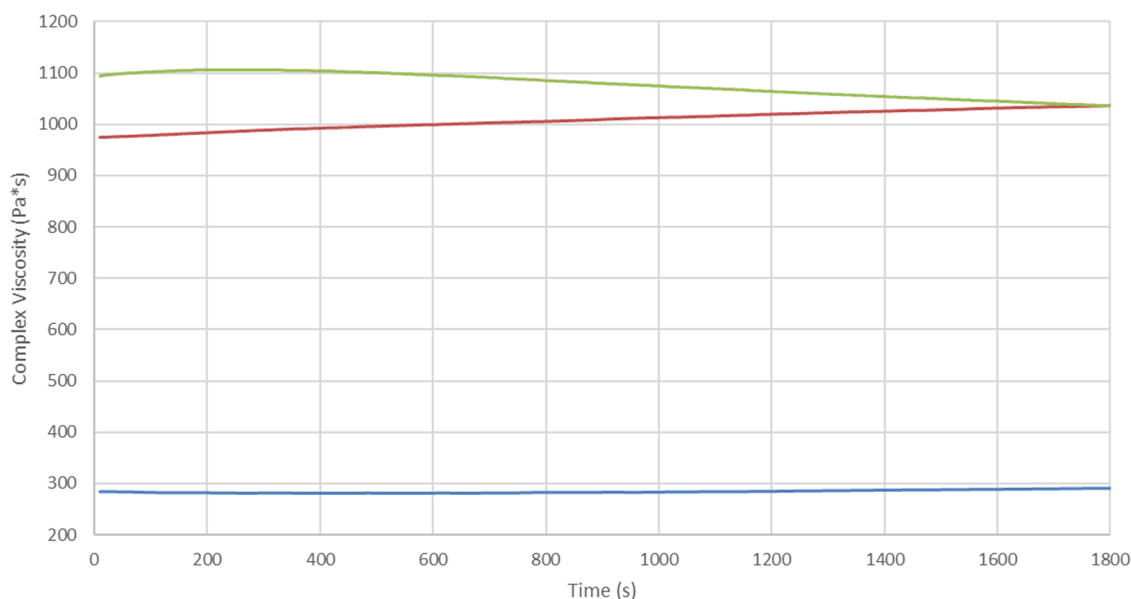


Figure 5. Constant frequency experiments: R-PET (blue), R-PET + MEDA 0.5% (red), and R-PET + PMDA 0.5% (green).

