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Highly efficient solid-state hydrolysis of waste polyethylene terephthalate by mechanochemical milling and vapour-assisted aging

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Abstract: Despite significant methodological and technological advancements in chemical recycling of synthetic polymers, an efficient and quantitative conversion of post-consumer polyethylene terephthalate (PET) into terephthalic acid (TPA) under ambient conditions of temperature and pressure still remains a challenge. In this respect, the application of mechanochemistry and multiple advantages offered by solid-state ball milling and vapour-assisted aging have remained insufficiently explored. To further expand their potential, the implementation of organic solvent-free milling as a superior methodology for successful alkaline depolymerization of waste PET (e.g. bottles and textile) into TPA monomer in near-quantitative yields is reported herein. The solid-state alkaline PET hydrolysis is also shown to proceed in excellent yields under aging conditions in humid environment or in the presence of alcohol vapours. Moreover, the performance of mechanochemical ball milling and aging in the gram-scale depolymerization of PET into TPA is demonstrated.

Introduction

Since the beginning of the so-called "plastic age" in the 1950s, when the mass production of plastics commenced, polymer materials have found application in almost every aspect of human activity.^[1] Their durability and chemical stability often represent a problem from the recycling point of view. As a result, an increasing production and consumption of non-biodegradable synthetic polymers imposes a great pressure on the environment. All ecosystems on Earth are affected, from terrestrial where landfills are occupying valuable space to aquatic where the scale of this ecological disaster is particularly visible. According to some estimates, by the year 2050 there will be more plastic waste than fish in oceans by total weight, with the annual production of plastic materials reaching more than 1.1 billion tonnes.^[2] Global production of plastics in 2015 was estimated to ca. 380 million tonnes, and the cumulative amount of waste generated from 1950–2015 was around 6.3 billion tonnes. Only 9% of the waste was recycled and a staggering 60% of all plastics ever made ended up in the environment.^[3] Rationalizing the use of plastic products and increasing the consumer awareness to sort and recycle waste is important in terms of pollution reduction, however finding technical solutions and methodologies to more efficiently process plastic waste and transform it into valuable chemicals is a great challenge. Polyethylene terephthalate or PET is a thermoplastic made of repeating units of terephthalic acid (TPA) and ethylene glycol

(EG), linked together via an ester bond. Therefore, PET is classified as a polyester, and many of its physical and chemical properties arise from such bonding.^[4] Since the ester linkage between TPA and EG units (as any other ester bond) can be cleaved by hydrolysis (or more generally solvolysis), this is the point where all chemical PET degradation pathways occur.^[5] These include alkaline, acidic or neutral hydrolysis, solvolysis reactions such as methanolysis and glycolysis, and aminolysis or ammonolysis with nitrogen nucleophiles.^[6] Different catalysts (e.g. metal salts, zeolites),^[7] reaction media (e.g. ionic liquids, supercritical fluids)^[8] and heating sources (e.g. microwaves)^[9] are used to promote the above mentioned transformations of PET. Currently, glycolysis in ethylene glycol and methanolysis are the most important PET depolymerization methods leading to bis(2-hydroxyethyl) terephthalate (BHET) and dimethyl terephthalate (DMT), respectively.^[6] These products are then used in the production of PET, a characteristic of closed-loop recycling. A common feature of all these depolymerization processes is the need for high temperatures (typically 100–300 °C) and pressures (even up to 200 bar) in order to accomplish reasonable levels of PET conversion.^[10] Enzymatic hydrolysis offers an interesting biotechnological route to PET degradation under mild conditions,^[11] but with serious limitations such as the requirement for amorphous or low-crystallinity PET necessary for the proper activity of PETase enzymes.^[12] Consequently, the enzymatic approach to PET depolymerization still suffers from relatively inefficient conversion and TPA yield, unless the plastic substrate underwent chemical pre-treatment.^[13]

The last decade has witnessed an immense interest in translating reactions from solution to the solid-state, which propelled mechanochemistry among the most promising fields of chemical science with "the potential to change the world", as recognized by the International Union for Pure and Applied Chemistry (IUPAC) in 2019.^[14] Following the discoveries of controlling the solid-state reactivity by adding liquid or solid additives, e.g. liquid- (LAG)^[15] or ion- and liquid-assisted grinding (ILAG),^[16] polymer-assisted grinding (POLAG),^[17] or ionic-liquid assisted grinding (IL-AG)^[18], the introduction of new methodologies such as liquid-assisted resonant acoustic mixing (LA-RAM)^[19] or mechanochemically-assisted solid-state photocatalysis (MASSPC),^[20] or by measuring the temperature effects during ball milling,^[21] mechanochemistry has emerged as a means of doing chemical reactions in a safe, efficient and green manner.^[22] Development of advanced *in situ* monitoring techniques,^[23] alongside *ex situ* measurements,^[24] has greatly

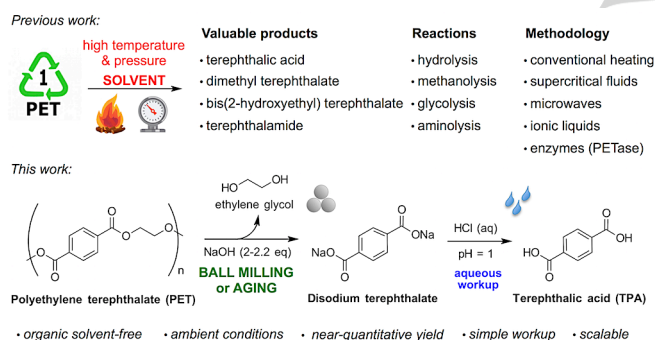
contributed to understanding of mechanochemical reactions on a microscopic level. In the years to come, these findings will undoubtedly form the foundation for scaling-up mechanochemistry by using technologies such as twin-screw extrusion,^[25] which shows promise for application even on the industrial scale.

