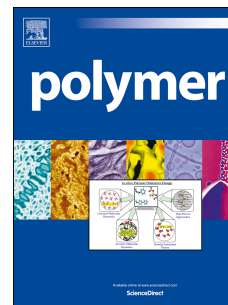


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Recent progress in carbon dioxide (CO₂) as feedstock for sustainable materials development: Co-polymers and polymer blends

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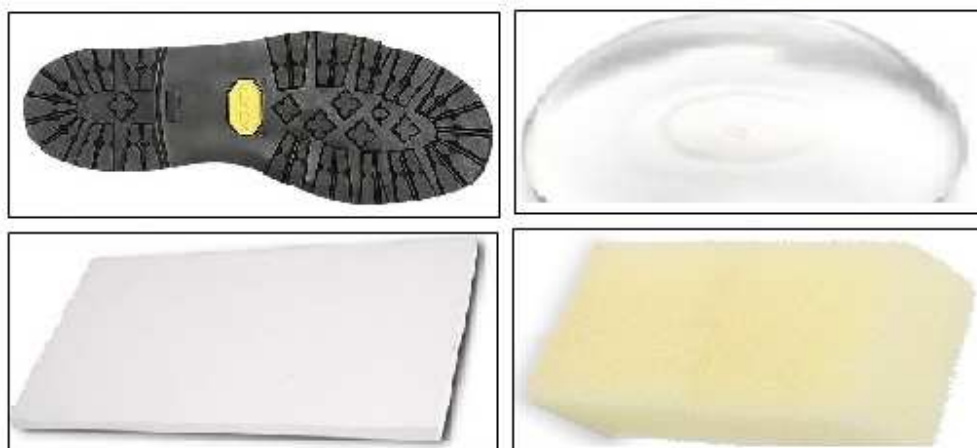
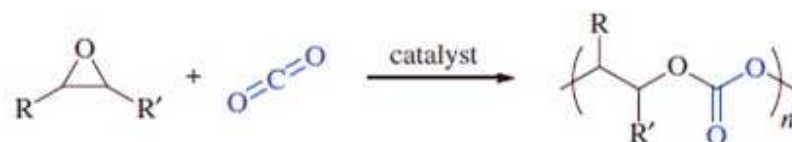
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Recent progress in carbon dioxide (CO₂) as feedstock for sustainable materials**development: co-polymers and polymer blends**Rajendran Muthuraj¹, Tizazu Mekonnen^{2*}

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**Recent progress in carbon dioxide (CO₂) as feedstock for sustainable materials
development: co-polymers and polymer blends**

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Abstract

Combustion of fossil fuels and many other industrial activities inevitably produces carbon dioxide (CO₂) that is released into the atmosphere and is currently deemed to be among the major contributors to global warming. One of the prominent solutions proposed to mitigate global warming concerns from CO₂, capture and storage (CCS), did not attract many CO₂ emitting industries as expected, mainly because of economic reasons. On the contrary, environmental pollution concerns associated with plastic waste, and the demand for sustainable feedstock for their production constitute grand challenges facing our society with regard to the production and use of plastics. As a result, the materials science community is striving to generate sustainable and biodegradable plastics to substitute conventional synthetic plastics from resources that do not pose direct competition with food production. This manuscript aims to provide a general overview of the recent progress achieved in CO₂ based polymers for sustainable biopolymers such as co-polymers, and polymer blends. The synthesis, material properties, processability, and performances of important CO₂ based co-polymers are critically reviewed. Furthermore, a critical review of CO₂ co-polymers as components of polymer blend with a focus on the most relevant CO₂ based aliphatic polycarbonates, poly (propylene carbonates) (PPC), is conducted.

Keywords: Carbon dioxide, poly (propylene carbonate), poly (ethylene carbonate), polymer blends, biodegradable polymers, packaging, biodegradability

1. Introduction

1.1. Carbon dioxide as a resource rather than a greenhouse gas burden

Carbon dioxide (CO₂) is produced by several anthropogenic activities, and it is considered as the major contributor to global warming because of its greenhouse properties. Current emission rate of CO₂ is about 35 billion tonnes per year with major sources from combustion of fossil fuel, utilization of biomass for energy and decomposition of carbonates (mainly in the steel and cement industries) [1]. Some reports showed that the accumulation of CO₂ in the atmosphere has increased from a concentration of 270 ppm at the beginning of the industrial revolution to more than 385 ppm today [2]. This increase is regarded as a possible cause for the greenhouse effect that brings about global warming, and its mitigation is a subject of environmental concern. While carbon dioxide is indispensable for the existence of all living organisms via photosynthesis of green plants, the utilization of carbon dioxide as a feedstock for industrial products is rather limited. More recently, the capture and utilization of CO₂, and its chemistry in general has attracted the attention of the scientific community.