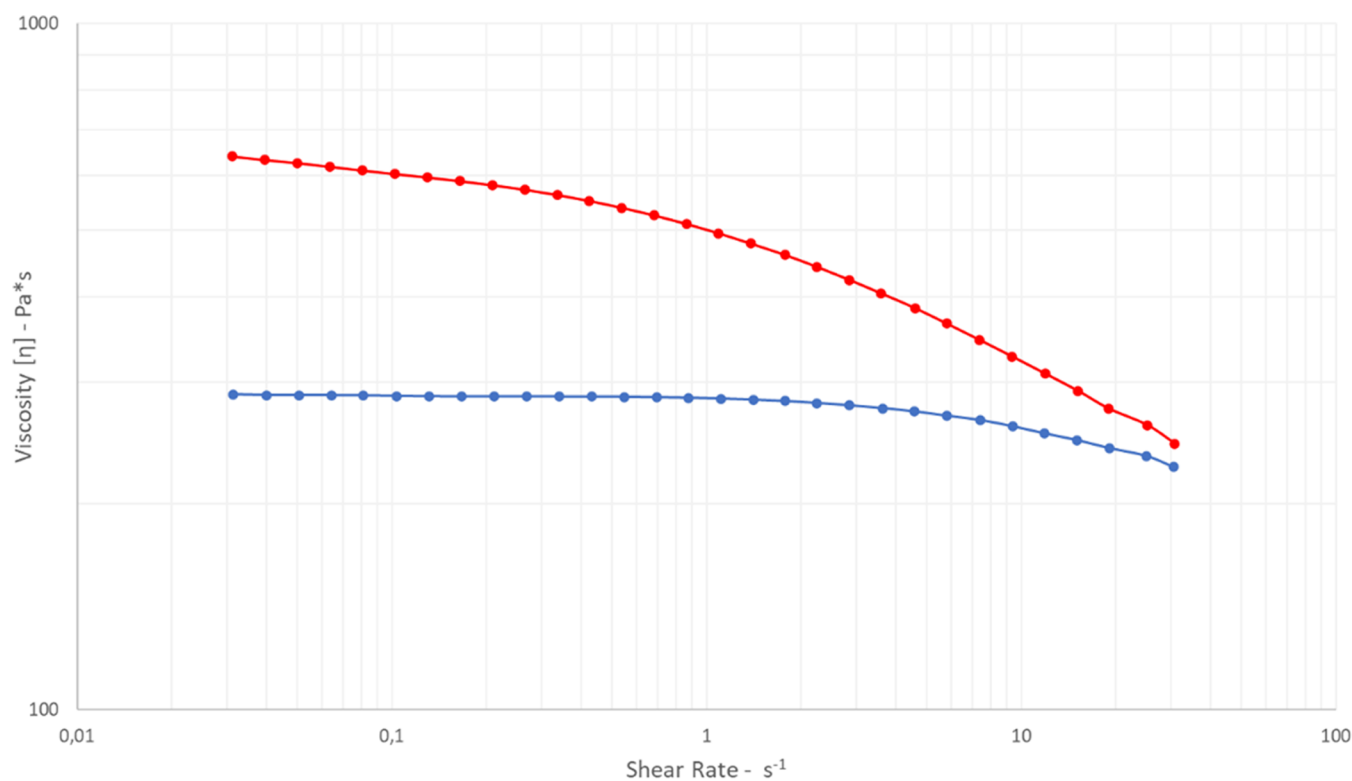
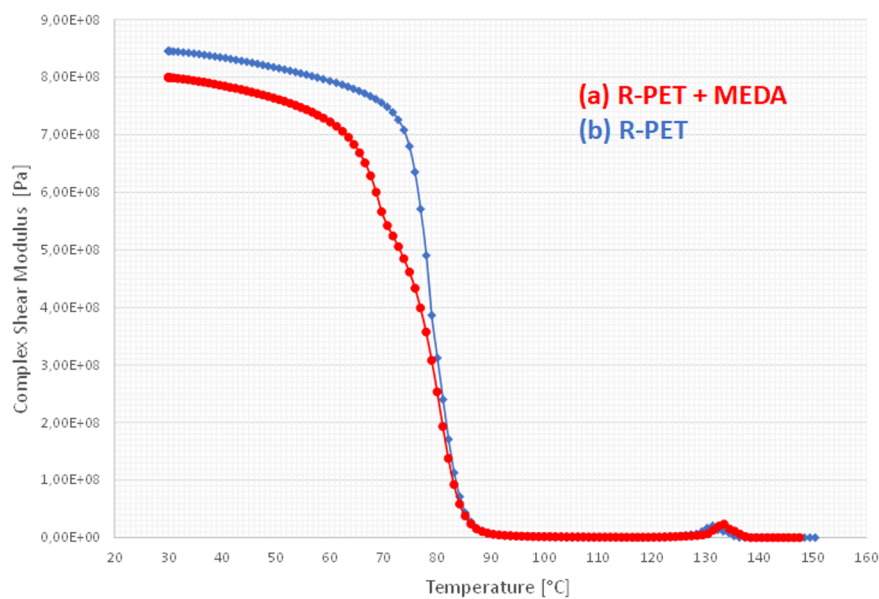


Figure 6. Melt viscosity of extruded R-PET (red) and extruded R-PET + MEDA (blue).



(a)



(b)

Figure 7. ISO 527-5A specimens and DMTA analysis: (a) R-PET + MEDA (6) and (b) R-PET.

Table 1. G^* Values at 30 and 100 °C of R-PET and R-PET + MEDA

sample	G^* (30 °C) [MPa]	G^* (100 °C) [MPa]	Δ (R-PET + MEDA vs R-PET)
R-PET	826 ± 6	1.43 ± 0.06	-2.6%
R-PET + MEDA	804 ± 2	1.69 ± 0.06	+18.8%

have a high technological impact because it could allow the downgauging (lower thickness) of the bottles, which could thus be lighter. The lower consumption of polymer and the

lower weight of the bottles clearly lead to a lower environmental impact.

