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# Environmentally benign chemical recycling of polycarbonate wastes: comparison of micro- and nano-TiO<sub>2</sub> solid support efficiencies

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**Abstract:** Polycarbonate (PC) wastes, including optical discs (CDs) and digital optical discs (DVDs), were chemically recycled into valuable materials such as 4,4'-(propane-2,2-diyl)diphenol (BPA) and etherified derivatives of BPA using sodium hydroxide (NaOH) as the alkali metal catalyst and nanostructured titanium dioxide (nano-TiO<sub>2</sub>) and microstructured titanium dioxide (micro-TiO<sub>2</sub>) as the solid supports in the binary green system consisting of water and 2,2'-oxydi(ethan-1-ol) (DEG) under conventional heating method, and data were compared. In this study, the effects of various parameters, such as solvent composition, concentration of NaOH, and solid support, were studied on the reaction progress. In these reactions, the importance of water as the green solvent was investigated in achieving pure BPA as the valuable material. When used with 20% aqueous DEG (pbw), a pure BPA can be obtained at 70% yield in the presence of nano-TiO<sub>2</sub> and micro-TiO<sub>2</sub> as the solid supports. According to the results, the use of nano-TiO<sub>2</sub> in comparison with micro-TiO<sub>2</sub> accelerates the chemical recycling of PC wastes. The nano-TiO<sub>2</sub> catalyst recovery shows that the recovered solid support is applicable for four cycles. The obtained products were characterized using spectroscopic methods, namely, <sup>1</sup>H NMR, <sup>13</sup>C NMR, and Fourier transform infrared spectroscopy as well as gas chromatography-mass spectrometry.

**Keywords:** bisphenol-A; chemical recycling; green chemistry; nano-TiO<sub>2</sub>; solid support.

## Abbreviations

<sup>1</sup> H NMR	proton nuclear magnetic resonance
<sup>13</sup> C NMR	carbon-13 nuclear magnetic resonance
BGA-BPA	mono glycerol ether of BPA
BHE-BPA	bis(hydroxy ethyl) ether of bisphenol-A
BPA	bisphenol-A
CDCl <sub>3</sub>	chloroform-d
CDs	optical discs
DGA-BPA	diglycerol ether of BPA
DMC	dimethyl carbonate
DVDs	digital optical discs
EC	ethylene carbonate
EG	ethylene glycol
FT-IR	Fourier transform-infrared spectroscopy
GC	gas chromatograph
GC-MS	gas chromatography-mass spectrometry
LCD	liquid crystal display
m.p.	melting point
MHE-BPA	mono(hydroxy ethyl) ether of bisphenol-A
Micro-TiO <sub>2</sub>	microstructured titanium dioxide
Nano-TiO <sub>2</sub>	nanostructured titanium dioxide
PC	polycarbonate
PUR	polyurethanes
THF	tetrahydrofuran
TMS	tetramethylsilane
XRD	X-ray diffractometer

## 1 Introduction

Polycarbonate (PC) as a useful engineering thermoplastic due to its unique properties is widely used in various applications such as in medical, security compounds, construction materials, data storage, phones, liquid crystal display (LCD) screens, electronic component, bottles, laboratory safety goggles, automotive, aircraft, optical discs (CDs), and digital optical discs (DVDs). Because of unprecedented increase in PC wastes, recycling expansion in recent years has become necessary. In general, there are two methods that have been developed for recycling of PC wastes, which are the physical and chemical methods. In the chemical method, the PC wastes can be turned into 4,4'-(propane-2,2-diyl)diphenol (BPA), bis(hydroxy ethyl) ether of BPA (BHE-BPA), and mono(hydroxy ethyl) ether of BPA (MHE-BPA) using ethane-1,2-diol (EG) as the solvent,

