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Medium chain glycerides of coconut oil for microwave-enhanced conversion of polycarbonate into polyols

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ABSTRACT

In this paper, the medium chain glycerides of coconut oil were used as solvolysis reagents for microwave-enhanced conversion of polycarbonate into recycled polyols. First, triglycerides of coconut oil were transesterified with glycerol to monoglycerides bearing functional hydroxyl groups, which were able to react with carbonate linkages resulting in cleavage of polycarbonate chain. The important accelerating effect of microwave irradiation on kinetics of polycarbonate solvolysis was observed. The developed recycling process produced a mixture of low-molecular weight polyols applicable for synthesis of novel polyurethanes.

1. Introduction

Polycarbonate (PC) waste might be as other thermoplastic wastes re-processed at elevated temperatures by means of physical (mechanical) recycling. However, the negative aspect of this relatively simple way how to re-use PC waste is connected with the unwanted degradation of PC during re-processing resulting from the presence of impurities and contaminants. As the example, siloxane coatings from waste automotive headlamps negatively affected the mechanical properties of the reprocessed PC [1]. Contrary to that, methods of chemical recycling might lead even in certain amount of present impurities to recover raw materials, monomers applicable for manufacture of new polymer materials.

A number of chemical recycling methods for PC waste have been mentioned in the literature. Alkali-catalyzed methanolysis of PC was firstly described by Yakubovich et al. [2]. Hu et al. studied the basic methanolysis of PC in toluene and dioxane [3]. The use of solvent led to significant decrease of reaction time (from 330 min to 70 min) and increase of yield 2,2-bis(4-hydroxyphenyl)propane, commonly called bisphenol A (BPA) up to 96%. Liu et al. also used the addition of organic solvents to accelerate the rate of basic methanolysis and hydrolysis of PC [4]. However, very high excess of solvent and high amount of catalyst (NaOH) had to be applied. The methanolysis of PC under mild conditions (105 °C) and in the presence of ionic liquid (1-*n*-butyl-3-methylimidazolium chloride) led to 95% BPA recovery and carbonate formation after 2.5 h of the reaction [5]. Non-catalyzed methanolysis and glycolysis of PC is described by Kim et al. [6,7]. The maximal yield of BPA was reached after 85 min of the reaction with ethylene glycol (EG) at 220 °C. However, the high excess of EG was applied; the used mass ratio of EG/PC was 4/1. Lin et al. reported the glycolysis process for PC waste in which the use of molar excess of urea and zinc oxide as the catalyst in the second stage of the process led to high yields of bishydroxyalkyl ethers of BPA [8]. The basic gly-

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colysis of PC using EG in combination with ethylene carbonate supported the formation of bishydroxyethyl ethers of BPA [9]. It is also known the basic methanolysis of PC in supercritical conditions [10], which led at temperatures of 100–140 °C and pressure of 9–10 MPa to the yield of BPA around 90%. The decomposition of PC using water in supercritical state and sodium bicarbonate as the catalyst led to undesirable cleavage of created BPA into phenolic derivates [11]. The high-pressure hydrolysis of PC is also reported [12–14]. The same catalyst was also used for the aminolysis of PC utilizing N,N′-dimethyl-1,2-diaminoethane [15]. The alkali-catalyzed hydroglycolysis was recently tested using the ternary mixture of glycerin, water and sorbitol [16]. The highest yield of BPA was obtained when the ratio of glycerin/water/sorbitol was 6/3/1. The steam hydrolysis of PC in a fluidized bed reactor was also described [17] producing BPA with maximal yield of 45%.