It is anticipated that carbon-based fossil fuels will continue to supply a sizeable portion of the energy consumption for at least the next few decades. Consequently, an increase in CO₂ emission resulting from the use of fossil fuel will continue to raise serious concerns in relation to its greenhouse effect, and as a result, there is a tremendous effort to reduce CO₂ accumulation. Direct reduction of CO₂ emission from the source, CO₂ capture and storage, and conversion of CO₂ into building block for platform chemicals and fuels are widely accepted approaches to mitigate the accumulation concerns. In this context, the use of CO₂ as a carbon building block to produce basic chemicals, plastics, inert solvents, fuels, and other high value products is desirable not only to limit its emission into the atmosphere, but also to partially replace fossil derived resources to produce

chemicals and materials. More recently, significant research and development effort is in place to investigate possible applications of CO₂ for value-added applications (Figure 1). CO₂ is an attractive feedstock because it is abundant, inexpensive, safe, non-flammable, non-oxidant, FDA approved for food related use, balanced geographic distribution, and renewable. In addition, it is suitable for the separation and extraction of thermally unstable materials, and can be used as a building block for making commodity chemicals, solvents, fuels and materials. However, it is a relatively low energy (C₁) and inert molecule. This is a major hurdle to the scientific community as it means that reactions involving CO₂ consume a lot of energy, and thus catalysts that overcome the low reactivity need to be developed [3].

The potential uses of CO₂ in chemical products such as carboxylates, carbonates, and carbamates are extensively reported in the literature [4]. CO₂ can also have applications as refrigerants, fire extinguishing gas, industrial solvent, and production of carbonated beverages. Several companies represent success stories on the utilization of CO₂. For instance, Covestro (former Bayer Material Science), launched a polyurethane foam product from their manufacturing plant near Cologne, Germany based on polyether polycarbonate polyol precursor partially derived from CO₂ [5]. In addition, Novomer Inc., a Cornell University spin-off, has filed several patents on conversion processes, catalysis, polymer synthesis and applications of CO₂ derived polyols [5–7]. The company has sold a portion of their technology (known as Converge®) to Saudi Arabia's Aramco for a \$100 million [8] Converge® is reported to provide high performance, cost competitive and more sustainable CO₂ based polyol for specialty coating, adhesive, sealant, foams, and elastomer applications. Petronas, a Malaysian multinational oil and gas company, has been capturing about 160 ton of CO₂ per day from steam reformers since 1999 [9]. The captured CO₂ from the reformers is then purified (especially from H₂S and SO_x pollutants) and used for urea fertilizer production in combination with ammonia.