Early studies of mechanochemical depolymerization of plastic materials published 50 years ago showed that ball milling can induce partial destruction of **PET** polymer chains.^[26] The authors observed a decrease in the average molecular weight of **PET**, where milling at lower temperature or in the presence of water was more efficient compared to dry samples milled at room temperature. Several radical-based mechanisms of partial **PET** depolymerization, grafting and polycondensation were proposed. Cagnetta et al. investigated the application of ball milling in dehalogenation of waste polypropylene in order to remove brominated flame retardants.^[27] Dry ball milling with iron or calcium oxide in the presence of silica was found to be an effective way to transform harmful organobromine compounds into an inorganic bromide. More recently, Frisčić and Auclair have developed the reactive aging ("RAGING") technique for enzymatic depolymerization of biopolymers, e.g. cellulose,^[28a] hemicellulose,^[28b] chitin,^[28c] cellobiose^[28d] and lignocellulosic biomass.^[28e] A combination of brief ball milling and aging in humid environment at mild temperatures, performed in several cycles, accelerates enzymatic hydrolysis and even improves enzyme reactivity to afford monomers in concentrations not achievable in dilute aqueous solutions.

milling in **PET** depolymerization seemed as an attractive research topic. Herein, an unprecedented, efficient and quantitative conversion of waste **PET** into **TPA**, achieved by organic solvent-free mechanochemistry at ambient temperature and pressure, is described. Also, the solid-state **PET** hydrolysis by vapour-assisted aging under different relative humidity levels and solvent vapours, as well as the potential of scaling-up milling and aging reactions, is further discussed.

Results and Discussion

Initially, a mixture consisting of 0.50 grams of pre-milled waste **PET** and stoichiometric amount of sodium hydroxide^[29] (1.0 eq) pellets was ball-milled in a 10 mL jar using a single 12 mm stainless steel ball (7.0 g) for 60 minutes. FTIR-ATR analysis of the crude reaction mixture revealed formation of **TPA** disodium salt as evidenced by the characteristic absorption peaks at 3068, 1545, 1320, 894, 823 and 741 cm^{-1} (Figure 1b). The crude mixture was next suspended in distilled water, the unreacted **PET** removed by filtration, and the filtrate containing the disodium terephthalate salt was acidified with diluted hydrochloric acid^[29] resulting in precipitation of **TPA**. Following this simple aqueous workup procedure, the **PET** conversion was high as 96% with excellent **TPA** yield of 93%. Almost quantitative values were reached by prolonging the reaction time, which led to significant reduction of the intensity of **PET** absorption bands at 1714, 1241 and 724 cm^{-1} (Figure 1c-d and Table 1). When milling was performed for 30 minutes, the conversion and yield plummeted by 50% (Figure 1a).



Scheme 1. Alkaline **PET** hydrolysis in the solid-state.

Although considered as a simple chemical reaction, reports in the scientific or patent literature on the transformation of **PET** waste into its monomer constituents in quantitative yields at ambient temperature and pressure, could not be found. Taking into account the multiple benefits of performing reactions in the solid-state,^[22] the hypothesis was that solid-state alkaline hydrolysis of ester linkages in **PET** polymer chains would lead to an efficient depolymerization and possibly result in practically quantitative yields of **TPA** monomer, regardless of **PET** properties such as crystallinity.^[12] This would also secure only stoichiometric (or slight excess) base to be added for hydrolysis, while high solubility of the terephthalate salt in water would completely eliminate the need for organic solvents in the process. Since another "chemical innovation that will change the world" on the same IUPAC list is monomer production from plastics and related circular economy,^[14] a utilization of ball

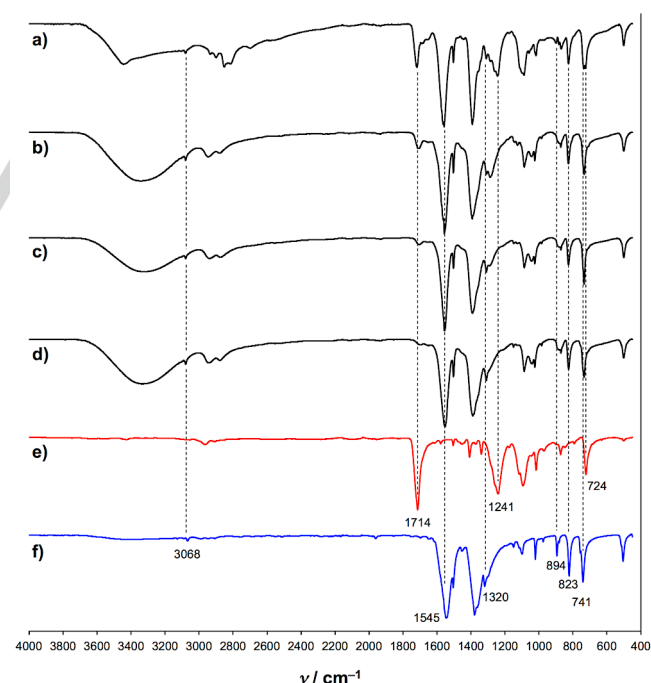


Figure 1. Optimization of reaction time using a single 12 mm ball during alkaline hydrolysis of pre-milled **PET** waste on 0.50 g scale monitored by FTIR-ATR. a) 30 min, b) 60 min, c) 120 min, d) 180 min, e) pre-milled **PET** and f) disodium terephthalate. Milling was carried out in a 10 mL stainless steel jar at 30 Hz.

