

PURIFICATION OF RECYCLED TEREPHTHALIC ACID AND SYNTHESIS OF POLYETHYLENE TEREPHTHALATE

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Abstract: *Plastic waste pollution presents one of the major environmental challenges in the 21. Century. Post-consumer textile waste is especially problematic since it is very hard to recycle mechanically due to the high content of various impurities. Therefore routes for chemical recycling needs to be developed. Depolymerization of polyethylene terephthalate (PET) usually yields terephthalic acid (TA) containing impurities that can negatively influence polymerization; thus purification of TA is an essential step in the chemical recycling of PET. In the present study, the purification method for recycled TA (rTA) was developed. Purification method involves dissolving rTA in sodium hydroxide solution, activated charcoal treatment, precipitation and recrystallization in dimethylacetamide (DMAC). The purity of rTA and purified rTA (prTA) was assessed by determining optical density at 340 nm (OD_{340}) of TA solution using UV-VIS spectroscopy. After the purification the OD_{340} decreased from 17.764 to 0.170, indicating significant improvement in purity of TA. PET from both rTA and prTA was synthesized in a custom-made 2.5 L stainless steel reactor and characterized using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). PET synthesized from rTA exhibited a low melting point (235 °C), indicating low molecular weight. FT-IR analysis revealed that unreacted TA was still present in the polymer. PET synthesized from prTA exhibited a significantly higher melting point (253 °C), indicating higher molecular weight compared to PET synthesized from rTA.*

Key words: chemical recycling, terephthalic acid, polyethylene terephthalate, purification, synthesis

1 INTRODUCTION

PET is a thermoplastic polyester that offers many good properties, such as high strength, high toughness, high transparency, and good barrier properties. Due to these properties, it is mostly used for the production of plastic bottles and textile fibers (Sinha, Patel and Patel, 2010). Production of PET is steadily increasing from 14 million tons in the late 1990s to 60 million tons in 2011 (Geyer, Lorenz and Kandelbauer, 2016). With the increased production also the PET waste increased, accounting for around 8 % of world solid waste, therefore it is necessary to develop PET recycling technologies in order to meet the principles of the circular economy (Atta *et al.*, 2006). The methods for PET recycling are primary recycling, mechanical or secondary recycling, chemical or tertiary recycling, and energy recovery or quaternary recycling. Although primary and secondary recycling is preferable, it is not possible to recycle all PET waste in this manner. Post-consumer waste is especially problematic since it is often highly contaminated and therefore difficult to recycle mechanically. There are many PET chemical recycling technologies developed, that can be divided into solvolysis and pyrolysis procedures. Chemical recycling can yield different chemicals such as monomers, petroleum liquids, and gases, depending on the used method. Hydrolysis is a commonly used method for depolymerization of PET that yields TA and ethylene glycol (EG) that can be again polymerized. After the hydrolysis, the obtained TA usually still contains impurities that need to be removed before the polymerization of PET (Al-Sabagh *et al.*, 2016). Liu used activated carbon treatment to increase the purity of TA recovered from alkali reduction wastewater (Liu *et al.*, 2010). Wu *et al.* purified TA recovered from alkali reduction wastewater by recrystallization using DMAC (Wu *et al.*, 2011).

The purity requirements of TA for polymerization of PET and methods for determination of purity are presented in ASTM D7976 standard. Another method for determining the suitability of TA for PET synthesis is also commonly cited in the literature. In this method, optical density at 340 nm (OD_{340}) or transmittance at 340 nm of a solution of TA is measured by UV-VIS spectroscopy (Ohkashi, Inary and Zaima, 1997). In the present study, the TA obtained by alkali hydrolysis was purified, the purity was assessed by UV-VIS spectroscopy and PET was synthesized and characterized both from unpurified and purified TA.

2 MATERIALS

rTA obtained from textile PET by alkali hydrolysis was provided by the University of Maribor. EG (purity of 99.5 %) was a product of Carlo Erba, germanium (IV) oxide (purity of 99.99 %) was a product of Sigma Aldrich, triphenyl phosphate (purity of 99 %) was a product of Sigma Aldrich, acetic acid (purity of 99.5 %) was a product of Sigma Aldrich, sodium hydroxide (purity of 99.4 %) was a product of Fisher Chemical, potassium hydroxide (purity of 85 %) was a product of Acros Organics, DMAC (99 %) was a product of Sigma Aldrich, acetone (purity of 99.8 %) was a product of Carlo Erba, activated charcoal was a product of Sigma Aldrich.

