CHEMICAL RECYCLING OF POLYETHYLENE TEREPHTHALATE (PET) WASTE USING SUB- AND SUPERCRITICAL WATER

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The chemical degradation of PET waste in sub- and supercritical water was investigated in this study. The hydrolysis reaction was carried out without stirring in a high alloy refractory stainless steel autoclave at high temperatures (300 and 385°C) and pressures (300 bar) for reaction times in the range 1-60 minutes. The reaction products were analyzed by using UV-Vis and FT-IR spectroscopy, X-ray diffraction, ^{1}H NMR, and ^{13}C NMR. Percent depolymerization of PET and recovery yields of terephthalic acid (TPA) were determined by gravimetry. In all cases depolymerization of PET waste was complete and TPA yields were between 62.9% and 93.5%.
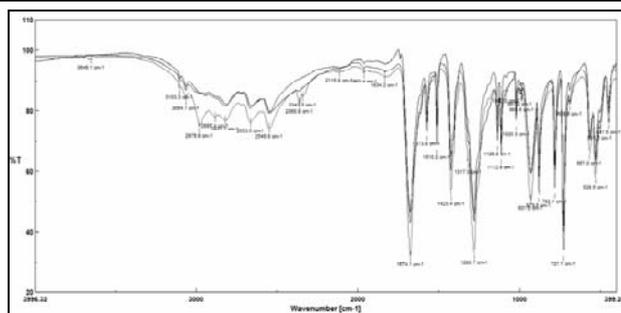
INTRODUCTION

Polyethylene terephthalate (PET) is an important thermoplastic polyester produced either by the esterification of terephthalic acid (TPA) with ethylene glycol (EG) or by trans-esterification of dimethyl terephthalate (DMT) with EG. It has excellent tensile and impact strength, chemical resistance, clarity, color ability, processability and reasonable thermal stability.[1] Polyethylene terephthalate has become one of the most valuable recyclable materials because of the wide range of applications such as manufacture of synthetic fibers, beverage, food and other liquid containers, X-ray films, thermoformed products, etc.[2,3]

The recycling industry of PET waste started as result of environmental pressure to improve waste management, considering that natural decomposition rate is very slow and the consumption is dramatically increasing at global level.

The various methods for recycling of PET waste can be divided into four main groups, namely primary (re-extrusion), secondary (mechanical), tertiary (chemical), and quaternary (involves energy recovery) recycling. Among the recycling methods, chemical recycling is the only one acceptable according to the principles of "sustainable development" because it leads to the formation of raw materials which the polymer is originally obtained.[2] Depending on the depolymerization agent, the chemical recycling of PET waste can be carried out through hydrolysis, glycolysis, methanolysis, aminolysis or ammonolysis.[3] These methods are mainly focused on obtaining monomers such as terephthalic acid (TPA), ethylene glycol (EG), bis(2-hydroxyethyl) terephthalate (BHET) and dimethyl terephthalate

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(DMT). The first two products can be obtained from PET waste by hydrolysis under neutral,[4,5] acidic,[6,7] or alkaline[8,9] conditions, the third product by glycolysis[10,11] and the last by methanolysis.[12,13] Special attention has been paid to glycolysis of PET and applications of the glycolysis products.[14,15] Also, as an environmentally friendly alternative to conventional recycling methods, the enzymatic degradation of PET has been studied.[16,17]

Sub- and supercritical fluids such as water[18,19] or alcohols[20-22] are excellent reaction media for depolymerization of plastics. By using sub- and supercritical fluids which acts both as reactant and as solvent, decomposition of polymers into their monomers occurs rapidly and selectively without catalysts.[23]

In this paper, the neutral hydrolysis of PET waste was studied in sub- (300°C, 300 bar) and supercritical (385°C, 300 bar) conditions without catalysts in order to obtain terephthalic acid. In order to investigate the influence of reaction time on the hydrothermal depolymerization of PET waste, the experiments were carried out at different reaction times in the range 1-60 minutes.

EXPERIMENTAL

Colorless post-consumer PET bottles were chosen for hydrolytic depolymerization in neutral conditions. The PET bottles were manually cut into small flakes (1÷3 mm × 1÷3 mm), then washed and dried. The hydrolysis reaction was carried out without stirring in a high alloy refractory stainless steel (12NiCr 250) batch-type autoclave reactor with inner volume of 27 mL.