It should be noted that high **PET** conversions and **TPA** yields are typically obtained only under harsh conditions of high temperature and pressure,^[10] so these results represent an exciting new opportunity for quantitative polyester hydrolysis by mechanochemical ball milling. For comparison, a mild **PET** hydrolysis (0.50 g scale) in NaOH aqueous solution ($c = 1 \text{ mol dm}^{-3}$, 5.2 mL, 1.0 eq) at room temperature afforded **TPA** in only 14%, while the same reaction in a closed 10 mL vial at 125 °C led to 85% after 24 hours.

Table 1. Optimization of mechanochemical **PET** hydrolysis.

Entry	Conditions ^[a]	Conversion / %	Yield / % ^[b]
1	0.5 h, 12 mm	51	50
2	1 h, 12 mm	96	93
3	2 h, 12 mm	99	98
4	3 h, 12 mm	99	99
5	1 h, 2x7 mm	13	11
6	1 h, 10 mm	75	71
7	1 h, 15 mm	98	97
8	2 h, 15 mm	>99	99
9	1 h, 12 mm, LiOH·H ₂ O	77	76
10	1 h, 12 mm, KOH	86	85
11	1 h, 10 mm PTFE ball and jar	13	12
12	1 h, 15 mm Si ₃ N ₄ ball and steel jar	79	78
13	1 h, 12 mm, LAG(H ₂ O) ^[c]	79	78
14	1 h, 12 mm, LAG(MeOH) ^[d]	94	93
15	1 h, 12 mm, LAG(MeCN)	97	96
16	1 h, 12 mm, LAG(1,4-dioxane)	58	57
17	2 h, 15 mm, 0.50 g NaCl	>99	99
18	2 h, 15 mm, 0.75 g NaCl	99	99
19	2 h, 15 mm, 1.1 eq base^[e]	>99	99
20	2 h, 15 mm, coloured PET mix. ^[f]	99	98
21	2 h, 15 mm, PET flakes ^[f]	95	95
22	2 h, 15 mm, PET textile ^[f]	96	94
23	2 h, 15mm, plastics mixture ^[g]	99	97
24	2 h, 15mm, plastics mixture ^[h]	57	54
25	2 h, 15mm, plastics mixture, LAG ^[i]	99	97
26	3 h, 2x15 mm, 2.00 g PET ^[f]	>99	99
27	3 h, 2x15 mm, 2.00 g PET textile ^[f]	99	97
28	3 h, 2x20 mm, 4.00 g PET flakes ^[f]	>99	99
29	3 h, 2x20 mm, 4.00 g PET mix. ^[f]	>99	99

[a] 0.50 g **PET**, 1.0 eq NaOH, milling frequency 30 Hz (unless otherwise stated). [b] Isolated **TPA** yield. [c] In LAG experiments, $\eta = 0.25 \text{ mL mg}^{-1}$. [d] 2% of monomethyl terephthalic acid (**MMT**) by-product was detected. [e] NaCl/**PET** weight ratio = 1.5. [f] NaCl/**PET** weight ratio = 1.5 and 1.1 eq base. [g] The plastics mixture consisted of 10 wt% **LDPE**, 10 wt% **PP**, 10 wt% **PS** and 70 wt% **PET**. The amount of NaOH added was 1.1 eq as if the mixture was pure **PET**. [h] The mixture consisted of 20 wt% **LDPE**, 20 wt% **PP**, 20 wt% **PS** and 40 wt% **PET**. [i] 40 wt% **PET**, LAG using water, $\eta = 0.10 \text{ mL mg}^{-1}$.

Other inorganic bases e.g. lithium hydroxide monohydrate (LiOH·H₂O) and potassium hydroxide were tested, but proved ca. 10–20% less efficient (entries 9 and 10). When a substoichiometric amount of NaOH (10 mol%) was used in the presence of stoichiometric water, 11% **PET** conversion and **TPA** yield of 10% were obtained. Next, the effect of milling material on alkaline **PET** depolymerization was assessed. For example, soft milling using polytetrafluoroethylene (PTFE or Teflon) jar and ball (10 mm, 1.7 g) gave a poor 13% **PET** conversion. A combination of stainless steel jar and silicon nitride ball (15 mm, 5.1 g) was much better than PTFE (entries 11 and 12), but still less effective than stainless steel media.

