



Chemical Depolymerization and Value Addition Study of Post-Consumer Polycarbonate Waste

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ABSTRACT: The post-consumer plastics become an issue to the environment due to their stable and non-biodegradable nature. Their management is essential today and starts from the source of utility through segregation to the place where a proper care can be taken place that includes landfills or energy recovery areas or place of recycling. The present work is a step towards the development of environmentally friendly and sustainable depolymerization method of bisphenol A based polycarbonate. The chemical recycling has come up with various advantages in comparison to the traditional recycling methods for plastics. The reaction has been performed with environmentally friendly green solvents and also with green reagents like alumina and montmorillonite clays.

Keywords: Plastic waste, Polycarbonate, Chemical recycling, Alumina, Bisphenol A.

I. INTRODUCTION

The plastic production and utility showed substantial growth due to its usefulness as essential materials for daily life [1-3]. The plastic production becomes so large that their post-consumer products started creating problems for the environment [4-6]. According to Statista, the global plastic production has increased from 0.35 million metric tons in 1950 to 335 in million metric tons in 2016 [7]. For this huge production, the safe disposal practice has not been developed as per requirement. The waste generated from its production to development of finished products leads to environmental damage. Hence, with due course of time, several legislations and restrictions have been introduced to curb the environmental pollution due to the plastics [8,9].

Polycarbonate (PC) is an engineering thermoplastic which is widely used for several applications [10]. This plastic has received a great upliftment in the plastic industry due to its high-performance nature. The polycarbonate products contribute substantially to the safety and well-being of consumers. The good physical and mechanical properties of PC plastic make it potential for a large amount of production and their introduction to our environment and created huge challenge for their waste management. The manufacturing of CDs and DVDs, baby bottles, water bottles along with automotive components are totally based on PC [10]. The polycarbonate has found its applications in varied fields like food contact applications (4%), medical applications (3%), consumer products (4%) along with optical media like DVD's (21%), houseware and electrical appliances (11%), automotive (12%), construction (17%) and electronics (20%) (PlasticEurope, 2010). However, due to the adverse effect of bisphenol A on human health, many manufacturers have reduced or stopped using polycarbonates for human related items [11,12]. The chemicals associated with PC get leach out leading to environmental damage

including damage to humans, animals and marine organisms. They enter into the food chain and directly or indirectly harms human beings. Polycarbonate is coded 7 suggesting difficulty in its recycle ability. However, a lot of research work has been done to recycle and/or degrade the polycarbonate bottles and CDs [13-16].

Chemical recycling converts plastic wastes to the corresponding monomers, oligomers and/or other value-added industrial relevant chemical compounds. The process involved includes thermal, photochemical, microbial, catalytic etc [17-21]. The recycling has been studied with catalysts and reagents like metal chlorides [22], high pressure high temperature steam [23], glycerol (Gly) using NaOH as catalyst [24], ethylene glycol (EG) in NaOH [25], zinc oxide nanoparticles (ZnO-NPs) [26]. Most of the above reactions are performed in closed vials and difficult reaction conditions. This difficult condition always create problem when subjected to high scale. We have attempted to perform the reaction in open vessel at atmospheric pressure. This work is a step towards the development of easy and durable method for the chemical depolymerization of waste PC.

II. EXPERIMENTAL SECTION

Materials and methods

The used and non-working CDs and DVDs for this study were collected from the students of DTU, Delhi, India. The obtained CDs were crushed into the arbitrary sizes and shapes, keeping the particle size minimum possible by manual crushing. The crushed samples were washed with acidic, basic and neutral water and dried before being charged into the round bottom flask. Commercial BPA, glycerol, sodium hydroxide (NaOH), BF₃-etherate, AlCl₃, acidic alumina, and montmorillonite clay were purchased and used without further purification. Melting point was determined on a laboratory capillary melting apparatus and are uncorrected. FTIR spectrum was recorded on a Perkin Elmer 1710 FTIR spectrophotometer. The ¹H NMR and ¹³C NMR were recorded on a Bruker Avance-300 spectrophotometer (300 MHz).