PET waste decomposition was carried out both in sub- and supercritical conditions at high temperatures (300 and 385°C) and pressures (300 and 1000 bar) for reaction times in the range 1-60 minutes. The working pressure was estimated using the Kennedy diagram[24] by the choice of temperature and the degree of filling. For each experimental test was used the same ratio PET:H$_2$O of 1:10 (w/v). In each case, the time required for the autoclaves to reach the required temperature has been set at 1 hour, and then maintained at this temperature for the desired reaction time. After the desired reaction time, the reactor was left to cooling at room temperature until the next day when it was opened and the reaction product was collected.

The post-reaction mixture was treated with sodium hydroxide in order to form sodium salt of terephthalic acid (water soluble) and then was filtered to separate unreacted PET.

The filtrate was acidified with concentrated HCl in order to precipitate TPA. The white precipitate of TPA was filtered, washed with double-distilled water, dried and weighed. The recovery yield of TPA was calculated according to the following formula:

$$\eta_{TPA}\ (\%) = W_{TPA}^{exp} / W_{TPA}^{t} \times 100 \qquad (1)$$

where W_{TPA}^{exp} is the weight of TPA obtained experimentally and W_{TPA}^{t} is the theoretical weight of TPA that could be obtained for complete depolymerization of PET.

The reaction products were analyzed by using UV-Vis spectroscopy (Jasco V-530), FT-IR spectroscopy (VERTEX 70, Bruker) and X-ray diffraction (X'Pert PRO MPD, PANalytical). Also, for verification of chemical structure of the final product, ^{13}C-NMR and ^{1}H-NMR spectra were recorded on a Bruker Avance DRX 400 device with the operating frequencies of 400.13 (for ^{1}H) and 100.61 (for ^{13}C) by using as solvents CDCl$_3$ for ^{13}C-NMR and DMSO-d$_6$ for ^{1}H-NMR. The results were compared with those obtained for authentic TPA.

RESULTS AND DISCUSSION

Waste PET was depolymerized with excess water in absence of catalysts in sub- and supercritical conditions. From a theoretical perspective, if PET degradation is complete, the reaction products consist of terephthalic acid (TPA) as the main product, ethylene glycol (EG) and water. The reaction pathway of TPA formation is shown in Fig. 1. In the case of incomplete degradation of PET the liquid phase is composed mainly of water, ethylene glycol and diethylene glycol, and the solid phase consist mainly of unreacted PET, oligomers and terephthalic acid.[25] Also, due to the drastic reaction conditions, it is possible the formation of other secondary products such as benzoic acid, 1,4-dioxane, acetaldehyde and crotonic acid.[23]

In this work we focus mainly on the study of solid fraction of post-reaction mixture and on the high-yield recovery of terephthalic acid. In all experimental tests performed in this work (Table 1), degradation of PET waste was achieved completely. The solid reaction product appears as light yellow crystals in subcritical conditions (Fig. 2) and light brown crystals in supercritical conditions (Fig. 3). Changing of crystals coloration toward brown in supercritical region could be due to the formation of some secondary products which are adsorbed on the TPA crystals.

The amounts of residual PET and TPA obtained after purification were determined gravimetrically. However, it was difficult to measure accurately the amounts of solid products obtained in each case, because of inevitable weight losses during the product processing. The influences of temperature and reaction time on the TPA yield are shown in Table 1. Higher TPA yields (>91%) were obtained at 300°C. Similar results have been reported by Sato *et al.*[18] where at 300°C all PET dissolved in water and TPA yield was 90%.
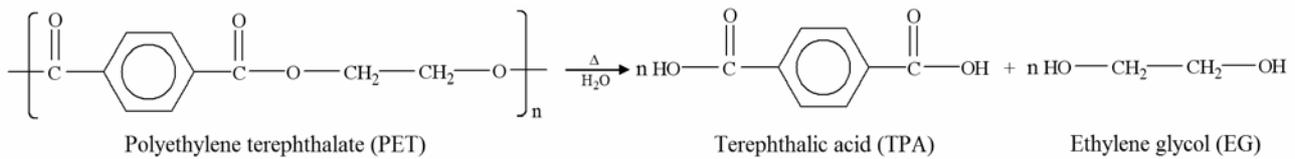
Fig. 1 – Hydrolytic depolymerization reaction of PET.