Liquid-assisted grinding (LAG),^[15] a well-established mechanochemical strategy to enhance the solid-state reactivity, did not lead to higher efficiency when water was used as the liquid additive ($\eta = 0.25$, 78% yield). Collins reported that methanolic NaOH solutions hydrolyzed **PET** more rapidly than aqueous did,^[30] so methanol was also tested in LAG. Indeed, substitution of water with methanol improved the conversion by 15% and reached the values of solvent-free reaction,^[31] which can even be slightly surpassed by LAG with acetonitrile (96% yield). Contrary to the alkaline **PET** hydrolysis in ethylene glycol solutions where ethereal solvents accelerated it,^[32] 1,4-dioxane proved less efficient in the solid-state with only 57% **TPA** yield. Despite positive results with methanol and acetonitrile, LAG was not further pursued since the initial intention was to optimize the depolymerization process as green as possible without using any organic solvents.

The levels of **PET** conversion and **TPA** yield were at last optimized by changing the number and size of balls, while keeping the milling time at 60 minutes for comparison (Table 1, Figure S9). As expected, two 7 mm balls (2x1.4 g), as well as a single 10 mm ball (4.0 g), were found to be detrimental to the conversion and yield, whereas one large 15 mm ball (13.6 g) increased the **PET** conversion to 98% and **TPA** yield to 97% after 1 hour. Near quantitative values were then achieved with 15 mm ball after 2 hours of milling. Presumably, an interplay of mechanical and thermal effects during ball milling^[33] could be responsible for more efficient performance of the reaction with increasing ball size.^[34] It was also observed that the appearance of crude reaction mixture changed from powdery to hard gum-like compressed mass as the conversion approached high levels (>95%).^[35] To facilitate the recovery of reaction products, as well as ensure high reproducibility of ball milling, sodium chloride (NaCl) was chosen as an inert and safe additive that keeps the mixture in powder form throughout the reaction.^[36] Additionally, NaCl was favoured since it was already formed during precipitation of **TPA** from alkaline solution by adding HCl(aq). The NaCl/**PET** weight ratios between 1–1.5 were found to be suitable, depending on the scale of **PET** hydrolysis.

Based on ¹H NMR analysis, the purity of isolated **TPA** samples was 89–96%.^[37] Two impurities were found, where the major one was identified as mono(2-hydroxyethyl) terephthalic acid (**MHET**) formed as a result of incomplete polymer hydrolysis and

co-precipitated with **TPA**. The signals at 3.72 and 4.31 ppm, together with the doublet signals around 8.08 ppm, are characteristic for ethylene glycol end-group and aromatic protons in **MHET**.^[13,38] Another set of low intensity aromatic signals from 7.64 to 8.48 ppm can be ascribed to isophthalic acid (**IPA**), an impurity typically found in recycled **TPA**.^[39] The presence of **IPA** is not surprising since it is used as a copolymer to modify the physical properties of **PET** during polymerization process.^[40] This compound was present in all samples in ca. 2%, while the content of **MHET** varied (except for LAG with methanol where 2% of monomethyl terephthalic acid (**MMT**) was also detected). Taking the ethylene CH₂ triplet signal at 4.31 ppm ($J=4.8$ Hz) as the diagnostic one, the relative amount of **MHET** (compared to reaction without the additive) increased by ca. 3x and 5x as the NaCl/**PET** weight ratio went from 0 to 1 and 1.5, respectively (Figure 2a-c). This observation is explained by the dilution effect due to presence of more NaCl additive, resulting in slower rate of alkaline hydrolysis. When milling was prolonged from 2 to 5 hours, the amount of **MHET** dropped as shown by ¹H NMR (Figure 2d). In order to avoid further **MHET** contamination and unnecessary prolongation to several hours of milling, a slight excess of NaOH was used (1.1 eq), thus ensuring quantitative depolymerization to **TPA** monomer with purity $\geq 98\%$ (Figure 2e).

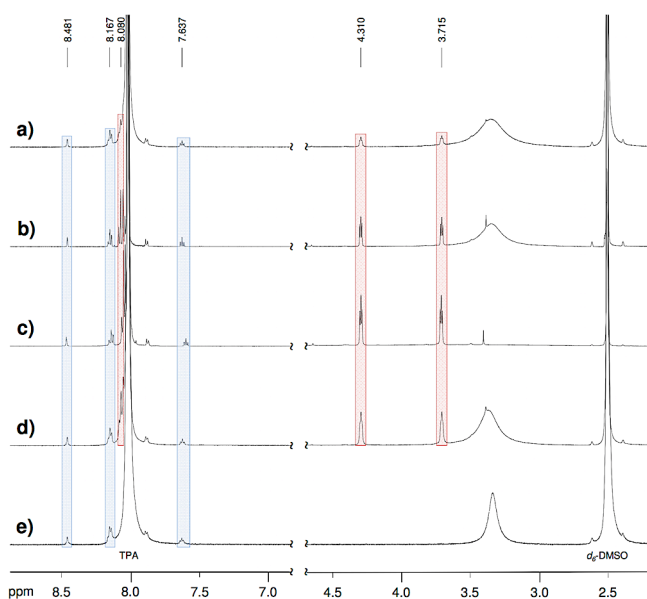


Figure 2. The effect of NaCl additive on the purity of crude **TPA** product monitored by ¹H NMR (*d*₆-DMSO). NaCl/**PET** weight ratios were 0 (a), 1 (b) and 1.5 (c-e). All reactions were carried out with one 15 mm ball and 1.0 eq of NaOH at 30 Hz for 2 h on 0.50 g **PET** scale, except for d) where milling time was 5 hours and e) where 1.1 eq NaOH was used. The signals of **IPA** are labelled in blue and **MHET** in red.