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sodium hydroxide (NaOH) as the alkali metal catalyst, and 1,3-dioxolan-2-one (EC) as the reagent [1]. Semi-continuous lab-plant is another chemical method, studied by using a destructive reagent, such as methanol and methanol-water mixtures, on PC that is converted to BPA (99.9%) and dimethyl carbonate (DMC, 35%) [2]. In another study, metal chlorides, namely, tin dichloride (SnCl<sub>2</sub>) and zinc chloride (ZnCl<sub>2</sub>), catalytic efficiencies had been studied on the thermal degradation of PC wastes [3]. Moreover, Pant studied recycling of PC wastes by using glycerol as the solvent in combination with mild catalysts such as zinc oxide (ZnO) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in the presence or absence of urea (CO(NH<sub>2</sub>)<sub>2</sub>). In these reactions, mono-glycerol ether of BPA (BGA-BPA), diglycerol ether of BPA (DGA-BPA), and BPA were obtained [4]. Iannone and his co-workers studied the efficiency of nanostructured ZnO and tetrabutylammonium chloride (ZnO-nanoparticles/NBu<sub>4</sub>Cl) as a recyclable catalyst on the PC depolymerization into BPA monomer under the following conditions: tetrahydrofuran (THF) as solvent, 7 h, 100°C, and nitrogen (N<sub>2</sub>) atmosphere [5]. In another study, Li et al. [6] described controllable PC depolymerization by using 1,4-dioxane/EG as the solvents and zinc acetate (Zn(O<sub>2</sub>CCH<sub>3</sub>)<sub>2</sub>) as the catalyst. In addition, in high temperature of 300°C, BPA was obtained in 91% yield under pyrolytic hydrolysis conditions of PC; when temperature is raised to 500°C, this product degraded [7]. Following an overview on recycling of PC wastes, recycling of PC wastes by alkali-catalyzed methanolysis and hydrolysis reactions led to recover BPA in 94% yield [8]. In the meantime, recycled PC via the methanolysis chemical method in the presence of *n*-butyl-3-methylimidazolium chloride ([Bmim][Cl]) as the ionic liquid at 105°C for 2.5 h without applying acidic or basic catalysts collected BPA and DMC in good yields [9]. Moreover, PC depolymerization using an alcohol such as supercritical ethanol has been studied [10]. BPA was recovered as the sole product using 1-butyl-3-methylimidazolium acetate ([Bmim][AC]) as the ionic liquid at 140°C [11]. In explaining the mechanism of glycolysis reactions in the destruction of PC, two mechanistic pathways were suggested by Kim's research group [12]. Beneš et al. [13] studied the two-step solvent-free recycling process of PC into suitable polyols for the synthesis of novel polyurethanes (PUR) using glycerol for oil transesterification, coconut oil as solvolysis reagent, and dibutylbis[1-oxo(dodecyl)oxy]stannane (DBTL) as a catalyst. Taguchi and co-workers studied the chemical recycling of PCs into BPA with 90% yield under hydrothermal conditions using a batch reactor in the presence of two crystallite sizes of cerium (IV) oxide (CeO<sub>2</sub>) crystal (75 and 74 nm) as the catalyst [14]. Moreover, more methods and studies are presented for the chemical recycling of PC involving

alcoholysis [15–17], aminolysis [18, 19], pyrolysis [20–22], hydrolysis [23–26], and hydrolysis/glycolysis [27]. In our previous works, the chemical recycling of PC wastes into BPA has been considered in the presence of green solvents such as (water, glycerol, and sorbitol) mixtures [28], (water and glycerol) mixtures [29], and water [30] under conventional heating method and (water and glycerol) mixtures [31], and EG [32] under conventional microwave irradiation using NaOH as alkali metal catalyst. In our previous researches, the amount of NaOH as alkali metal catalyst (0.5% to 2% based on total waste and solvent weights) and the weight ratios PC pellets:solvent was 1:1. In addition, in one of the last studies mentioned, the effects of the nanostructures such as Closite 30B, silicon dioxide (SiO<sub>2</sub>), and titanium dioxide (TiO<sub>2</sub>) as solid supports (2% based on total waste and solvent weights) on the chemical recycling of PC wastes have been studied [30]. In this case, we decided to estimate the efficiency of titanium dioxide (TiO<sub>2</sub>) in two scales of nanostructure (nano-TiO<sub>2</sub>) and microstructure (micro-TiO<sub>2</sub>) as the eco-friendly, non-toxic, low-cost, chemically stable, and recyclable solid supports in the chemical recycling of PC wastes. Our main goal in the current report is the chemical recycling of PC wastes to pure BPA as the valuable material in accordance with the main goals of green chemistry and synthesis using green solvent composition, namely, 2,2'-oxydi(ethan-1-ol) (DEG) and water, in combination with a least amount of alkali metal catalysts in an easy and eco-friendly method in the presence of nano- and micro-TiO<sub>2</sub> as an efficient solid support at atmospheric pressure. In these reactions, valuable materials such as BPA and etherified derivatives of BPA were identified. In this study, the presence of water is known as an eco-friendly solvent to achieve pure BPA. According to the results, when nano-TiO<sub>2</sub> as the solid support are used in the reaction mixtures, the chemical recycling of PC wastes is accelerated compared with the experimental conditions using micro-TiO<sub>2</sub> as the solid support. The nano-solid support can be recovered for four cycles and used in the next reaction.

## 2 Materials and methods

### 2.1 Materials

NaOH, methanol (MeOH), DEG, acetic acid (MeCOOH), and acetone (C<sub>3</sub>H<sub>6</sub>O) were purchased from Merck company (Darmstadt, Germany) and used as received without further purification. PC pellets were obtained from CD and DVD wastes, and the thin layer of aluminum was separated completely. Then, the large particles of PC wastes were broken into the arbitrary sizes and shapes (very tiny pieces), washed with NaOH solution and hot water for several times, and then dried.

The water for doing the reactions was twice distilled. Nano-TiO<sub>2</sub> were purchased from Kemira company (Helsinki, Finland) with the average crystallite size of 34.68 nm, 79.75% rutile, and 20.25% anatase phases and specific surface area of 59 m<sup>2</sup>/g. Moreover, micro-TiO<sub>2</sub> was supplied from the Crimea Titan company (Crimea, Ukraine).