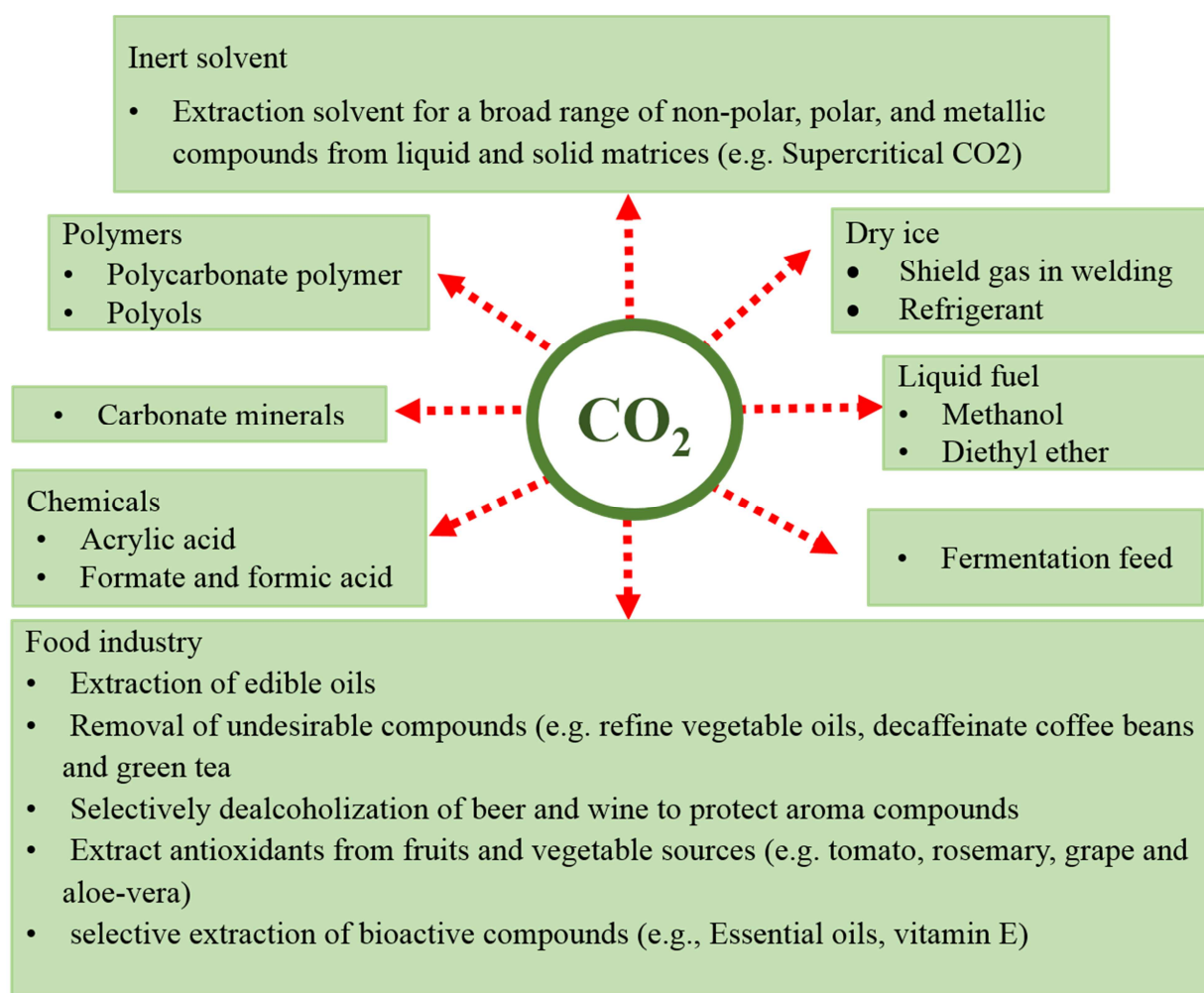


Figure 1. CO₂ as a renewable feedstock in common consumer applications

Furthermore, CO₂ has the potential to become a strategic molecule for the progressive introduction of renewable chemicals and materials [10] that are not based on agricultural feedstock, which currently are competing with food production [11]. The objective of this paper is to critically review the recent progress in the utilization of carbon dioxide for bio-based plastics development. It highlights brief updates on the capture and utilization of CO₂, and provide a detailed overview of CO₂ based co-polymers, and their potential applications. Polymer blends obtained from carbon dioxide based polymers are also critically reviewed.

1.2. Carbon dioxide capture, storage and availability as a resource

To reduce CO₂ emissions and prevent its concentrations in the atmosphere, it can be separated from the flue gas of; for example, a fossil fuel based power plant and subsequently sequestered (Figure 2). Carbon capture and sequestration (CCS) is considered as one of the proposed technics as a means to enable continued use of fossil fuels. CCS technology involves three major process steps: capture, transport and sequestration. Capture is currently the most expensive process step and a target of vital technology research focusing on cost reduction. Some reports show that CO₂ capture can contribute up to 75% of the overall CCS cost [12–14]. Suitable CCS technology storage sites include depleted gas fields, oceans, and saline aquifers. Such sites require a highly impermeable rock layer to prevent CO₂ leakage from the storage reservoir. Despite the significant advances made in CCS, there are still inherent limitations to it. These limitations include excessive energy consumption and associated economics for CO₂ capture, low capture efficiency and slow sorption kinetics [1], uncertainties in storage life time of sites, seismic instability and accidental leakage safety concerns from storage sites [1,15], and capacity constraints [15].

