

# Green Chemical Recycling of Waste Polycarbonate Plastic

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**Abstract**– Polycarbonates (PCs) are basically polymers containing carbonate group & has significant properties such as good stability and durability. PC plastics are widely used in manufacturing of Compact Discs (CDs), plastics, baby bottles, electric and electronic equipments and packaging. Increased use of polycarbonate creates the problem for environment as they are non-biodegradable so it is necessary to decompose it with suitable methods. A number of techniques have been developed in order to separate and sort polycarbonates. On burning Plastics, polythene, PVC etc. produce highly toxic products such as dioxin and furans in flue gases. Increasing cost of high temperatures combustion and decreasing space of landfills are forcing considerations of alternative options for polycarbonates disposal. Chemical recycling is a way to convert waste plastic to valuable chemical. In this paper we are focusing on recycling process of polycarbonates in an eco friendly way via Green Chemical Recycling. In Green Chemical recycling, Low Temperature require and Using Non-hazards solvent and reagent.

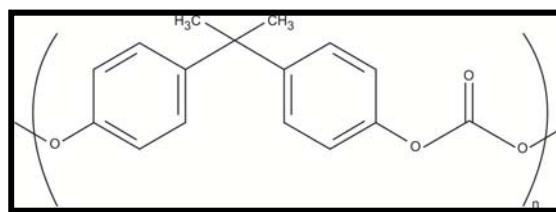
**Keywords:** Polycarbonate, Compact Discs (CDs), Chemical recycling, Green Chemical Recycling.

## 1. INTRODUCTION

The problem of polycarbonate plastic wastes at both the post-manufacturer and post-consumer stages is now an important issue in the global conservation of carbon resources and in the protection of petroleum resources from depletion. In many countries, the major technologies that are used to address this problem are electricity generation, substitute for coke at blast furnaces, and liquefaction to fuel oil. However, these methods do not solve the problem of depletion of petroleum resources, which are not renewable. To address the deplorable worldwide trend of treating plastic wastes as refuse, rather than as recyclable plastic resources, we proposed that plastics be recycled by means of retro-polymerization to monomers and that their reuse as plastics should be the primary solution to this problem, since this would conserve large amounts of manufacturing energy which are inherited in the waste plastics.

**1.1 Chemical recycling is a process to reproduce the constituting unit from the virgin plastic and when it is performed by using green solvents, the process is said to be Green Chemical Recycling.**

Polycarbonates have excellent solvent resistance property. Polycarbonates are long-chain linear polyesters of carbonic acid and dihydric phenols, such as bisphenol A. Polycarbonate resins have excellent clarity and heat resistance, and a low water absorption, making them ideally suited as optical grade material.



Structure of Polycarbonate

The world's first process succeeded in development and industrialization by Asahi Kasei Corp. for producing an aromatic polycarbonate (PC) using CO<sub>2</sub> as starting material. The carbonate group of PC links directly to the residual aromatic groups of the bisphenol. Until Asahi Kasei's new process is revealed, all of carbonate groups of PC in the world were derived from CO as starting material. Furthermore, more than about 90% of PC has been produced by so-called "phosgene process", and the PC contains Cl-impurities. It needs to use not only highly toxic and corrosive phosgene made from CO and Cl<sub>2</sub> as a monomer, but also very large amounts of CH<sub>2</sub>Cl<sub>2</sub> and water, and needs to clean a large amount of waste water. The new process enables high-yield production of the two products, Cl-free and high-quality PC and high-purity monoethylene glycol (MEG), starting from ethylene oxide (EO), by-produced CO<sub>2</sub> and bisphenol-A. PC produced by the new process has many excellent properties compared with conventional PCs. The new process not only overcomes drawbacks in the conventional processes, but also achieves resource and energy conservation. The reduction of CO<sub>2</sub> emissions is also achieved in the new process, because all CO<sub>2</sub> is utilized as the component consisting main chains of the products. The newly constructed commercial plant of Chimei-Asahi Corp. (Taiwan), a joint venture between Asahi Kasei Corp. and Chi Mei Corp., has been successfully operating at

full-production since June 2002. The initial capacity (PC: 50,000 t/y) is now increased to 150,000 t/y. A typical example of the Green and Sustainable Chemistry (GSC) contributing to society and mankind has been realized [4].