CONCLUSIONS

This work demonstrates that the bio-based mellophanic dianhydride (MEDA), obtained from galactaric acid, can be successfully used as a chain extender for R-PET. Aldaric acids derive from carbohydrates that are largely available as a waste of agriculture and food industry. The synthesis was characterized by the fact that all of the carbon atoms present

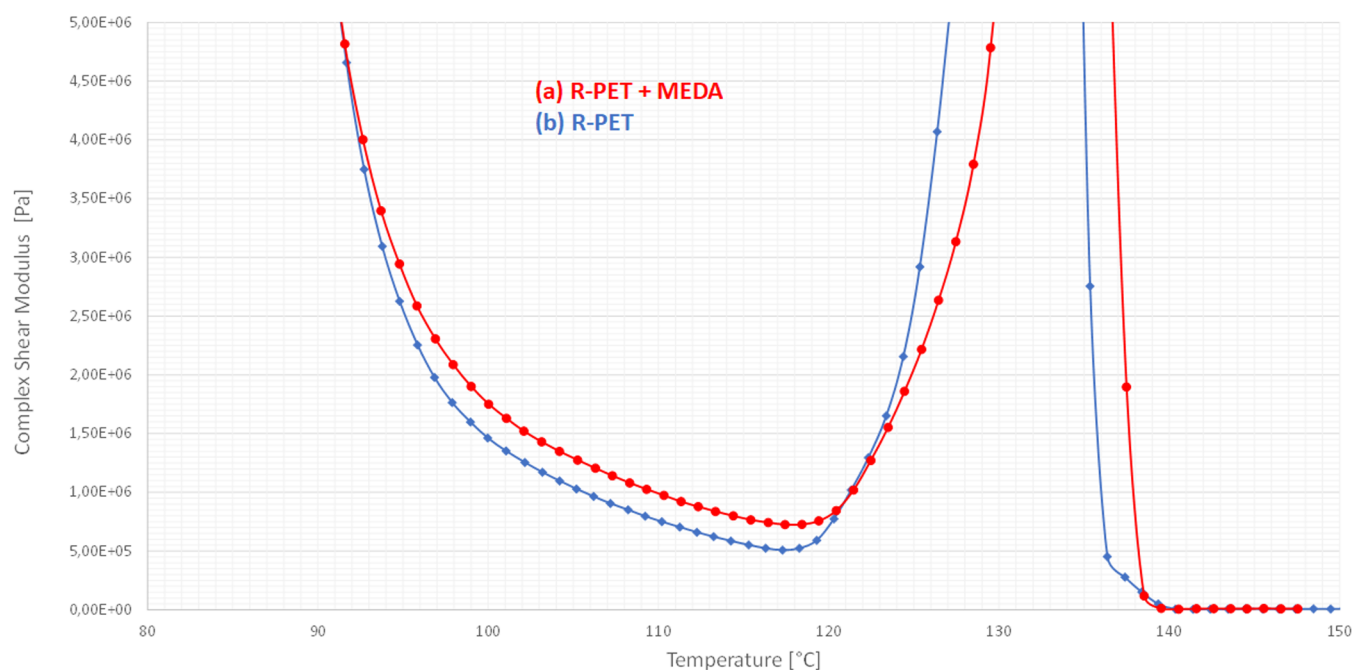


Figure 8. Magnification of Figure 7 between 90 and 120 °C.

in the starting galactaric acid are preserved in the dianhydride. Furthermore, the thermal dehydration of the tetracid could represent an improvement to obtain MEDA in a more sustainable way. The rheological studies, performed *via* frequency sweep experiments, revealed that PET + MEDA had viscosity and shear sensitivity that were higher than those of pristine R-PET and comparable to those of R-PET + PMDA. DMTA analysis on samples after extrusion and injection molding revealed that R-PET + MEDA had a higher modulus than the pristine R-PET in the temperature range (from 90 to 120 °C) commonly used for blow molding. This could result in the downgauging of the bottles: a lower amount of PET would be used and lighter bottles would be obtained. The results reported in this manuscript indicate that MEDA might be used as a chain extender of PET, in place of an oil-based one, favoring the recycling of PET.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.3c01636>.

Representative ^1H NMR and ^{13}C NMR spectra, TGA–DTA, complex viscosities, and DMTA plots are reported (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. All of the authors contributed equally.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

MEDA, mellophanic dianhydride; PMDA, pyromellitic dianhydride; R-PET, recycled poly(ethylene terephthalate); CEs, chain extenders

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