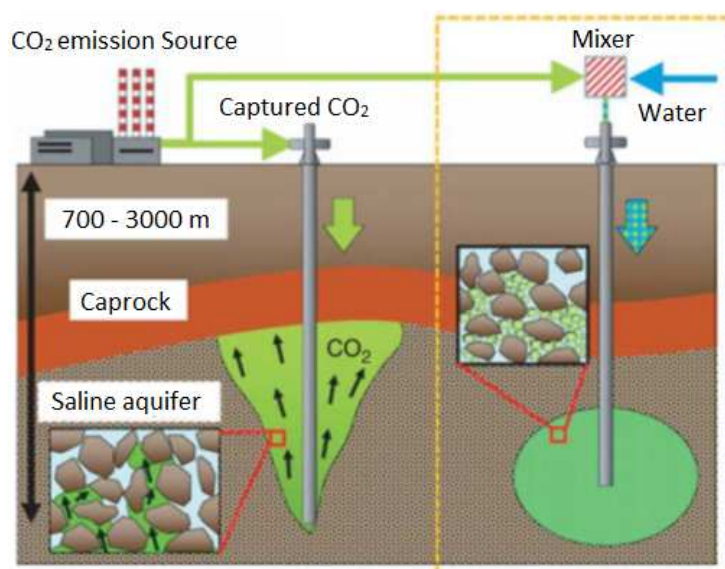


Figure 2. Schematic image of CCS. Adapted from ref. [16] Wiley copyright © 2014.

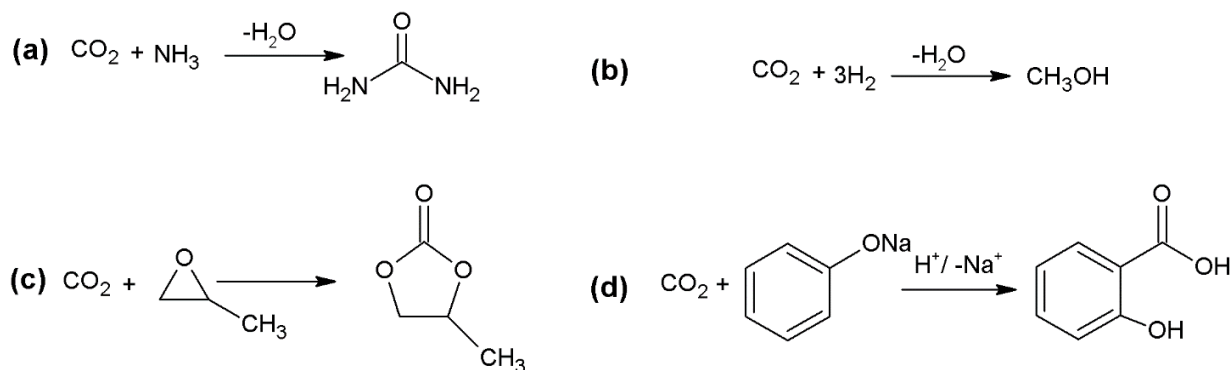
Also, underground injection of CO₂ into reservoirs is widely accepted as a visible means for reducing anthropogenic CO₂ emissions. In this technology, CO₂ is injected into an oil and gas

reservoirs to mobilize and displace oil and gas known as the enhanced oil recovery (EOR) platform to create economic gains that partly offset sequestration costs [15]. One of the most popular such projects is the Weyburn EOR project in Saskatchewan, Canada that employs both EOR and CCS [17]. In this project, 5000 tonnes/day of CO₂ (95% pure) is injected, and a total of approximately 20 million tonnes of CO₂ is expected to be stored in the reservoir over the EOR project life. It is important to highlight here that CO₂ based EOR cannot be applied to all oil reservoirs because of mainly economic constraints. For its efficient use in oil and gas reservoirs, large quantities of pure CO₂ need to be obtained at a reasonable cost that includes CO₂ separation, transportation and injection installations. More recently, cheaper CO₂ obtained from gas fields is gaining more popularity particularly in the US because of the availability of CO₂ gas fields, such as the Bravo Dome and McElmo Dome gas fields [16]. Other technologies proposed to mitigate CO₂ release include CO₂ capture via anion-functionalized liquids capture [18,19], mineral CO₂ sequestration in which CO₂ is chemically stored in solid carbonates by the carbonization of minerals into a geologically stable final form [16]. Leung *et al.* [13] conducted an extensive literature review on the current status of CO₂ capture and storage technologies.