3 CHARACTERIZATION

3.1 UV-VIS spectroscopy

The OD_{340} was determined according to the procedure described in literature (Ohkashi, Inary and Zaima, 1997). The sample was prepared by dissolving 0.32 g of TA in 4 ml aqueous solution of 2N potassium hydroxide. The absorbance of the solution was measured on UV-VIS spectrometer (Perkin Elmer Lambda Bio 20). The samples were measured from 400 nm to 300 nm, with 1 nm resolution and 240 nm/min scan speed. The absorbance was measured by the use of water as a control in 10 mm cell. The measured absorbance at 340 nm (A_{340}) was normalized to the standard 50 mm path length to get OD_{340} .

3.2 Thermogravimetric analysis

Thermal decomposition was measured using Perkin Elmer TGA 4000 thermogravimetric analyzer. Samples were heated from 40 °C to 600 °C in a nitrogen atmosphere (20 ml/min) and from 600 °C to 900 °C in an oxygen atmosphere (20 ml/min). The heating rate was 10 °C/min.

3.3 Differential scanning calorimetry

Thermal properties were determined by Mettler Toledo DSC 2 calorimeter. Samples were measured from 25 °C to 280 °C, with 10 °C/min heating and cooling rate in a nitrogen atmosphere (20 ml/min). First cooling run and second heating run were evaluated.

3.4 Fourier transform infrared spectroscopy

FTIR spectra were recorded with a Perkin Elmer Spectrum 65 infrared spectrometer using attenuated total reflectance (ATR) technique. Samples were measured from 4000 cm^{-1} to 600 cm^{-1} , with 4 cm^{-1} resolution. The spectra were averaged over 10 scans.

4 PURIFICATION OF TPA

2.3 kg of rTA was dissolved in 19.6 L of an aqueous solution of sodium hydroxide (concentration of 11.4 wt.%) and filtered in order to remove insoluble compounds. 90 g of activated charcoal was added to the filtrate and stirred for around 1 h; afterwards, the activated charcoal was removed by filtration. Acetic acid was added to the filtered solution to precipitate the TA until the pH value of a solution reached approximately 3. The precipitated TA was filtered, washed with water and dried to constant mass (yield was approximately 58 %). The resulting product was recrystallized in several batches by dissolving approximately 20 wt.% of precipitated TA in boiling DMAC. After dissolving the solution was filtered and slowly cooled to around $5\text{ }^{\circ}\text{C}$ to obtain TA crystals. Resulting TA was filtered and washed (cold DMAC, water and acetone) and dried to constant mass (yield of recrystallization was approximately 70 %).

5 SYNTHESIS OF PET

PET was synthesized in custom-made 2,5 L stainless steel reactor. The reactor was equipped with helix agitator, a system of 2 condensers, vacuum pump and a heated valve at the bottom for releasing the polymer. The simplified process scheme of the used reactor is presented in Figure 1. Synthesis of PET was done in four stages: mixing, transesterification, pre-polymerization, melt polycondensation. The molar ratio of TA to EG was 1:1.3. Germanium (IV) oxide was added as a catalyst (0.05 wt.% on TA mass), and triphenyl phosphate (0.08 wt.% on TA mass) was added as a thermal stabilizer to prevent degradation during the synthesis. The purpose of the mixing stage is to dissolve the TA in EG to obtain a homogeneous mixture. During this stage, the reagents were put in the reactor, and the reactor was evacuated with a high vacuum oil rotation pump (absolute pressure of 50 mbar) and filled with nitrogen (5 bar) in order to remove the oxygen from the reaction mixture. This procedure was repeated 3 times. After the purging the reactor was pressurized with nitrogen to approximately 5 bar, heated to $60\text{ }^{\circ}\text{C}$ and stirred at 200 rpm for 1h. After mixing the reaction mixture was heated to $240\text{ }^{\circ}\text{C}$ and water was in-situ distilled under pressure (3 bar – 5 bar) with two condensers. The first condenser was set to $160\text{ }^{\circ}\text{C}$ to condense the EG and the second condenser was cooled with water