With optimized milling conditions on 0.50 g **PET** scale determined (15 mm ball, 2 hours at 30 Hz, 0.50 g waste **PET**, 0.23 g NaOH (1.1 eq) and 0.75 g NaCl grinding auxiliary), the protocol was found to work equally well for coloured waste **PET** (e.g. green and yellow bottles), but also for a mixture of transparent and coloured plastic mimicking real samples (98% **TPA**). Furthermore, excellent conversion and isolated yield of 95% were observed when **PET** flakes (cut to 0.5–0.8 cm size)

were used instead of pre-milled plastic. In order to verify that the high efficiency of mechanochemical **PET** hydrolysis is not affected by the crystallinity of the substrate, a sample of post-consumer black polyester textile was milled under the optimized conditions. Unlike plastic bottles where the desired crystallinity of **PET** is around 30%,^[41] polyester **PET** fibers used in textile industry have higher degree of crystallinity, typically around 40%.^[42] Gratifyingly, it was found that the polyester textile in the form of pre-cut flakes could also be successfully depolymerized by milling, producing **TPA** in 94% after 2 h on the 0.50 g scale (Table 1, entry 22).

The selectivity of alkaline hydrolysis towards polyester materials was investigated by milling mixtures of different plastics such as low density polyethylene (**LDPE**), polypropylene (**PP**), polystyrene (**PS**) and **PET**. The content of **PET** in mixtures was 40 and 70 wt% (Table S1), while the amount of NaOH was adjusted as if pure **PET** were reacted. NaCl auxiliary was not added in these experiments since **LDPE**, **PP** and **PS**, as plastics stable under hydrolytic conditions, took over the role of inert grinding support. After ball milling for 2 hours, the pre-milled mixture consisting of 10 wt% **LDPE**, 10 wt% **PP**, 10 wt% **PS** and 70 wt% **PET** led to 97% **TPA**, corresponding to 99% **PET** conversion. However, the mixture with lower **PET** content afforded **TPA** in only 54%. To improve the efficiency in this case, LAG using water ($\eta = 0.10 \mu\text{L mg}^{-1}$) was successfully employed, resulting in almost quantitative hydrolysis with 99% **PET** conversion as evidenced by FTIR-ATR analysis (Figure 3 and Table 1, entries 24 and 25). The characteristic **PET** absorption bands at 1714, 1241 and 1096 cm⁻¹ disappeared, whereas the remaining signals could all be assigned to **LDPE**, **PP** and **PS**, demonstrating that solid-state hydrolysis by milling can selectively remove polyester waste from mixtures containing different types of plastic materials.

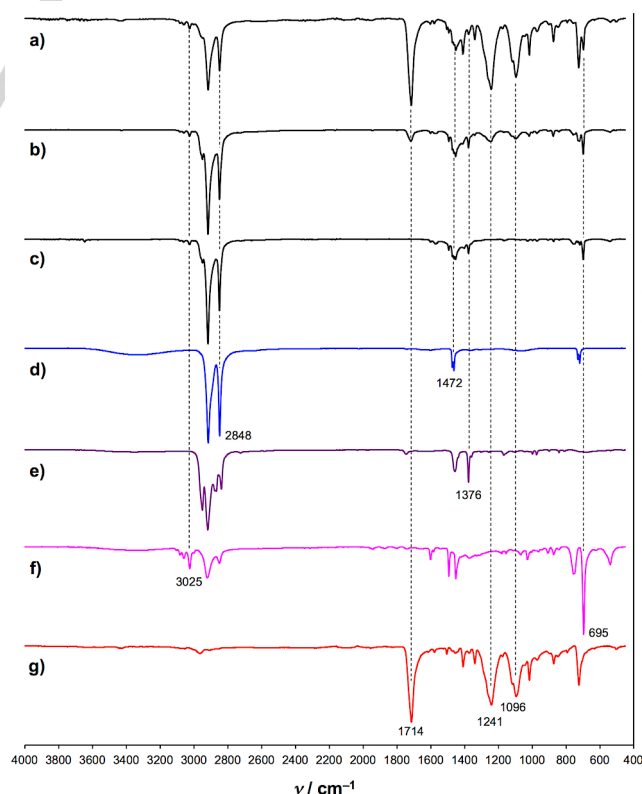


Figure 3. Selective depolymerization of waste **PET** in mixtures with different plastics monitored by FTIR-ATR. a) Initial mixture containing 20 wt% **LDPE**, 20 wt% **PP**, 20 wt% **PS** and 40 wt% **PET**, b) unreacted plastics under solvent-free conditions, c) unreacted plastics after LAG(H_2O), d) **LDPE**, e) **PP**, f) **PS** and g) **PET**.

Similarly to mechanochemical milling, an alternative solvent-free and low-energy method that promotes solid-state chemical transformations, but in the presence of inorganic (e.g. H_2O , NH_3) or organic (e.g. alcohols) vapours, is vapour-assisted aging, also known as vapour digestion or accelerated aging.^[43] To investigate the behaviour of **PET**/NaOH system in humid atmosphere by aging, mixtures of ~100 mg of pre-milled waste **PET** and ~42 mg NaOH (1.0 eq) were briefly homogenized with a spatula and distributed into five vials (Figure S2). The relative humidity (RH) levels in aging chambers were set to 0% (P_2O_5), 8% (sat. $ZnBr_2$), 43% (sat. K_2CO_3), 75% (sat. NaCl) and 100% (H_2O). In this way, the effects of RH, aging time (1, 3, and 7 days), temperature (25, 45 and 60 °C)^[44] and treatment method on waste **PET** depolymerization were studied.