General procedure for chemical degradation of PC

Method – I: Crushed polycarbonate sample (5 g) was taken in round bottom flask (250 mL). The glycerol and water were added in the ratio as given in tables 1 and 2. Further, an aqueous solution of NaOH (0.5 M, 50 mL) was added to the system. This mixture is heated on oil bath at a temperature of 150-160°C for time period ranging from 6 to 36 hours, with continuous stirring on a magnetic stirrer. The reaction mixture was filtered at hot and cooled to room temperature. This filtrate was kept in refrigerator overnight. The obtained precipitate was filtered and re-crystallized from hot water. The product was characterized by chemical test and spectroscopic data. The chemical test was done with ferric chloride.

Method – II: In a round bottom flask (250 mL), bisphenol-polycarbonate (5 g) was suspended in THF (200 mL) and put under vigorous stirring for 1 hour. To this reaction mixture ethanol (20 mL) was added and further refluxed for 12 hours. The reaction mixture was filtered at hot and cooled to room temperature. The reaction mixture was further treated with aqueous HCl. This was extracted with diethyl ether (CH₃CH₂OCH₂CH₃). The solvent was passed through anhydrous Na₂SO₄ and evaporated under reduced pressure. The recrystallization from hot water gave bisphenol A (BPA).

Mp. 160°C (Lit. mp. [27] 158-159°C); IR (KBr, cm⁻¹): 3397, 2973, 2960, 2870, 1612, 1598, 1510, 1435, 1362, 1218, 826; ¹H NMR (CDCl₃) ppm: 1.70 (s, CH₃), 5.40 (s, OH), 6.75 (m, ArH) and 7.01 (m, ArH); ¹³C NMR (CDCl₃) ppm: 31, 42, 113, 128, 140, 158.

III. RESULTS AND DISCUSSION

The chemical depolymerization of waste PC have been carried by two different methods. In the first method, the waste CDs and DVDs were manually crushed into small pieces. The sample was treated with glycerol and water in the ratio given in table 1. Further, an aqueous solution of sodium hydroxide was added to the reaction mixture as an alkaline catalyst. This mixture was heated from 100-250°C for 6 to 36 hours to optimize the time and

temperature (Tables 1 & 2). The reaction failed to give any product till 160°C for 6 hours, however 5-10% of BPA was isolated between 170-250°C. From 12 hours onwards, the formation of BPA was observed. The best result was obtained at 150°C after 24 hours. There was no increase in the yield observed beyond 24 hours. There was decrease in the yield have been observed beyond 170°C (Table 1).

Table 1. Yield (%) for temperature and time optimization for depolymerization

S. No.	Temp. (°C)	Time (h)→ Yield* (%)↓					
		6	12	18	24	30	36
1	100	0	27	30	30	38	40
2	130	0	40	52	60	60	61
3	150	0	40	50	65	65	65
4	160	0	37	48	60	60	60
5	170	5	35	45	52	55	50
6	200	8	35	42	46	46	46
7	250	10	41	42	49	50	49

*isolated yield of BPA; reaction condition: PC 5g, G:H₂O 2:1

Table 2. Optimization of solvent system for depolymerization

S. No.	G:H ₂ O	Yield* (%)	S. No.	G:H ₂ O	Yield (%)
1	1:0	35	8	2:5	28
2	1:1	30	9	3:5	32
3	1:2	28	10	4:5	39
4	1:3	25	11	6:5	45
5	1:4	23	12	7:5	58
6	1:5	23	13	8:5	60
7	0:5	20	14	2:1	60