(around 20 °C) to condense the water. This stage (transesterification) was finished when the total amount of distilled water reached a plateau (usually around after 3 h – 4 h). In the next step, the reactor was heated up to 260 °C, and the pressure was reduced to 100 mbar in order to remove unreacted EG and stirring speed was reduced to 50 rpm to decrease the shear. This stage (pre-polymerization) lasted for 1 hour. After pre-polymerization, the reactor was heated to 280 °C and pressure was further decreased to 50 mbar. This stage (melt polycondensation) lasted for 3 h. After the polymerization, the PET was released from the reactor through the heated valve and quenched in cold water. Sample synthesized from rTA was designated as PET1 and sample synthesized from prTA as PET2.

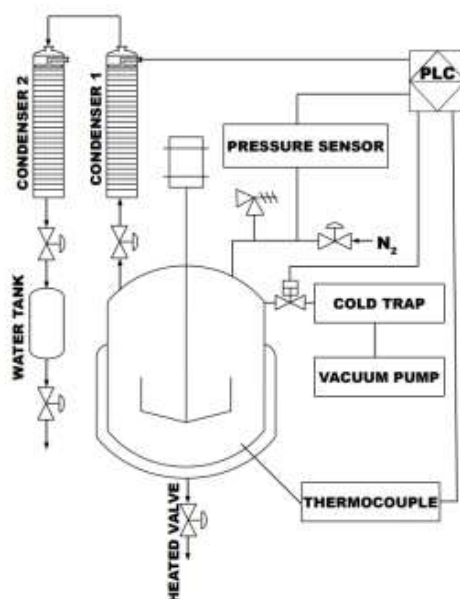


Figure 1: Process scheme of a reactor used for polymerization of PET

6 RESULTS AND DISCUSSION

6. 1 UV-VIS spectroscopy

The OD₃₄₀ results of the samples are summarized in Table 1. The higher is OD₃₄₀ is the lower is the purity of TA. Reported values of OD₃₄₀ for highly pure TA are around 0.100 (Ohkashi, Inary and Zaima, 1997). Unpurified rTA exhibited OD₃₄₀ of 17.764, indicating that rTA contains a very high content of impurities. After the purification the OD₃₄₀ number significantly decreased to 0.170, indicating significant improvement in purity of TA. Although the obtained prTA had higher

values of OD_{340} as values reported for highly pure TA, further improvement of the purity of rTA may be possible with the optimization of the purification process.

Table 1: OD_{340} of samples determined by UV-VIS spectroscopy

Sample	OD_{340} (-)
rTA	17.764
prTA	0.170

6. 2 Differential scanning calorimetry

Thermal properties determined by DSC are summarized in Table 2. DSC thermograms of the second heating run of samples are shown in Figure 2. Both PET polymers exhibited glass transition temperature (T_g) in the same range as reported in the literature (Awaja and Pavel, 2005). PET2 exhibited slightly higher T_g (+ 1.7 °C) and a larger change in specific heat at constant pressure (ΔC_p) (+ 0.079 J/gK). It is well-known phenomena that with higher molecular weight, the T_m increases. PET2 exhibited a significantly higher melting temperature (T_m) (+ 18.8 °C). T_m of the PET2 is in the same range as reported in the literature for high molecular weight PET (Hsu, 1967). Since the T_m of polymer chains, if affected by molecular weight, the melting peak width provides indirect information about the molecular weight distribution. PET1 exhibited a much broader melting peak width (+ 13.0 °C), indicating broader molecular weight distribution. PET1 exhibited higher crystallization temperature (T_c) (+ 3.3 °C) as well as higher crystallization enthalpy (T_c) (+ 1.5 J/g) and melting enthalpy (T_m). This phenomenon was ascribed to easier rearrangement of molecules during the cooling due to lower molecular weight. The result indicated that the purification process of rTA successfully removed impurities that inhibit the polymerization of PET.