For reactions carried out at 25 °C for 3 days, aging under high RH led to about 65% **PET** conversion and 64% **TPA** yield. Significantly lower turnover was observed for reactions done at 8% and 43% RH. Prolonging the aging time from 3 days to one week raised the conversion to 80% at high RH, while a short one-day aging barely reached 20% under the same conditions (Figure 4a). Elevating the temperature to 45 °C caused the **PET** conversion and **TPA** yield to reach ca. 50% even at low (8%) and 85% at high RH (75% and 100%). In general, higher RH levels and mild heating promoted the solid-state alkaline **PET** hydrolysis (Figure 4b). Most notably, aging in dry atmosphere where RH = 0% led to 1-2% **PET** conversion and did not afford **TPA** regardless of reaction time or temperature (Table S3). Moreover, 1H NMR analysis of **TPA** samples after aging revealed purity $\geq 98\%$ without **MHET** by-product.

Inspection of the unreacted **PET** samples after aging experiments and comparison with the starting pre-milled **PET** by light microscopy revealed moderate changes in particle size, however as the samples aged at higher RH they appeared more translucent and thinner than the ones aged at lower RH (Figures S3–S5). Since aging takes place on the surface of reacting particles, it was expected that treatment of the reaction mixture by short 5-minute milling before aging might improve the overall efficiency, similar to mechanoenzymatic hydrolysis of biopolymers^[28] or catalytic transfer hydrogenation of nitroaromatics^[45] reported earlier. The background reaction in this case resulted in 13% of **TPA**, but significantly changed the **PET** reactivity profile where 66% of **TPA** was isolated even at low 8% RH at 25 °C after 3 days. For higher RH, the conversion and yield >84% were obtained (Figure 4c). Another treatment method included pre-heating of the reaction mixture at 100 °C for one hour. It turned out that pre-heating alone can induce alkaline depolymerization as the extent of the background reaction was found to be around 20%, consequently increasing the hydrolysis efficiency by roughly 15–20% compared to manual mixing (Figure 4c). This finding also underpins a possible contribution of thermal effects during milling with different ball sizes.^[35] Overall, these experiments showed that pre-milling, in combination with aging under conditions of high RH,^[28] could be employed as a strategy to enhance **PET**

reactivity through more efficient homogenization, introduction of structural defects and partial breakage of polymer chains.^[26]

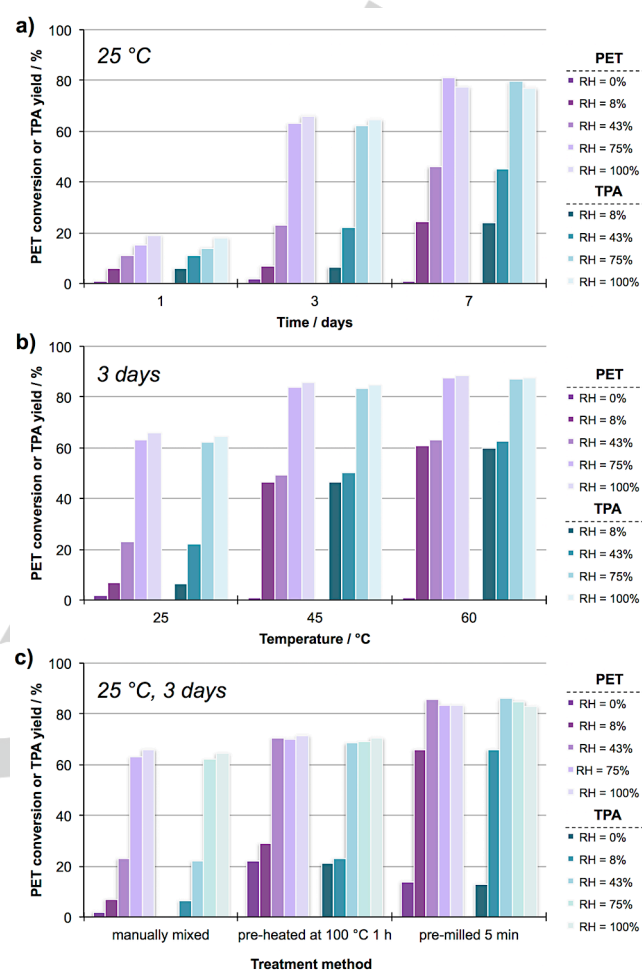


Figure 4. Solid-state hydrolysis of waste **PET** by aging under different relative humidity levels. The effect of a) aging time, b) temperature and c) reaction mixture treatment method on **PET** conversion and **TPA** yield.