Table 1

Experimental data for PET depolymerization in sub- and supercritical conditions

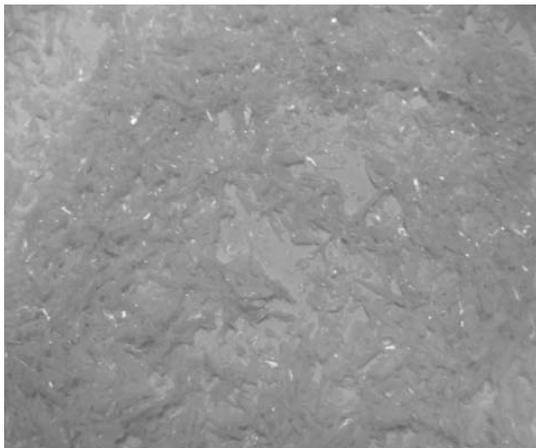| No	T [°C]	p [bar]	t [min]	w_{PET} [g]	$W_{TPA\ teoretic}$ [g]	$W_{TPA\ exp.}$ [g]	η_{TPA} [%]
1	300	300	60	2.022	1.748	1.599	91.44
2	300	300	30	2.025	1.750	1.599	91.36
3	300	300	15	2.022	1.748	1.624	92.92
4	300	300	1	2.023	1.749	1.637	93.46
5	385	300	60	1.532	1.327	0.833	62.86
6	385	300	30	1.536	1.328	1.057	79.59
7	385	300	15	1.531	1.324	1.036	78.27
8	385	300	1	1.532	1.325	1.122	84.72

Fig. 2 – Hydrolysis solid product (300°C) before purification.

Fig. 3 – Hydrolysis solid product (385°C) before purification.

It is noted that increasing the reaction time both at 300°C and 385°C, the recovery yield of terephthalic acid decreases. Although, in each case, the PET depolymerization was complete, the decrease of the recovery yield of TPA can be attributed to the formation of secondary products resulting both from the decomposition of terephthalic acid and ethylene glycol which can be catalyzed by the formed TPA.

Compared with neutral hydrolysis of PET at autogenious pressure and high temperatures (250°C)[5] where the time required to complete depolymerization of PET is very long (> 2 h), the method proposed in this study is convenient in reducing the reaction time without the use of a catalyst for complete depolymerization of PET and high recovery yields of TPA.