## 2.2 Instruments

Fourier transform-infrared spectroscopy (FT-IR) spectra (KBr pellet press in a weight ratio of 1:100 sample/KBr) were recorded on a BRUKER Tensor 27 spectrometer (Bruker, Billerica, MA, USA) between 400 and 4000 cm<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a BRUKER CRX 300 spectrometer (at 300 MHz, Bruker, Billerica, MA, USA) employing indicated solvents CDCl<sub>3</sub> and tetramethylsilane (TMS) and the internal standard, respectively. Chemical shifts are expressed in ppm ( $\delta$ ) values and coupling constants in Hz ( $J$ ). Melting point was determined on a Gallenkamp electrothermal 9100 (CO, USA). The nanostructure (nano-TiO<sub>2</sub>) was characterized on an X-ray diffractometer (XRD, Model: GNR, Novara, Italy). The XRD data were collected on an APD-2000 diffractometer (Cu K $\alpha$  radiation,  $\lambda = 1.54 \text{ \AA}$ , GNR, Novara, Italy) from 20° to 80° ( $2\theta$ ). Nanostructure recycling processes were done on a centrifuge (Centromix, JP Selecta s.a., Kyoto, Japan, 5890g) instrument. Moreover, materials and products were dried using a vacuum oven (Wisd, WOV-70, DAIHAN Scientific, Seoul, South Korea) in the reactions. The obtained products were characterized using an Agilent/HP 6890 gas chromatograph (GC) combined with a 5973 MSD (Mass Spec, Mass Spectrometer, Mass Selective Detector, MS, GC-MS, Agilent, Santa Clara, CA, USA). In addition, samples for GC-MS analysis were dissolved in MeOH. The temperature program of the GC column used was as follows: temperature kept at 60°C for the first 1 min and then increased to 285°C for 14 min using a heating rate of 20°C min<sup>-1</sup>.

## 2.3 General procedure

In this section, the process was carried out in a 50 ml two-necked bottom equipped with a magnetic stirrer, and a reflux condenser and filled with 5.0 g of PC wastes pellets, DEG and water (total weight of solvents 5.0 g), and NaOH (2% based on total weights of the PC waste and solvent = 0.2 g) as the alkali metal catalyst. In addition, micro- or nano-TiO<sub>2</sub> as the solid support (2% based on total weights of the PC waste and solvent = 0.2 g) was added to the reaction vessel. As a general procedure, the reaction vessel was heated under reflux, and complete dissolution of the PC wastes was considered as the reaction end point. The weight ratios (PC pellets:solvents) and (alkali metal catalyst or solid support:PC pellets) were 1 and 0.04, respectively. In the next step, the reaction mixture was cooled to room temperature and neutralized with acetic acid as noted in Tables 1 and 2. Product recovery yields are obtained using Eq. (1). Moreover, purification of the obtained products was performed by methanol:water 1:1 mixture solution (30 ml), and the product was separated by filtrating, washed with twice distilled water for several times, dried at 80°C in vacuum oven for 5 h, and then characterized by using spectroscopic methods (<sup>1</sup>HNMR, <sup>13</sup>CNMR, and FT-IR) and GC-MS.

$$Y = \frac{b}{a} \times 100\% \quad (1)$$

**Table 1:** DEG/water composition role using nano-TiO<sub>2</sub> as the solid support in chemical recycling of PC wastes.

Entry	DEG:water (Pbw)	<i>t</i> (min)	Product recovery yield (%)
1	100:0	13	85
2	90:10	22	75
3	80:20	88	70
4	70:30	95	65
5	60:40	251	53
6	50:50	332	40

**Table 2:** DEG/water composition role using micro-TiO<sub>2</sub> as the solid support in chemical recycling of PC wastes.

Entry	DEG:water (Pbw)	<i>t</i> (min)	Product recovery yield (%)
1	100:0	17	80
2	90:10	53	73
3	80:20	110	70
4	70:30	160	63
5	60:40	320	52
6	50:50	360	40

where  $Y$  is the product recovery yield (%),  $b$  is the amount of recovered products in the chemical recycling of PC wastes (g), and  $a$  is the amount of PC wastes used in the chemical recycling of PC wastes (g).