It is evident from data in Figure 4 that water vapour content plays an important role in the aging process. In the absence of milling-induced effects (e.g. mass transfer, pulverization, stress, etc.), the reactivity under purely "static" aging conditions appears to be related to properties like hydrogen bonding and nucleophilicity of the liquid phase used to create the desired atmosphere, as suggested by experiments conducted in acetonitrile, 1,4-dioxane, methanol and ethanol vapours. In the case of acetonitrile (polar aprotic solvent) and 1,4-dioxane (nonpolar solvent), vapour-assisted aging at 25 °C for three days resulted in only 1–2% **PET** conversion. Surprisingly, methanol and ethanol vapours induced **PET** hydrolysis at 25 °C even more efficiently than pure water with 93–99% **PET** conversion and **TPA** yield. Similarly to LAG with methanol, the formation of monomethyl terephthalic acid (**MMT**) by-product in ca. 11% was observed.^[46] Likewise, aging in ethanol vapours led to ~3% of monoethyl terephthalic acid (**MET**) in the crude **TPA** according to the 1H NMR analysis. Such behaviour is tentatively explained by greater solvent nucleophilicity of methanol and ethanol against water,^[47] their ability to participate in hydrogen bonding,

as well as deprotonation of alcohol molecules upon contact with NaOH in the reaction mixture. The alkoxide anions formed could act as nucleophiles and assist in cleaving the ester bond in **PET** to afford monomethyl- or monoethyl-ester intermediates. The absorption bands at 1721 and 1104 cm^{-1} in FTIR-ATR spectra (Figure S11) and the signals of methoxy (3.88 ppm) or ethoxy group (1.33 and 4.34 ppm) and the corresponding aromatic protons (8.06 ppm) in the NMR spectra of crude **TPA** after vapour digestion using alcohols are clear indication of such transesterification reactions (Figures S18 and S19).

Finally, the mechanochemical **PET** hydrolysis was successfully scaled up to 2.00 and 4.00 g, whilst keeping the almost quantitative levels of **PET** conversion and **TPA** yield (Table 1, Entries 26–29). In both cases, milling was performed in three one-hour cycles with cooling pauses to prevent excess heat formation resulting from an increased total ball mass in large volume jars.^[34,48] The reactions took place in 25 and 50 mL stainless steel jars with 1.1 eq NaOH and NaCl/**PET** ratio 1.5. Besides transparent plastic and black polyester textile pieces, green **PET** flakes (0.5–0.8 cm size) as well as a 1:1 mixture of pre-milled green and yellow **PET** were also efficiently depolymerized on 4.00 g scale to produce **TPA** in 99% yield (Figure S7). The described gram-scale procedure proved robust and reliable, affording **TPA** in excellent isolated yields and purity $\geq 98\%$, demonstrating that ball milling has the potential for large scale processing of waste **PET** under solid-state alkaline hydrolytic conditions.

Based on the results shown in Figure 4, a gram-scale aging experiment starting from 4.00 g of the substrate (a mixture of transparent and green waste **PET** and stoichiometric amount of NaOH) was attempted. Pre-milling the mixture for 5 minutes, followed by aging at 75% RH and 45 °C for 3 days resulted in 95% **PET** conversion and isolation of **TPA** in high 94% yield (3.24 g) and $\geq 98\%$ purity (Figure S8).

Conclusion

Mechanochemical ball milling has been demonstrated for the first time as a superior method to achieve clean and efficient depolymerization of waste **PET** to **TPA** monomer in near quantitative yields. While this protocol uses a strong base such as sodium hydroxide, the possibility to reduce its amount to (near) stoichiometric, offered by solid-state ball milling, helps diminish its environmental impact. Mechanochemical hydrolysis of **PET** does not depend on the properties of plastic substrate such as crystallinity, which is still a major obstacle for other eco-friendly methods, e.g. enzymatic hydrolysis in aqueous solutions. In addition to ball milling, aging in humid environment or solvent vapours, as an alternative solid-state and low-energy approach to **PET** depolymerization, has also been investigated and showed high performance in both **PET** conversion and isolated **TPA** yield. A systematic study of the effect of relative humidity on the conversion of waste **PET** into **TPA** during aging has revealed an optimum performance under moist atmosphere in combination with mild heating and short pre-milling treatment of the reaction mixture. On the other hand, room temperature-aging in alcohol vapours was even more productive with near-quantitative conversions, but at the expense of **TPA** purity as monoester derivatives were also formed. The depolymerization reactions by ball milling and aging have also been carried out on

gram-scale to verify that this approach is not limited to only milligram-scale experiments. The possibility to isolate **TPA** from post-consumer **PET** in almost quantitative yields and high purity by solid-state ball milling or aging in humid environment, represents an important step forward in the implementation of **PET** production paradigm which is based on starting directly from **TPA** instead of prevailing conventional precursors such as bis(2-hydroxyethyl) terephthalate or dimethyl terephthalate.^[6] On the other hand, considering the vast amount of waste **PET** which is almost an inexhaustible source of **TPA** circulating in the environment, the herein presented mechanochemical alkaline **PET** hydrolysis could potentially form a basis for the development of more efficient, organic solvent- and catalyst-free sustainable production of this industrially important chemical.^[49]

Experimental Section

Materials

All chemicals were purchased from commercial sources (Sigma Aldrich, Kemika and T.T.T.) and were used as received. Post-consumer waste polyethylene terephthalate (**PET**) soft drink or water bottles (transparent, green and yellow) were washed with detergent, warm water and dried, cut into flakes ca. 0.5–0.8 cm size and milled in a 50 mL jar (ca. 3 g **PET**) using a 20 mm stainless steel ball for 2 hours (in 30-minute cycles) until powder was obtained. Post-consumer black tracksuit pants (kindly provided by Mr. Dominik Štrukil) made of 100% **PET** polyester were cut in smaller pieces (ca. 0.5–0.8 cm size) and used as such. **LDPE** (from transparent shopping bags), **PP** (from food container) and **PS** (from coffee cups) were cut into flakes and pre-milled with **PET** to obtain mixtures of different plastics.