*isolated yield of BPA; reaction condition: PC 5g, Temp. 130°C, Time 24h

Table 3. Optimization of reaction condition with acidic catalyst

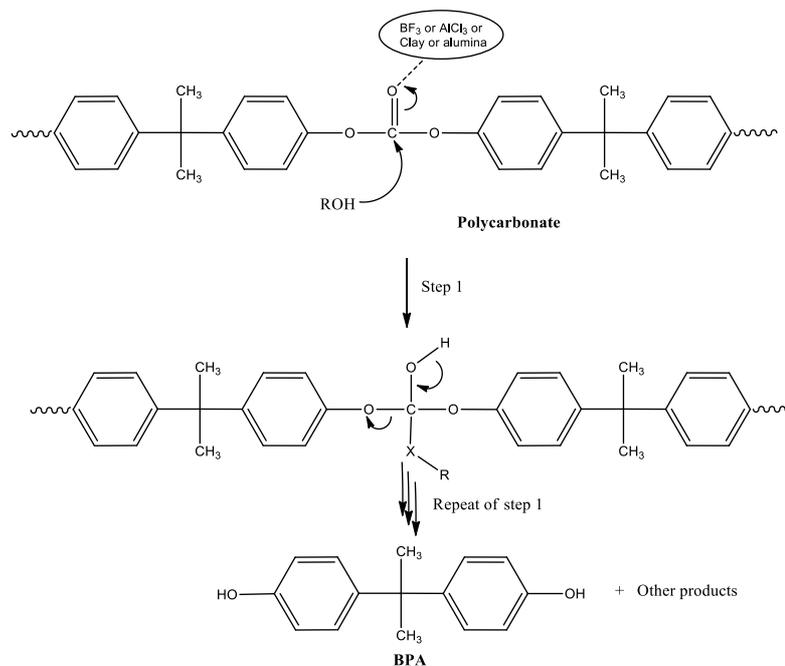
S. No.	Catalyst	Amount of catalyst	%Yield of BSA*
1	BF ₃ -etherate	0.5 mL	25
2		1.0 mL	28
3		1.5 mL	30
4		2.0 mL	45
5		2.5 mL	45
6		3.0 mL	46
7	AlCl ₃	1.0 g	22
8		1.5 g	30
9		2.0 g	34
10		2.5 g	39
11		3.0 g	48
12	Acidic alumina	2.0 g	20
13		4.0 g	37
14		5.0 g	48
15		6.0 g	50
16		7.0 g	55
17	Montmorillonite clay	2.0 g	25
18		4.0 g	35
19		5.0 g	49
20		6.0 g	55
21		7.0 g	61

*isolated yield

The combination of solvents also played very important role in the depolymerization of polycarbonate. The use of sodium hydroxide with glycerol gave alkoxide ion which was instrumental in the shortening of reaction times as mentioned in method I. The alkoxide acted as nucleophile that helped in depolymerization. In order to optimize solvent composition possessing high water content to make the process environmentally friendly, different ratios of water and glycerol were studied and the results are given in table 2.

The increase in water content causes decrease of BPA recovery yields. The usage of water alone calls the procedure totally green but it increases reaction time which is not economically interesting. Therefore, reaction needs the application of glycerine as a co-solvent [25]. While with increasing water content at constant amount of glycerine, there is negligible difference in yield. The increase in glycerine content afforded considerable increase in yield of depolymerized product (Table 2, Entry 14).

The second method was based on the acid catalyzed depolymerization of PC. In this method, the PC was suspended in THF and treated with acids such as BF_3 -etherate, AlCl_3 , Acidic alumina and montmorillonite clay. This was followed by the addition of ethanol to get BPA and other unidentified products (Scheme 1). The use of montmorillonite was found to be suitable catalyst for depolymerization (Table 3, entry 21). The recovered BPA was characterized by spectroscopic methods and comparison with the literature [28].



Scheme 1. Depolymerization of polycarbonate under acidic condition

IV. CONCLUSIONS

Chemical depolymerization is the potential method for plastic waste to get the corresponding monomers and other value-added products. Glycerol/water system in the ratio 2:1 was found to be a green solvent composition for the chemical depolymerization of PC based CDs and DVDs to get high yield BPA by heating at 150°C for 24 hours using NaOH as basic catalyst. We have also successfully performed acid catalyzed depolymerization in open vessel at atmospheric pressure. The best result for depolymerization was obtained under montmorillonite clay.

Acknowledgments

Authors SS and RS are thankful to Delhi Technological University (DTU) for financial support and infrastructure respectively.

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