In order to characterize the liquid fraction of post-reaction mixture, UV-Vis spectra were recorded (Fig. 4). Although, the liquid fraction should contain mainly water and ethylene glycol which do not absorb in UV, in the spectra of all samples two absorption bands were found. These can be assigned to some byproducts formed during the depolymerization reaction. λ_{max} values indicates the presence of some aromatic ring compounds bearing carboxyl substituents. The composition of the liquid fraction and the possibilities of leading the hydrolysis process of PET waste in order to reduce the formation of byproducts will be the subject of further studies.
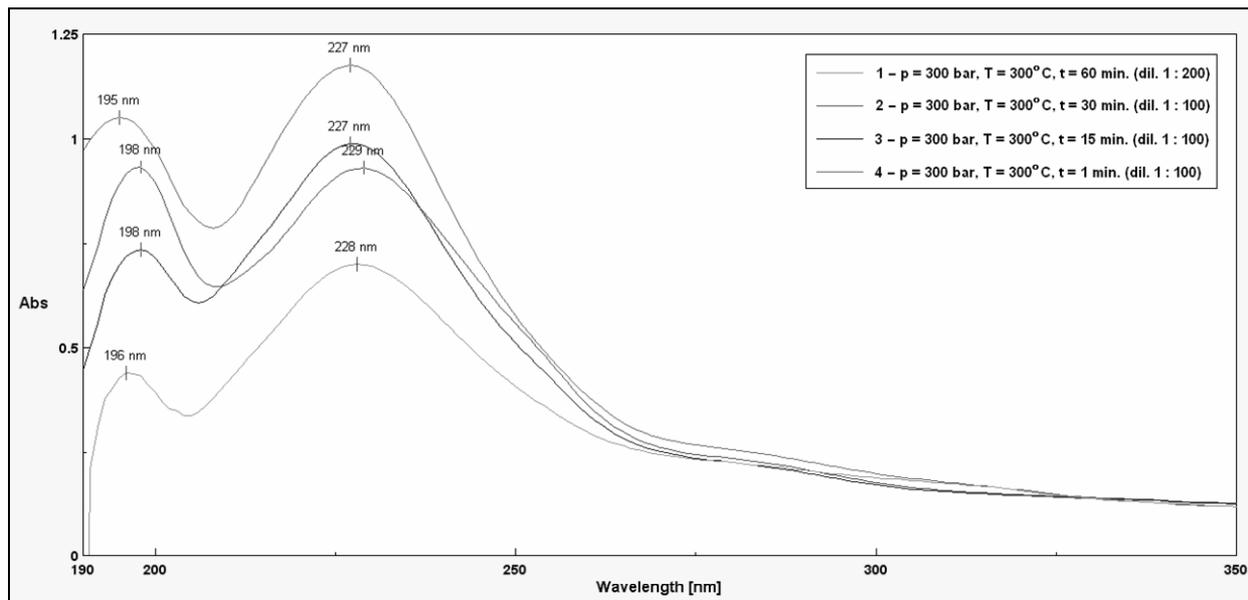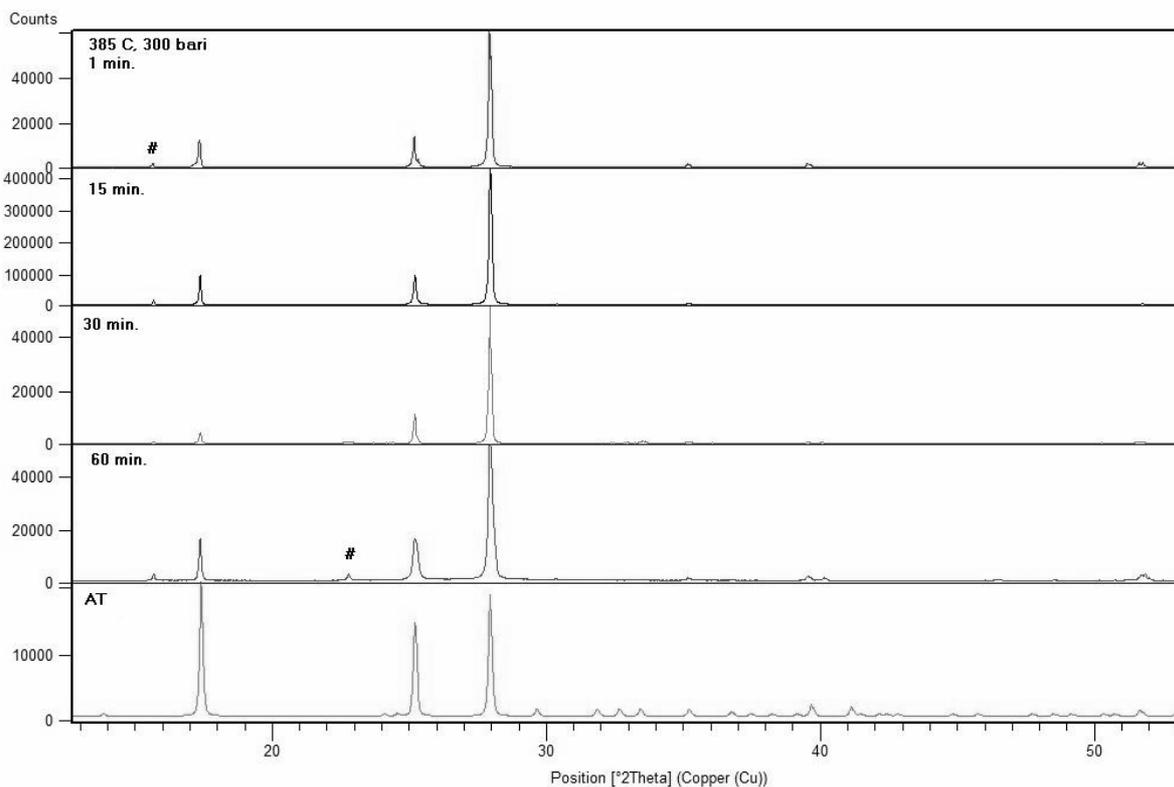
Fig. 4 – UV-Vis spectra of liquid phase.