Mechanochemical hydrolysis of waste **PET**

A mixture of 0.50 g of waste **PET** and stoichiometric amount (0.21 g, 1.0 eq) or slight excess NaOH (0.23 g, 1.1 eq) was ball-milled in a 10 mL jar using stainless steel balls (2x7 mm, 10 mm, 12 mm or 15 mm) for the respective time under conditions in Table 1. The crude mixture was suspended in 20 mL of distilled water and the unreacted **PET** removed by filtration, followed by drying at 70 °C overnight. The filtrate containing the disodium terephthalate salt was acidified with diluted HCl ($c = 1 \text{ mol dm}^{-3}$) until $\text{pH} \approx 1\text{--}2$ resulting in precipitation of terephthalic acid (**TPA**), which was collected by filtration, washed with distilled water and dried at 70 °C overnight.

In scale-up experiments, a mixture of waste **PET** (pre-milled powder or flakes) and NaOH (1.1 eq) at NaCl/**PET** weight ratio = 1.5 was ball-milled in 25 mL jar using 2x15 mm stainless steel balls (2.00 g scale) or in 50 mL jar with 2x20 mm balls (4.00 g scale) for 3 hours, carried out in three 1-hour cycles with intermittent cooling to prevent excess heat formation. The crude mixture was suspended in distilled water (80 or 160 mL) and worked up as described above.

PET hydrolysis in the presence of different plastics: A 0.50 g sample of the plastics mixture was ball-milled with NaOH (0.23 g) using a 15 mm stainless steel ball for 2 hours. In the case of LAG, water was used as the grinding liquid at $\eta = 0.10 \text{ } \mu\text{L mg}^{-1}$.

The crude mixture was suspended in 20 mL of distilled water, unreacted plastics removed by filtration and the filtrate acidified. The precipitated **TPA** was collected by filtration, washed and dried at 70 °C overnight.

Waste PET hydrolysis by vapour-assisted aging

Manually mixed samples: Mixtures of waste **PET** (ca. 100–106 mg) and sodium hydroxide (ca. 41–45 mg, 1.0 eq) were briefly manually homogenized with a spatula and distributed into five vials. The vials were placed in aging chambers with the relative humidity levels set to 0% (P₂O₅), 8% (sat. ZnBr₂), 43% (sat. K₂CO₃), 75% (sat. NaCl) and 100% (dist. H₂O). For aging in organic vapours, dry acetonitrile, 1,4-dioxane, methanol or ethanol were used. After aging at 25, 45 or 60 °C for the respective reaction time, each reaction mixture was suspended in 4 mL of distilled water and worked up as described above.

Pre-milled samples: A mixture of waste **PET** (600 mg) and NaOH (250 mg) was milled with a 12 mm ball for 5 minutes. Aliquots of the pre-milled mixture (140–145 mg) were then distributed into five vials and left in aging chambers in a controlled humid atmosphere at 25 °C for 3 days. Each reaction mixture was worked up as described above.

Pre-heated samples: Mixtures of waste **PET** (ca. 100–106 mg) and sodium hydroxide (ca. 41–45 mg, 1.0 eq) were briefly manually homogenized with a spatula and left in an oven at 100 °C for 1 hour, followed by placing the reaction vials in aging chambers at 25 °C for 3 days. Each reaction mixture was worked up as described above.

In the scale-up aging experiment, a mixture of transparent and green waste **PET** (4.00 g) and NaOH (1.0 eq), which was pre-milled for 5 minutes, was placed in a plastic air-tight container made of polypropylene with saturated sodium chloride aqueous solution (RH = 75%) and left at 45 °C for 3 days. The crude mixture was suspended in 160 mL of distilled water and worked up as described above.

Terephthalic acid (**TPA**): ¹H NMR (600 MHz, [D₆]DMSO, 25°C, TMS): δ=13.28 (brs, 2H; COOH), 8.04 ppm (s, 4H; Ar-H). ¹³C NMR (150 MHz, [D₆]DMSO, 25°C, TMS): δ=166.7 (COOH), 134.5 (C), 129.5 ppm (CH). IR (ATR): ν= 3104, 3064, 2816, 2657, 2539, 1674, 1574, 1509, 1423, 1280, 1136, 1112, 927, 879, 780, 726, 525 cm⁻¹.

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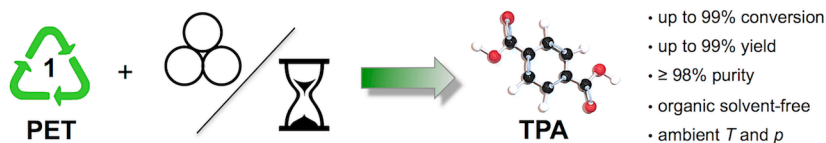
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Entry for the Table of Contents



The New Equation for PET Depolymerization: An efficient and clean solid-state alkaline depolymerization of waste PET into terephthalic acid (TPA) under organic solvent-free conditions has been developed. By employing mechanochemical ball milling, aging or their combination, near-quantitative PET conversion and TPA yields are achieved at ambient temperature and pressure which is hardly attainable by traditional solution-based methods.