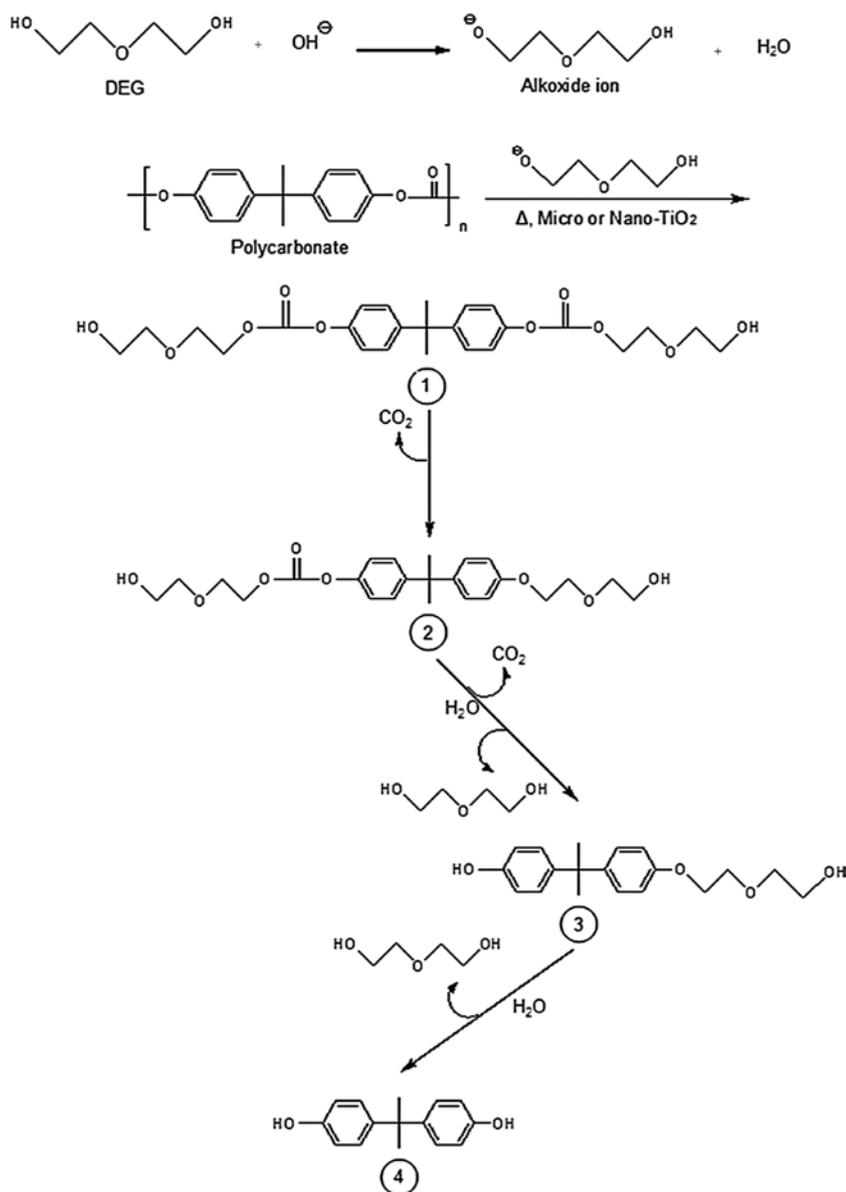
## 3 Results and discussion

### 3.1 Reaction scheme

According to all identified products, the proposed hydroglycolysis reaction of PC wastes under alkali metal catalyzed is shown in Scheme 1. As shown in the scheme, the reaction was explained with a Brønsted-Lowry acid-base reaction and conversion of DEG molecules to the corresponding alkoxide ion that is responsible for acting as a nucleophile with attaching to the carbonate functional group of PC and formation of products 1. In the next step, the other products were made in the reaction media.

### 3.2 Solvent composition studies

According to our results, by increasing the water content in the solvent composition (0%–50% based on total solvent weights), the concentration of the hydroxide ion as a nucleophile increases and competes with the alkoxide ion from DEG molecules in reacting with the carbonate functional group resulting in an extended reaction time due to its lesser nucleophilicity when compared by



**Scheme 1:** Reaction and mechanism: (1) Bis(2-(2-hydroxyethoxy)ethyl)(propan-2,2-diybis(4,1-phenylene))dicarbonate (MW = 490); (2) 4-(2-(4-(2-(2-hydroxyethoxy)ethoxy)phenyl)propan-2-yl)phenyl(2-(2-hydroxyethoxy)ethyl)carbonate (MW = 448); (3) 4-(2-(4-(2-(2-hydroxyethoxy)ethoxy)phenyl)propan-2-yl)phenol (MW = 316); (4) 4,4'-(propane-2,2-diy)l)diphenol (MW = 228); DEG 2,2'-oxydi(ethan-1-ol);  $\Delta$  = heat; MW = molecular weight.

the alkoxide ion. In order to find a green solvent composition in accordance with the main goals of green chemistry and synthesis containing higher levels of the water, the effects of various ratios of DEG and water were studied in chemical recycling of PC wastes, and data are collected in Tables 1 and 2 using nano-TiO<sub>2</sub> and micro-TiO<sub>2</sub> as the solid support, respectively. As one can see, the highest recovery of product was achieved under the conditions remarkable in entry 3 in Tables 1 and 2 using 20 pbw aqueous DEG (in Section 3.6, it will be discussed that the purpose of the highest recovery of product in entry 3 in Tables 1 and 2 is

pure BPA as a valuable material). Product recovery yields are reduced by increasing the amount of water in the reaction media.

### 3.3 Study on alkali metal catalyst concentration

To study the role of alkali metal catalyst concentration in the reaction progress as well as product formation, a set of experiments was carried out using additional 0.5 to

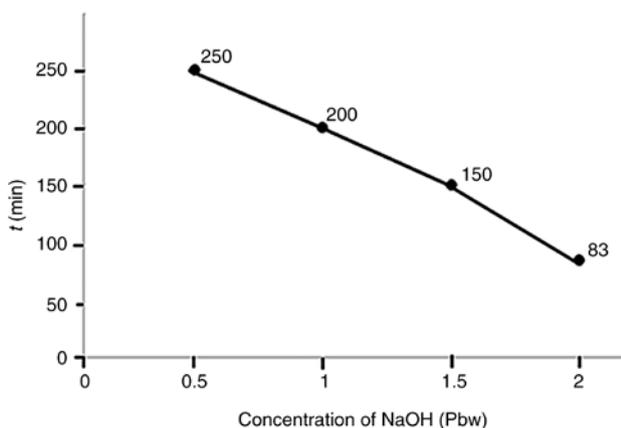
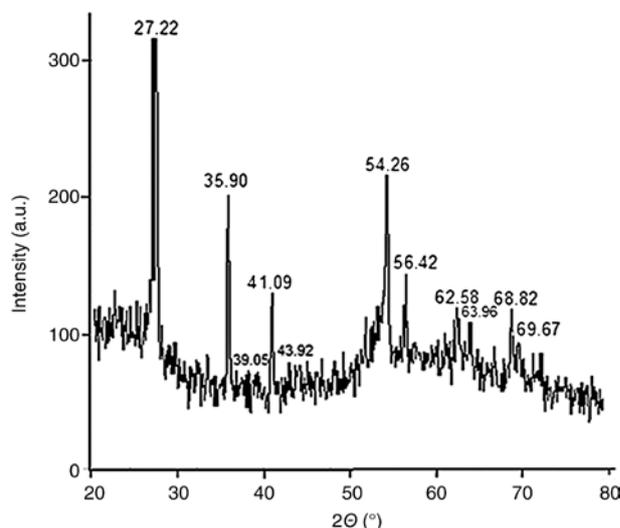
**Table 3:** Catalyst concentration role using nano-TiO<sub>2</sub> as the solid support in chemical recycling of PC wastes.