Polycarbonate is one of the most widely used engineering plastics because of its superior physical, chemical, and mechanical properties. Understanding the biodegradation of this polymer is of great importance to answer the increasing problems in waste management of this polymer. Aliphatic polycarbonates are known to biodegrade either through the action of pure enzymes or by bacterial whole cells [2]. Very little information is available that deals with the biodegradation of aromatic polycarbonates. Biodegradation is governed by different factors that include polymer characteristics, type of organism, and nature of pretreatment. The polymer characteristics such as its mobility, tacticity, crystallinity, molecular weight, the type of functional groups and substituents present in its structure, and plasticizers or additives added to the polymer all play an important role in its degradation. The carbonate bond in aliphatic polycarbonates is facile and hence this polymer is easily biodegradable. On the other hand, bisphenol A polycarbonate contains benzene rings and quaternary carbon atoms which form bulky and stiff chains that enhance rigidity. Even though this polycarbonate is amorphous in nature because of considerable free volume, it is non-biodegradable since the carbonate bond is inaccessible to enzymes because of the presence of bulky phenyl groups on either side. In order to facilitate the biodegradation of polymers few pretreatment techniques which include photo-oxidation,  $\gamma$ -irradiation, or use of chemicals have been tested. Addition of biosurfactants to improve the interaction between the polymer and the microorganisms, and blending with natural or synthetic polymers that degrade easily, can also enhance the biodegradation. A variety of biodegradable plastics have been developed in order to obtain useful materials that do not cause harm to the environment. Among the biodegradable plastics, aliphatic polyesters such as: poly(3-hydroxybutyrate) (PHB), poly( $\epsilon$ -caprolactone) (PCL), poly(butylene succinate) (PBS), and poly(L-lactide) (PLA) have become the focus of interest because of their inherent biodegradability [11]. The biodegradation of several polymers that had been buried under soil for over 32 years was examined by [7]. No evidence of biodegradation was found for polystyrene, polyvinylchloride, and urea formaldehyde resin. A remarkable degradation was indicated for low density polyethylene thin films which were directly in contact with soil. Severely degraded parts of the film is characterized by whitening. Many small holes were recognized on the surface of the whitened part. The whitened part is specific for the growth of hyphae. FT-IR spectra of the whitened part showed a characteristic band in the vicinity of  $1640\text{ cm}^{-1}$  which was assigned to the stretching vibration of  $\text{C}=\text{C}$  bond. Although the part which was not in contact with soil was clear, it also showed evidence of degradation from the presence of carbonyl band in FT-IR. It was suggested that the degradation of the

clear part is due to the usual thermo-oxidative process, while the degradation of the whitened part is due to the biotic process. Poly(bisphenol-A carbonate) (PC) was degraded in solution at various temperatures ( $26\text{--}70^\circ\text{C}$ ) by different lipases, *Candida Rugosa* (CR), Hog Pancreas (HP), Lipolase (LL), and Novozyme (NV), in various solvents. The degradation of PC was monitored using gel permeation chromatography (GPC). The molecular weights of oligomers obtained were around  $\sim 1,400$  irrespective of the lipases used. Continuous distribution kinetics was proposed to determine the rate coefficients of the polymers and deactivation of the enzyme. The FTIR analysis of the polymer before and after degradation showed that there is large reduction of carbonate linkages and generation of hydroxyl and acidic groups in the broken chains. The optimal temperatures for HP and other lipases were  $50$  and  $60^\circ\text{C}$ , respectively. HP showed higher degradation activity at lower temperatures and the overall degradability of the lipases was in the order of  $\text{LL} > \text{CR} > \text{NV} > \text{HP}$ . The effect of viscosity and polarity of the solvents on the degradation of the polycarbonate was also investigated by [10].

The effect of biofouling on physical, chemical and mechanical changes of Bisphenol A polycarbonate immersed at a depth of three meters at two different locations (Port and FSI, Chennai, India) in the Bay of Bengal Sea over a period of six months was studied by [3]. Biofouling in terms of total suspended solids, organic matter and total viable count was higher at Port than at FSI, probably because of higher dissolved oxygen at the former than at the latter site. An increase in glass transition temperature (from  $133^\circ\text{C}$  to  $147$  and  $144^\circ\text{C}$  at Port and FSI respectively) was observed in the samples indicating loss of amorphous region and conformational change in the polymer. A two fold decrease in tensile strength, a 33% decrease in contact angle and, a reduction in the tertiary methyl and carbonate carbonyl indices were observed. These findings indicate that polycarbonate undergoes a combination of biodeterioration and biodegradation under these conditions.

## 1.2 Thermal and photochemical degradation of polycarbonates: Reaction conditions and reaction mechanisms

Recent publications on the thermal decomposition behaviour of polycarbonates have reached divergent conclusions regarding mechanism was reported by [6]. The conflicting explanations are considered in relation to the differences in degradation conditions and methods of determining the nature of the reaction products. Criticisms made of the homolytic routes which have been proposed for the thermal degradation of some polycarbonates (notably bisphenol A polycarbonate) are answered.

Differential scanning calorimetry studies of the temperature and molar mass dependences for the primary and secondary crystallization behavior of bisphenol A polycarbonate (BAPC)

was reported by [1]. The molar mass dependence of the crystallization rate is found to be much stronger during primary than during secondary crystallization, confirming our earlier claims that primary and secondary processes occur by significantly different mechanisms. Investigations of the secondary crystallization process suggest the existence of a crossover phenomenon from secondary crystal formation at low temperatures to isothermal lamellar thickening at high temperatures. While the results of our low-temperature studies of BAPC provide further support for the model developed in a previous publication on poly(arylene ether ether ketone), evidences from atomic force microscopy and calorimetry of isothermal lamellar thickening above the crossover temperature lead us to anticipate a more unified view of polymer crystallization.