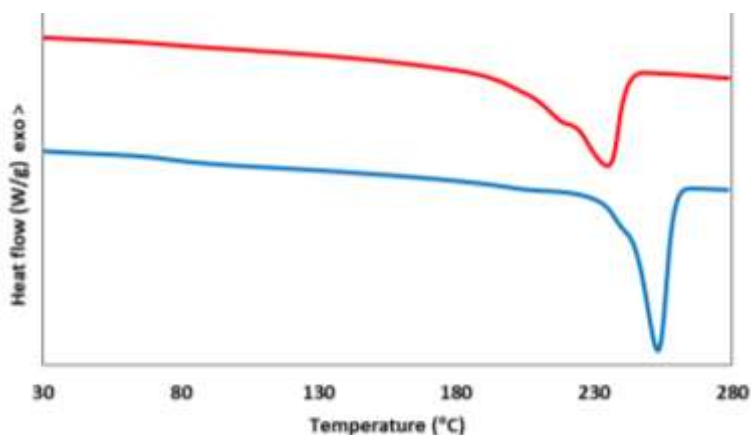


Figure 2: DSC thermograms of the second heating run of samples (PET1 – red curve, PET2 – blue curve)

Table 2: Thermal properties determined by DSC

Sample	T_g (°C)	ΔC_p (J/gK)	T_c (°C)	ΔH_c (J/g)	T_{m2} (°C)	ΔH_m (J/g)	Peak width (°C)
PET1	76.0	0.012	207.2	55.4	234.5	55.4	22.9
PET2	77.7	0.091	203.9	53.9	253.3	54.0	9.9

6. 3 Thermogravimetric analysis

Thermal properties determined by TGA are summarized in Table 3. Both samples exhibited a single decomposition step. PET2 exhibited a slightly higher decomposition temperature (T_d) (+ 4 °C). PET1 exhibited slightly higher char content (+ 2 %) and an ash content of 2 %, ascribed to impurities in rTA.

Table 3: Thermal properties determined by TGA

Sample	T_d (°C)	ΔY (%)	Char (%)	Ash (%)
PET1	443	79	19	2
PET2	447	83	17	/

6. 4 Fourier transform infrared spectroscopy

The FT-IR spectrums of both samples are shown in Figure 3. The carbonyl group (C=O) gives a band at 1713 cm^{-1} , ether bond (C-O) give bands at 1242 cm^{-1} and 1096 cm^{-1} , aromatic C-C bond gives a band at 1506 cm^{-1} , aliphatic C-H bond gives a band at 1341 cm^{-1} , aromatic C-H bonds give bands at 871 cm^{-1} and 722 cm^{-1} . Unreacted TA gives broad absorption band of a hydroxyl group (O-H) at around 2650 cm^{-1} and 2550 cm^{-1} . Both samples exhibited characteristic

absorption bands for PET. PET1 exhibited absorption bands characteristic for TA, indicating that TA was not fully converted during the polymerization.

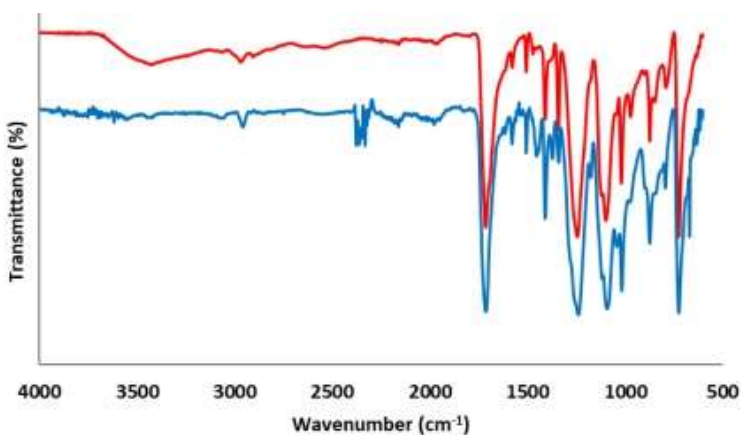


Figure 3: FT-IR spectrum of samples (PET1 – red curve, PET2 – blue curve)

7 CONCLUSION

rTA obtained from alkali hydrolysis of textile PET was successfully purified by using developed procedure. Purification process yielded TA with much higher purity compared to unpurified rTA, but still not in the range of highly pure TA commercially used in PET synthesis. PET was synthesized both from rTA and prTA. PET synthesized from prTA yielded PET with significantly higher melting point compared to PET synthesized from rTA, indicating higher molecular weight. Results showed that it is possible to synthesize high molecular weight PET from rTA, but only when rTA is purified using a suitable process. Developed purification process didn't yield highly pure TA, but with further optimization of the purification process, it may be possible to obtain highly pure TA from rTA.

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