Entry	Catalyst concentration (Pbw)	t (min)
1	1.5	150
2	1	200
3	0.5	250

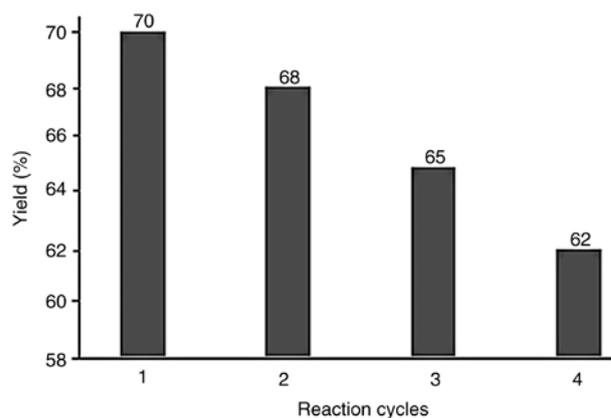
1.5 pbw NaOH as alkali metal catalyst and nano-TiO<sub>2</sub> 2 pbw as the nano-solid support and the DEG:water two systems as 80:20 ratio. The results are collected in Table 3, and data are compared by obtaining data in the Table 1. By comparison of the results, it is concluded that by decreasing of the NaOH concentration in the chemical recycling of PC wastes, the reaction completed in the prolonged times when compared with high concentrated reactions (Scheme 2). It is also quite clear that by increasing the catalyst concentration from 2 pbw, the time to complete the reaction will be reduced. On the other hand, the significant increase in reaction time in the case of reduction of the alkali metal catalyst concentration is not appropriate for the main goals of green chemistry and synthesis. According to the main goals of green chemistry and synthesis, regarding these experiments, the base catalyst concentration was set as 2 pbw in all reactions.

### 3.4 The role of the solid support at nanoscale

The X-ray diffraction pattern of nano-TiO<sub>2</sub> at positions ( $2\theta$ ) 27.22, 35.9, 39.05, 41.09, 43.92, 54.26, 56.42, 62.58, 63.96,

**Scheme 2:** The effect of alkali metal catalyst concentration in the PC dissolution time: DEG (4.0 g); water (1.0 g); DEG/water (80:20 pbw); PC wastes (5.0 g); NaOH and nano-TiO<sub>2</sub> (2 pbw); PC wastes:solvent (1:1).**Scheme 3:** XRD spectra of nanostructured TiO<sub>2</sub>.

68.82, and 69.67 as main angles are shown in Scheme 3. The average nano-TiO<sub>2</sub> diameter was calculated to be 34.68 nm from the XRD results by using the Debye-Scherrer's Eq. (2) and  $2\theta = 27.22^\circ$  in the Supplementary Material. Moreover, the observed XRD peaks were well assigned to rutile TiO<sub>2</sub> mainly [33]. In the presence of about 79.75% rutile and 20.25% anatase, phases were determined approximately in the XRD analysis (Supplementary Figure S22). The number of positions ( $2\theta$ ) in XRD of nano-TiO<sub>2</sub> (Scheme 3) is due to the combination of two phases of the rutile and anatase. In the following, in order to investigate the role of solid support at the nanoscale, experiments were carried out by using micro-TiO<sub>2</sub> 2 pbw, and NaOH 2 pbw as alkali metal catalyst (Table 2), and the data were compared with nominated experiments of nano-TiO<sub>2</sub> in the Table 1. These

**Scheme 4:** The effect of reuse of nano-TiO<sub>2</sub> as the solid support on the chemical recycling of PC wastes: DEG (4.0 g); water (1.0 g); DEG/water (80:20 pbw); PC wastes (5.0 g); NaOH and nano-TiO<sub>2</sub> (2 pbw); PC wastes:solvent (1:1); reaction time (83 min).