The properties and structure of Bisphenol A polycarbonate (PC) under hydrothermal aging were investigated [12]. The results of mechanical testing indicate that there is obvious elongation at break on the curve of PC samples before hydrothermal aging and no elongation at break after aging. After aging, the bending strength and the tensile strength of PC increase. According to scanning electron microscopy photographs of fracture surfaces, after hydrothermal aging, there are many fragments linked to the fracture surface and the length of deformation at break disappears. Differential scanning calorimetry analysis shows that the glass transition temperature ( $T_g$ ) of polycarbonate increases after hydrothermal aging. Fourier transform infrared spectroscopy shows hydrolytic degradation after hydrothermal aging. The mechanism of the photochemical evolution of bisphenol-A polycarbonate (PC) was probed using different FTIR and UV techniques along with several post-irradiation treatments of irradiated samples, including chemical derivatization reactions, physical treatments and mass spectrometric analysis of the low molecular weight fragments [9]. The absorption maxima that were found in the carbonyl and hydroxyl regions of the infrared were assigned, and the corresponding photoproducts were identified. These studies show that the photochemical evolution of PC mainly involves two successive photo-Fries rearrangements, a photo-induced oxidation on the side-chain and a phenyl ring oxidation. These multiple reaction pathways are shown to be largely dependent upon the spectral distribution of the excitation light source and whether oxygen is present.

### 1.3 Chemical recycling of polycarbonate

Alkali-catalysed depolymerization of polycarbonate (PC) wastes by alcoholysis in supercritical or near critical conditions has been studied in order to recover the essential monomer bisphenol A (BPA) and dimethyl carbonate (DMC) as a valuable by-product. This work aims to study the continuous process and possible scale-up for decomposition of both commercial PC and PC plastic wastes using methanol as solvent/reagent and NaOH as alkali catalyst. Total

depolymerization of PC has been achieved working at a temperature range of 75–180 °C and pressures from 2 to 25 MPa. The influence of operation conditions on product yield, selectivity and reaction rate has been studied, including temperature, pressure, methanol/cosolvent ratio and catalyst concentration. BPA yields of 80–90% (kg product/kg PC) were achieved with a further crystallization and separation of the final product, resulting in BPA pure crystals (99.9%). DMC yield reached 35% (kg DMC/kg PC) and was proved to be strongly dependent on pressure and methanol/H<sub>2</sub>O ratio. Non desired by-product yield was negligible when pure methanol was used as solvent and selectivity decreased with increasing methanol/H<sub>2</sub>O ratio [8].

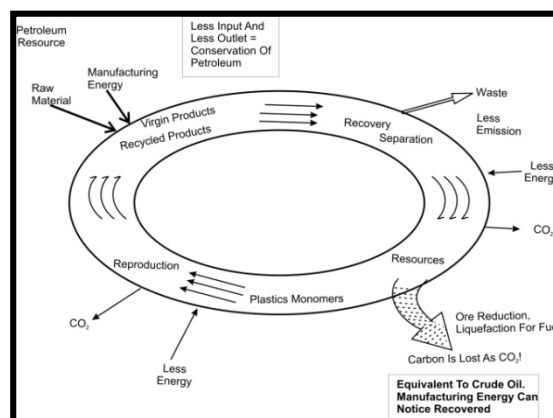


Fig. 1.1: Chemical Recycling of Polycarbonate

An efficient process for the chemical recycling of polycarbonate (PC) waste into diols of bis-phenol A (BPA) for use as raw materials in PU production has been developed [5]. Digestion of PC waste in alkylene glycols, *i.e.*, ethylene glycol (EG) and propylene glycol (PG), with a catalytic amount of sodium carbonate at 180 °C under normal atmospheric pressure afforded partial alkoxylation products of BPA. This initial product mixture was found to consist of BPA (28%) and monohydroxyethyl ether (MHE-BPA, 40%) and bishydroxyethyl ether of bisphenol A (BHE-BPA, 25%) when digested in EG solution. Whereas, in PG digestion solution, the corresponding digestion products consist of monohydroxypropyl ether of BPA (MHP-BPA, 53%) and bishydroxypropyl ether of BPA (BHP-BPA, 21%), with the rest being un-propoxylated BPA. When these digested solutions were further treated with molar excess of urea with a catalytic amount of zinc oxide at 180 °C, BHE from EG or BHP-BPA from PG was produced in high yields. In both digestion processes, cyclic alkylene carbonates, *i.e.* ethylene carbonate (EC) or propylene carbonate (PPC), were observed as the transient intermediates which eventually disappear during the prolonged alkoxylation conditions. ZnO was added to the second step as the catalyst to accelerate urea's transesterification process. Both BHE and BHP products have been successfully utilized in making PU polymers with good

mechanical properties. This chemical approach thus provides a viable alternative for PC recycling.

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