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Recycling of waste poly(ethylene terephthalate) with castor oil using microwave heating

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ABSTRACT

The chemical recycling of waste poly(ethylene terephthalate) (PET) using castor oil (CO) as a reagent is reported. CO presents a renewable alternative to petrochemical based reagents, e.g. glycols, and enables also substantial modification of final physico-chemical properties of a received product. Advantageously, microwave irradiation was used to accelerate the depolymerization of PET. A composition of obtained product was strongly influenced by the reaction temperature. When the decomposition of PET was performed at temperature higher than 240 °C, then a significant extent of side products based on PET oligomers and transesterified CO was observed due to dehydration and hydrolysis of CO. Contrary to that, PET decomposition took place at slow rate below 230 °C and the optimal reaction temperature range did not contain any high molecular weight PET oligomers. MALDI-TOF mass spectrometry enabled to identify the structures included in the obtained polyol product. The maximum number of six repeating monomeric unit of PET was found in the product, which confirmed practically the complete depolymerization of PET chain and good reactivity of the acylester hydroxyl groups of CO.

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1. Introduction

A global production of poly(ethylene terephthalate) (PET) is ca 26 million tons/year. According to PETcore, European post-sorting PET collection reached 1.59 million tons in 2011, an increase of 140 kilotons (9.4%) on 2010 [1]. Therefore, the challenge lies in finding a suitable way of reusing or recycling this waste.

The PET waste due to the presence of ester groups can be a subject of chemical recycling. During the last years, several methods of chemical recycling of PET have been tested, such as hydrolysis [2], glycolysis [3–7], methanolysis [8,9], aminolysis [10–12], etc. Generally, long reaction time and high energy demand are the common features of the above mentioned methods preclusive their spreading into the practice.

Microwave reactors could be a new way how to overcome the problem of high energy demanding recycling processes. Microwave (or dielectric) heating involves the conversion of electromagnetic energy into heat. Contrary to convective heating with steam and hot-air, or even radiation heating in general, the microwave heating generates heat directly inside the exposed material. The conversion

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of electric energy to heat results from the dielectric losses of the electric non-conducting material, which is usually also a poor thermal conductor [13]. The origin of the microwave heating lies in the ability of the electric field to polarize the charges in the material and the inability of this polarization to follow extremely rapid reversals of the changing electric field. The field interaction with the molecular dipoles and charged ions causes rapid rotation of these molecules or ions. Friction of this motion leads to a heat evolution and increased temperature in the material [14,15].

The first mention about the use of microwave heating for decomposition of PET appeared in the papers of Kržan [16,17]. He performed PET glycolysis with ethylene glycol, propylene glycol and zinc acetate (ZnAc) catalyst, in the microwave reactor at the constant power of 500 W. A complete PET dissolution was observed after 10 min of the reaction. Pingale and Shukla mentioned substantially reaction time reduction when a based catalyzed glycolysis of PET was performed in the microwave reactor. The final product was obtained after 35 min, whereas in a conventionally heated reactor the glycolysis was complete after 16 h [18]. Nikje and Nazari published a hydro-glycolysis of PET in microwave field, during which the main products, terephthalic acid and ethylene glycol, were obtained within less than 1 h [19,20]. A fast PET glycolysis with diethylene glycol in a pressure microwave reactor leading to the complete PET dissolution after 2 and 5 min at the







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constant power of 150 W and 100 W, respectively, was also reported [21]. A PET total hydrolysis to monomers (terephthalic acid and ethylene glycol) in high-pressure microwave reactor at 180 °C within 30 min was described by Siddiqui et al. [22]. Similarly, Liu et al. reported complete hydrolysis of PET within 120 min at the pressure of 20 bar (ca 204 °C) [23]. A microwave assisted aminolysis of PET performed at high temperature (260 °C) led to the PET dissolution after 5 min even without any catalyst addition [24]. Shukla and co-workers used a relatively high microwave oven power (700 W) and low temperature (170 °C) for the microwave assisted aminolysis of PET [12,25].

Recently in the field of polymer chemistry, much effort has been spent on substitution of petrol-based raw materials for naturalbased renewable ones, such as natural oils. For example, natural oils and their derivates bearing active functional hydroxyl groups, called oleochemical or oleic polyols, have been successfully applied as raw materials in polyurethane (PUR) synthesis [26–28]. Nevertheless, only few mentions have been published about the use of natural oil-based chemicals for polymer decomposition. Kržan et al. reported the unsuccessful PET decomposition using castor oil (CO) but without mentioning any experimental details about this experiment [17]. In our previous paper, we reported that CO and the fish oil-based polyol are reactive enough in order to be applied as the reagents for PUR decomposition [29]. New types of recycled polyols were obtained and applied for a preparation of new PUR materials [30].