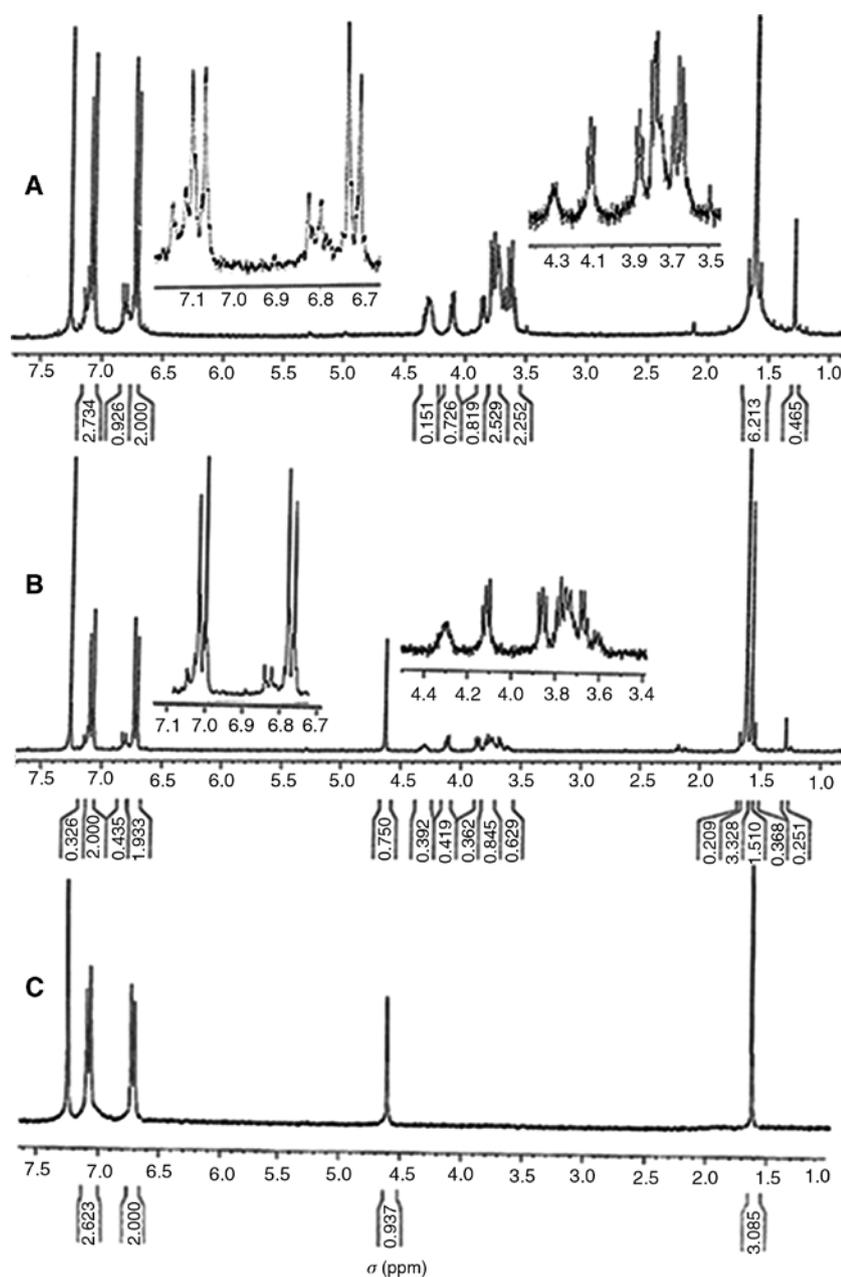
results show significant increments in reaction times due to a reduction of the surface to volume ratio when micro-TiO<sub>2</sub> was used as the solid support.

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

where  $k$  is generally considered as 0.94;  $\lambda$  is the wavelength of Cu K $\alpha$ , 1.54 Å;  $\beta$  is the full-width at half-maximum; and  $\theta$  is the Bragg's angle (°) [34].

### 3.5 Recycling of nano-TiO<sub>2</sub> as the solid support

As the catalyst recovery is one of the main goals of the green chemistry and synthesis, the recycling of nano-TiO<sub>2</sub> as the nano-solid support was examined under the conditions remarkable in entry 3 in Table 1. In the first step, the PC wastes dissolved completely within 83 min, and then the order of the purification steps described in Section 2.3

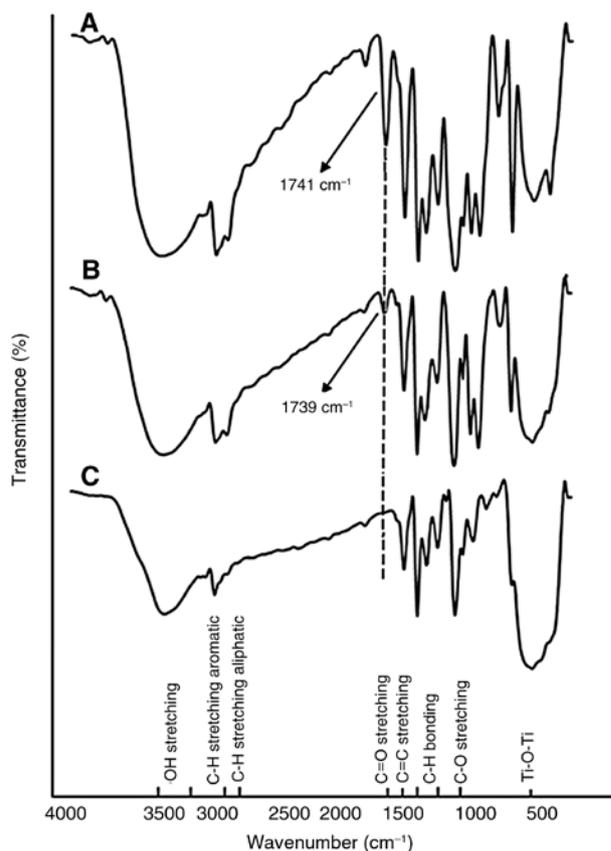


**Scheme 5:** <sup>1</sup>H NMR spectra in the CDCl<sub>3</sub> solvent: (A) Blended product resulting from the absence of water; (B) (BPA + byproduct) is resulting from the 10% water; (C) BPA resulting from more amount of water in the reaction medium.