Fig. 5 – X-ray spectra of standard TPA and PET hydrolysis products in supercritical conditions (before purification).

In order to characterize the solid fraction of post-reaction mixture, X-ray diffraction spectra were recorded both for intermediate products (crystals) and purified final products. In Fig. 5 are shown the X-ray spectra for unpurified products obtained under supercritical conditions. Comparing the X-ray spectra for experimental samples and standard TPA was confirmed the crystalline phase of terephthalic acid for the experimental products. In addition to TPA it was found the presence of some impurities (indicated by #), especially for unpurified products obtained at 300°C. These impurities/byproducts could be benzoic acid, hydroquinone, etc. After purification, the presence of impurities was not observed in the X-ray spectra.
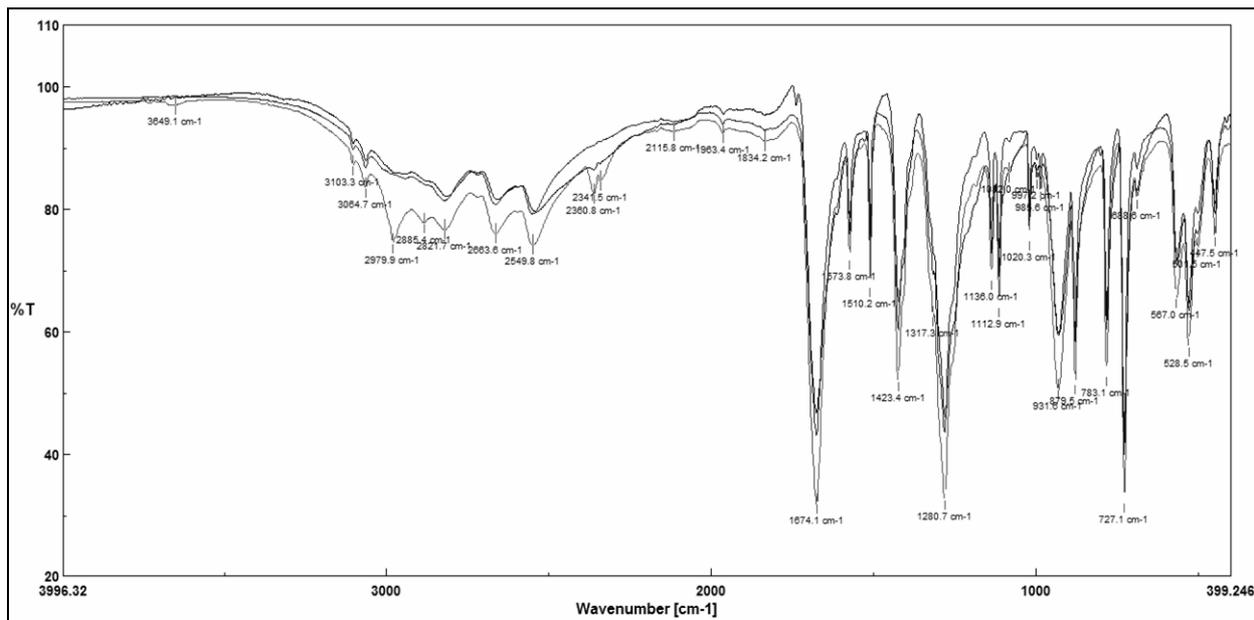
Fig. 6 – FT-IR spectra of standard TPA (−) and final product in subcritical conditions (sample 1 (−) and sample 4 (−)).
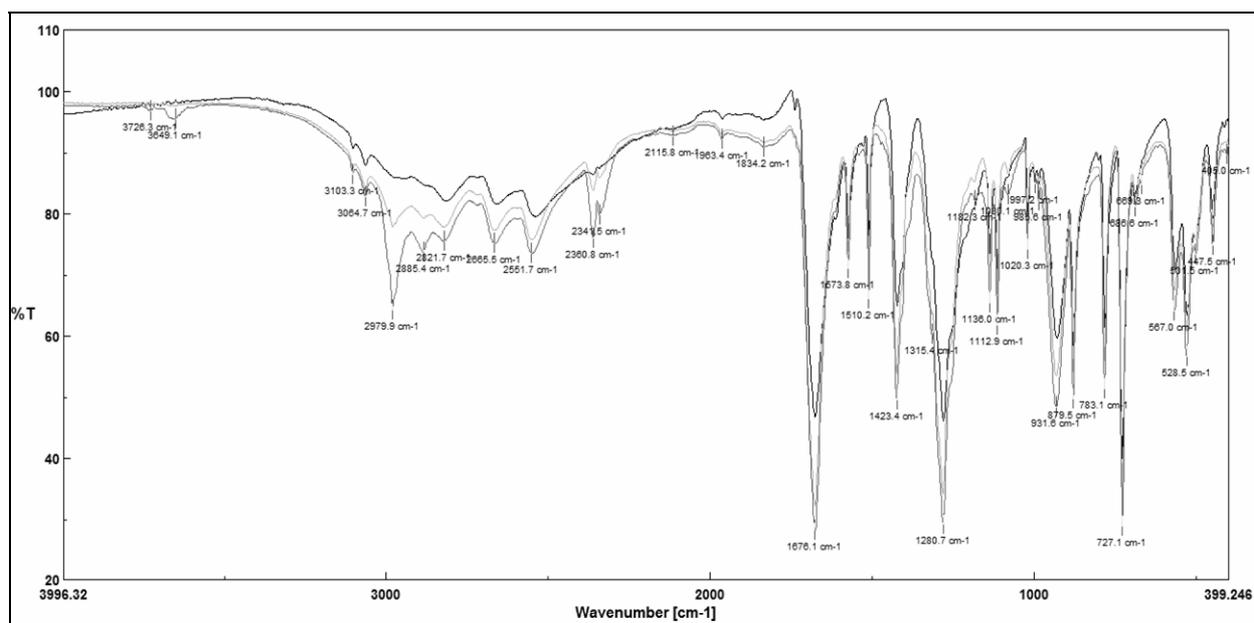