Common drawbacks of the above mentioned processes comprise (i) too long reaction time, (ii) the presence of solvent, (iii) the use of concentrated bases and (iv) demanding technology often requiring a high-pressure reactor and supercritical conditions. There are many examples in a number of reviews [18–26] demonstrating the benefits associated with the use of microwave heating, e.g. reaction time reduction, solvent-free conditions, enhancements in conversions, etc. The application of microwave irradiation to polymer degradation was recently reviewed [18]. The alkali-catalyzed glycolysis of PC in microwave field was firstly described by Nikje [27]. The optimal conditions can be summarized as following: 2 wt.% of NaOH, the reaction temperature of 180 °C and the reaction time 8.3 min, which led to ca 92% yield of BPA. Tsintzou et al. described the microwave-assisted alkaline hydrolysis of PC in the presence of phase-transfer catalyst (PTC), 1-hexadecyl trimethylammonium bromide [28]. The hydrolysis conversion of PC was greater than 80% after 40 min at 160 °C. The role of PTC catalyst seemed to be essential for the fast PC hydrolysis since the hydroxide anion (bonded via ionic interactions with the cation part of PTC) could easily attack the carbonate group of PC macromolecules placed on the PC-water interphase. Another microwave-assisted hydrolytic degradation of PC was performed with the addition of tetrahydrofuran as co-solvent [29]. The highest yield of BPA (94%) was achieved after 12.5 min of the hydrolysis at 110 °C, when the weight ratio of water/NaOH/tetrahydrofuran was 3.5/0.5/20. Rosi et al. reported hydrolysis/glycolysis of PC under microwave heating leading to complete PC conversion in 10 min [30]. BPA, mono- and di- hydroxyalkyl ethers of BPA were formed together with partially degraded compounds (phenol, isopropylphenol, and isopropenylphenol) as the results of probably too high applied power (3 kW).

In this paper, a novel two-step chemical recycling method of polycarbonate (PC) waste is described advantageously utilizing as decomposing agents two by-products - glycerol from biodiesel production and medium chain triglycerides of coconut oil (CCO) from soap industry. In the first "transesterification" step, glycerol and CCO are used to prepare a transesterified coconut oil (TCCO). In the second step, TCCO containing hydroxyl end-groups reacts with carbonate linkages of PC, which results in cleavage of PC chain. Applying microwave (dielectric) heating in the both steps makes the whole recycling process environmentally friendly and energy-saving, since no solvent or elevated pressure is required and the significantly reduced time compared with conventional heating is achieved. The prepared polyol product is suitable as replacement of petrochemical polyols in polyurethane (PUR) formulations.

2. Experimental part

2.1. Materials and reagents

The low molecular weight fraction of coconut oil (CCO), the by-product from soap industry, was kindly received from Environ Ltd. (Czech Republic). CCO was first filtered to remove solid impurities. Thus purified CCO, the liquid at room temperature with viscosity of 26 mPa·s (25 °C) and density of 911 $kg \cdot m^{-3}$ was used for all experiments. Glycerol (99.5%, Preol, Czech Republic), the by-product from biodiesel production, was used as received for the oil transesterification. Dibutylbis[1-oxo(dodecyl)oxy]stannane, DBTL (95%, Sigma-Aldrich), was used as a catalyst without further purification. The granules (particle size: 5–10 mm) of technological PC scrap from automotive headlamp production (Varroc Lighting Systems, Ltd., Czech Republic) was applied for solvolysis.

2.2. First step: microwave-assisted oil transesterification

The transesterification of CCO was conducted in a multimode microwave reactor (Romill, Ltd., Czech Republic) working at a frequency of 2.45 GHz and a maximum power of 1000 W. The reactor was equipped with a double temperature control using an IR pyrometer and a shielded Pt100-thermometer inserted directly into the reaction medium. The experiments were performed at constant temperature using alternating powers and the reaction temperature was controlled by the Pt100-thermometer. All experiments were performed under atmospheric pressure and inert atmosphere. In typical experiment, CCO (200 g, 0.4 mol), glycerol (100 g, 1.1 mol) and catalyst (in the amount of 0.06–0.3 wt.%) were combined in a 500 mL three-neck flask equipped with nitrogen inlet, reflux and mechanical stirrer. The reaction time was reported from the beginning of heating. During the heating, the mixture was regularly sampled, checked visually and analyzed using size exclusion chromatography (SEC) and MALDI TOF mass spectrometry.