in recovering the product was carried out. In the next step, the product was dissolved in acetone, and the nano-solid support was separated with a centrifuged colloidal solution and were washed with acetone and water for several times and dried. Other reactions were performed with the recycled nano-TiO<sub>2</sub> as the solid support. Scheme 4 shows the activity of nano-TiO<sub>2</sub> as the solid support in product recovery after four cycles, and the recovery yield drops dramatically.

### 3.6 Characterization of products using identification methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and GC-MS)

Products resulted from chemical recycling of PC wastes were analyzed using identification methods (<sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and GC-MS). The <sup>1</sup>H NMR and FT-IR spectra of products from all accomplished reactions are presented in Schemes 5 and 6, respectively. According to the results of the <sup>1</sup>H NMR spectroscopic method (Scheme 5A), a blended product was formed in the resulting reaction at (100:0) DEG:water ratio at 85% and 80% yields using nano-TiO<sub>2</sub> and micro-TiO<sub>2</sub>, respectively (entry 1 in Tables 1 and 2; Supplementary Figure S1). Also, increasing the amount of water in the reaction medium at the ratio of (90:10) DEG:water, BPA as the main product and a blended product as a byproduct were formed (Scheme 5B) with a total yield of 75% and 73% using nano-TiO<sub>2</sub> and micro-TiO<sub>2</sub>, respectively (entry 2 in Tables 1 and 2; Supplementary Figure S2). In addition, the identification of carbonyl functional groups (1741 and 1739 cm<sup>-1</sup>) shown in the FT-IR spectrum (Scheme 6A, B) led to the presence of certain products in these ratios (entries 1 and 2 in Tables 1 and 2; Supplementary Figures S3 and S4). To identify the product quality in these ratios (entries 1 and 2 in Tables 1 and 2), without doing the purification steps described in Section 2.3, we used the GC-MS method for the mentioned ratios. The spectra resulting from the GC-MS do not exist in the other literature and are usually unavailable in the mass spectral libraries. However, according to the results GC-MS, all chemical structures of the corresponding compounds were derived from BPA certainly. On the other hand, based on a principle of symmetry, chemical structures may have symmetrically failed during the GC-MS process. Thus, due to the instability of the chemical structures according to mass spectrums, elucidation of the chemical structures of mass spectrums was made with the help of molecular ion peaks (M<sup>+</sup>), important peaks and base peaks in the mass spectrums, and the mass spectrum of BPA. In Table 4 chemical structures identified by



**Scheme 6:** FT-IR spectra in the KBr pellet: (A) Blended product resulting from the absence of water; (B) (BPA + byproduct) is resulting from the 10% of water; (C) BPA resulting from more amount of water in the reaction medium.

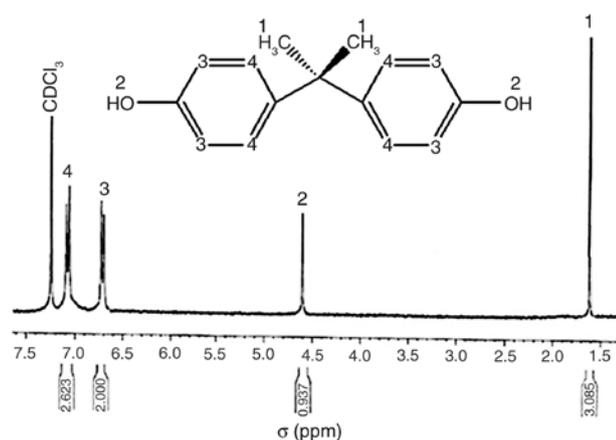
GC-MS method are labeled. According to the results, the depolymerization reaction of PC wastes was not carried out completely in the (100:0) ratio of DEG:water (entry 1 in Table 1) due to lack of water in the reaction medium and only release of carbon dioxide (CO<sub>2</sub>) from some of the products have taken place. Further, a mixture of diols such as etherified derivatives of BPA with molecular weight (MW) of 448–746 was detected in this ratio (Table 4, 1–6; Supplementary Figures S5–S10). According to the results of GC-MS, by increasing the water content at a ratio of (90:10) DEG:water, the reaction of depolymerization occurs incompletely in the BPA recovery (entry 2 in Table 1). Of course, a mixture of diols such as BPA and etherified derivatives of BPA with MW of 228–746 were identified in this ratio (Table 4, 7–14; Supplementary Figures S11–S18). Consistent with the main goals of the research, by adding more than 10% water to the reaction medium at other existing ratios in Tables 1 and 2, only pure BPA as the valuable material was obtained (entries 3, 4, 5, and 6 in Tables 1 and 2; Scheme 5C). Regarding the main goal of the research, to achieve the highest yield of BPA as a pure product, solvent