Fig. 7 – FT-IR spectra of standard TPA (−) and final product in subcritical conditions (sample 5 (−) and sample 8 (−)).

The FT-IR spectra of purified final products obtained in sub- (Fig. 6) and supercritical (Fig. 7) conditions and standard TPA were recorded and found to be similar, experimental products present the same characteristic bands as standard TPA. The characteristic bands specific to aromatic dicarboxylic acids are 3065 cm^{-1} (ν_{C-H} arom), 1676 cm^{-1} ($\nu_{C=O}$), 1280 cm^{-1} (ν_{C-O}) and the vibrations specific to 1,4-disubstituted benzene ring are 447-529, 1136, 1020 cm^{-1}.

The ^{13}C-NMR and ^{1}H-NMR for purified final product vs. standard TPA are shown in Fig. 8 and Fig. 9. The ^{13}C-NMR spectra for sample and standard TPA are identical: δ129.4 (unsubstituted C of the aromatic ring), 134.4 (C of the aromatic ring to where are attached the carboxyl groups), 166.6 (COOH). The ^{1}H-NMR spectra prove that the experimental product is terephthalic acid. Besides the signals corresponding to terephthalic acid: δ8.04 (s, 4H, *aromatic* H), 13.3 (s, 2H, COOH), in spectra also appear shifts in the range 7.8-8.4, indicating the presence of some aromatic impurities both in standard and experimental products (<10%).

Fig. 8 – ^{13}C-NMR spectra of standard TPA and final product (sample 6).

Fig. 9 – ^{1}H-NMR spectra of standard TPA and final product (sample 6).

CONCLUSIONS

In each case PET depolymerization was carried out completely and TPA was recovered from the post-reaction mixture in the range 62.86-93.46%. The best results were obtained for 1 minute of reaction both in subcritical (η_{TPA} =93.46%) and supercritical conditions (η_{TPA} =84.72%).

Although the degradation of PET was carried out completely, the decrease of the TPA recovery yields with increasing reaction time can be attributed to the formation of some secondary products resulting both from the decomposition of terephthalic acid and ethylene glycol which can be catalyzed by the formed TPA.

The recorded FT-IR, X-ray and NMR spectra confirmed that the solid product obtained during neutral hydrolysis in sub- and supercritical conditions was terephthalic acid.

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