This paper is focused on the decomposition of PET waste by means of CO in a microwave reactor. Our effort was to develop a low-energy demanding and efficient recycling process for PET using microwave heating for faster PET decomposition. At the same time, the use of renewable natural oil-based reagent (CO) was tested in order to modify physico-chemical properties of the obtained polyol product. Influence of the reaction parameters, such as temperature, type and amount of catalyst, as well as reaction time, on the PET decomposition is discussed. The reaction mixture and the obtained products are characterized by SEC, FTIR, titration methods (hydroxyl and acid number), dielectric spectroscopy (DS), TGA and MALDI-TOF MS.

2. Experimental

2.1. Materials

PET waste of clear drink bottles was washed, dried and chopped to pieces ca 5 mm. The melting temperature of the PET flakes determined as the onset temperature of melting endotherm on DSC record was 234 $^\circ$ C.

CO (purum, Aldrich, Germany) with hydroxyl number 162 mg KOH g⁻¹, acid number 0.9 mg KOH g⁻¹ and iodine value 88 g $I_2/100$ g was used as received as a reagent for the PET decomposition. The determination of its fatty acid composition by GC–MS was described in our previous paper (see Ref. [30]). The used CO had the following composition: 99.4% ricinoleic acid, 0.3% oleic acid and 0.2% linoleic acid. Zinc acetate dihydrate (ZnAc, Lachner, Czech Republic), sodium carbonate (Lachner, Czech Republic) and sodium bicarbonate (Lachner, Czech Republic) were used as the catalysts for the PET decomposition.

2.2. Decomposition of PET waste

The decomposition of PET waste was performed in a 3-necked round bottom flask fitted with a stirrer, a reflux and a nitrogen inlet. A commercial multimode microwave oven (Panasonic NN-GD566M, f = 2.45 Hz) operating at four constant (unpulsed) power levels (250 W, 440 W, 660 W and 900 W) rebuilt for laboratory

experiments was used as a microwave reactor. The reagent (CO), the chopped PET flakes and the catalyst were put into the flask and placed into the reactor. The decompositions were performed either at a constant power level or at alternating powers by switching of different power levels during experiment in order to keep a desired temperature. All decompositions were performed under atmospheric pressure. A temperature profile of the reaction mixture during decomposition was measured at regular time intervals using an infrared (IR) thermometer (FLUKE 568, USA) with accuracy \pm 1.0 °C. Before the experiments, the IR thermometer was calibrated according to a procedure described in details in Annex. The dissolution time of PET was visually observed and reported from the beginning of heating until no solid material remained in the reaction mixture. After the reaction, the product was cooled down to room temperature and filtered under vacuum to remove solid residues. All performed decompositions were repeated at least three times in order to exclude experimental errors and to determine reproducibility of the experiments.

For comparison, several experiments were also conducted in a conventionally heated reactor at constant temperature and at atmospheric pressure. In this case, the flask containing the reaction mixture was placed into a melted salt bath pre-heated to required temperature. All other operations were the same as those for the microwave reactor.

2.3. Characterization

Size exclusion chromatography (SEC) was used for evaluation of the progress of PET decomposition. The reaction mixture was sampled at different reaction times and Modular GPC System equipped with a refractive index detector RIDK-102 (Laboratorni pristroje Praha, Czech Republic) and an UV-vis photometric detector LCD 2084 (ECOM, Czech Republic) operated at $\lambda = 254$ nm, and a set of two columns PLgel 10E3 Å and 50 Å, 10 µm particle size, 300 mm \times 7.5 mm (Polymer Laboratories, UK) was used. Chromatographic data were collected and treated using Clarity software (Data-Apex, Czech Republic). Tetrahydrofuran and toluene were used as a mobile phase and a flow marker (retention time of toluene was 18.2 min) at a flow rate of 1 ml min⁻¹, respectively. The elution time corresponding to column void volume was 9.2 min. Polystyrene standards with weight-average molecular weights (Mw) of 500, 1000, 3000 and 10 000 were used for calibration. SEC analyses of pure CO (retention time: 13.3 min) and ethylene glycol (retention time: 16.6 min) were also done and compared with SEC results of the analyzed products.

Hydroxyl number of the prepared products was experimentally determined by acetylating method according to ISO 2554:1974 using a titrator SCHOTT TITRONIC[®] universal (SCHOTT-GERÄTE GmbH, Germany).

Acid number determination of the prepared products was determined according to ASTM D 4662-93 using an titrator SCHOTT TITRONIC[®] universal (SCHOTT-GERÄTE GmbH, Germany).

Infrared (IR) spectra of the prepared products were measured using Spectrum 100 FTIR spectrometer (Perkin–Elmer, USA) equipped with a mercury–cadmium–telluride (MCT) detector. The samples were measured in transmission mode as liquid films between two NaCl glasses. Spectral resolution was 4 cm⁻¹ with 16 scans taken for each spectrum.

Matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF MS). MALDI-TOF mass spectra of the prepared samples were recorded on a Bruker Reflex III (Bruker Daltonik, Bremen, Germany) in the positive ion mode. For ionization, a nitrogen laser (337 nm, 3 ns pulse width, 3 Hz) was used. All spectra were measured in the reflector mode using external calibration. For optimization of the mass spectra, the laser was aimed Download English Version:

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