**Table 4:** The molecules characterized using GC-MS.

Entry	Molecules	MW	Retention time (min)
1	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O COO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>a</sup>	746	15.055
2	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO- C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>a</sup>	658	13.246
3	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> - C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>a</sup>	570	12.474
4	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> -OCOO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>a</sup>	492	10.167
5	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> - C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OH <sup>a</sup>	482	11.248
6	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>a</sup>	448	10.167
7	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O COO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	746	15.535
8	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO- C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	658	15.106
9	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> -OCOO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	614	13.992
10	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> - C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	570	12.2
11	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> -OCOO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	492	10.125
12	HO-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OCOO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> - C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	448	8.487
13	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub> -OH <sup>b</sup>	316	15.106
14	HO-C <sub>6</sub> H <sub>4</sub> -C(CH <sub>3</sub> ) <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -OH <sup>b</sup>	228	11.214

<sup>a</sup>In the absence of water (entry 1 in Table 1). <sup>b</sup>In the presence of 10% water (entry 2 in Table 1).

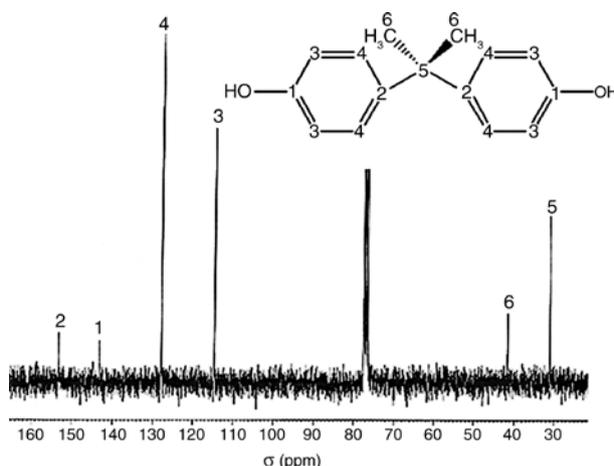
mixture at (80:20) DEG:water ratio has been introduced as an environmentally friendly solvent mixture because pure BPA as a valuable material is achieved with the highest yield of 70% using nano-TiO<sub>2</sub> and micro-TiO<sub>2</sub> as the solid supports (entry 3 in Tables 1 and 2).



**Scheme 7:** <sup>1</sup>H NMR spectrum of recovered pure BPA in the CDCl<sub>3</sub> solvent.

### 3.7 Spectra analysis of recovered BPA

4,4'-(Propane-2,2-diyl)diphenol (BPA). White powder, melting point (m.p.) 158°C, <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, δ): 7.10 (d, *J*=8.4, 4H; ArH), 6.71 (d, *J*=8.4, 4H; ArH), 4.60



**Scheme 8:** <sup>13</sup>C NMR spectrum of recovered pure BPA in the CDCl<sub>3</sub> solvent.

(s, 2H; OH), 1.61 (s, 6H; CH<sub>3</sub>) (Scheme 7; Supplementary Figure S19). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>, δ): 153.26, 143.26, 127.94, 114.69, 41.68, 31.07 (Scheme 8; Supplementary Figure S20). FT-IR (KBr pellet press): 1360–1507 cm<sup>-1</sup> (C-H bending), 3100 cm<sup>-1</sup> (C-H stretching aromatic), 2962 cm<sup>-1</sup> (C-H stretching aliphatic), 3150–3450 cm<sup>-1</sup> (OH stretching), 1178–1236 cm<sup>-1</sup> (C-O stretching), 1602 cm<sup>-1</sup> (C=C stretching), 679 cm<sup>-1</sup> (Ti-O-Ti) (Scheme 6C; Supplementary Figure S21). The FT-IR spectrum fully corresponds with NMR data.

## 4 Conclusion

In summary, in this study the performance of nano- and micro-TiO<sub>2</sub> as an efficient solid support in the chemical recycling of PC wastes by using a binary system (DEG/water) mixture as green solvents and NaOH as alkali metal catalyst for the recovery of BPA and etherified derivatives of BPA were investigated. As is fully explained, the main goal of this research is to achieve pure BPA as the valuable material. According to the results, using micro-TiO<sub>2</sub> as a solid support compared with the nano-TiO<sub>2</sub> with lowering of the surface area and active sites required for the reaction, due to a reduction of the surface to volume ratio, a significant increase occurs in the reaction time. Moreover, when increasing the amount of DEG in mixture solvents because of the higher power of the alkoxide ion than hydroxide ion as the nucleophile, the reaction time decreases. On the other hand, the increase of DEG in the solvent mixture leads to the chemical recycling of PC wastes into a blended product or mixed products (BPA + etherified derivatives of BPA), which is not optimal for the main goals of the research. In these reactions, water is known as an important agent in order to complete the depolymerization reaction of PC wastes in achieving the pure BPA as the valuable material. In addition, when decreasing the NaOH concentration as an alkali metal catalyst in the reaction medium, the reaction time for chemical recycling of PC waste increases significantly. The effect of recovering nano-TiO<sub>2</sub> from products for four cycles without significantly reducing the yields of products has been investigated. This method is an appropriate way to convert PC wastes into pure BPA as valuable materials with features such as inexpensive cost, high-efficiency products, recyclability of solid support, safe, eco-friendly, simple, easy, and using green solvents and available in atmospheric pressure. Finally, our research group hopes to look at the performance of other reagents, nanoparticles, and green solvents on the chemical recycling of PC wastes in the future.

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