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Emerging technologies, such as zero emission power plants, are expected to significantly reduce the complexity of separation, which is perhaps the costliest process step in recovering CO₂. Membrane separation processes, also provide several advantages over other conventional separation techniques. For instance, membrane materials that provide high selectivity for CO₂ over oxygen or nitrogen using polymeric and inorganic materials [12] are plausible options. Porous membranes with supporting amine solutions were also shown to be effective for the separation of CO₂ [20]. The use of specifically designed sieves, also known as molecular sieves, that separate molecules based on molecular weight or size have shown a potential for CO₂ adsorption. Efforts to enhance the adsorption of CO₂ by molecular sieves include incorporation of amine functional group on the sieves that has the prospect to interact with CO₂ resulting in the formation of, for example surface ammonium carbamate in anhydrous conditions, and carbonate species in hydrous conditions [12,21].

Although it is unlikely that CO₂ utilization could consume significant quantities to mitigate the emission concerns, development of products and processes for chemical transformation of CO₂ into useful compounds would be of immense importance from the standpoint of green and sustainable chemistry [1]. This is because CO₂ is attractive as an environmentally friendly chemical reagent [3,22,23]. While large-scale utilization of CO₂ is still limited, production of urea is currently the largest use of CO₂ in organic synthesis. It is also used to produce industrial scale salicylic acid and several carbonates (Scheme 1). The rapidly increasing interest in using supercritical CO₂ as a natural product extraction and fractionation agent, and its use as a hydrophobic solvent that is capable of replacing organic solvents in several applications presents important uses of CO₂. For example, the use of dense CO₂ as one of the few reaction medias used for the direct synthesis of hydrogen peroxide from H₂ and O₂ is notable [24].



Scheme 1. Utilization of CO_2 as a feedstock for chemical synthesis of: (a) Urea; (b) Methanol; (c) Cyclic carbonate; (d) salicylic acid [25–27].

The capture and conversion of CO_2 to produce sustainable, synthetic hydrocarbon or carbonaceous fuels, most notably for transportation purposes as a mid- to long-term option is also being investigated. In this regard, four major strategies involving CO_2 conversion by physico-chemical approaches are highlighted: sustainable (or renewable) synthetic methanol, dimethyl ether, syngas production derived from coal-, gas- or oil-fired electric power stations flue gases, and photochemical production of synthetic fuels [28]. Olah and co-workers [29] presented a detailed literature review analysis of the chemical recycling of CO_2 to methanol and dimethyl ether. Other researchers have reported the employment of genetically modified cyanobacterium to consume carbon dioxide and produce liquid fuel isobutanol that has the potential to complement gasoline [30]. Table 1 summarizes key CO_2 transformation pathways to chemicals and fuels. The recent advancement in carbon capture and sequestration as a key element in the global effort to mitigate emissions is providing substantial quantities of CO_2 as a renewable feedstock for conversions to commodity chemicals, fuels, and polymeric materials at a reasonable cost.

Table 1. Conversion process of CO_2 to fuels, and chemicals [31–35].

Transformation Process	Examples of Applications	Comments
Artificial photoreduction	- Carbon monoxide (CO), formic acid, synthesis gas (CO/H ₂)	- Products of photoelectrochemical reduction of CO ₂ is dependent on the metal photoelectrodes.
Electrochemical reduction	- Numerous products including CO, HCOOH, alcohols and light hydrocarbons can be reduced from CO ₂ .	- There is a significant thermodynamic efficiency improvement need
Hydrogenation	- Heterogeneous catalytic hydrogenation of CO ₂ may produce a wide variety of products including methane, methanol, dimethyl ether, higher hydrocarbons, and alcohols.	- Cost of hydrogen could be a challenge
Synthesis of organic carbonates	- Synthesis of carbonates such as dimethyl carbonate, dialkyl carbonates with longer chains (e.g. diphenyl carbonate, cyclic carbonates)	- Very few metal oxides are catalytically active for the direct carbonate synthesis from alcohol and CO ₂
Reforming	- Involves the reaction between hydrocarbons (C _n H _m) and CO ₂ to form synthesis gas	- Suitable catalyst development is still at its infancy
Photocatalytic reduction of CO ₂ with water	- Renewable and carbon-neutral fuels, CO and CH ₄ can be produced when water vapor serves as the electron donor.	- Reduction of CO ₂ by typical catalyst TiO ₂ is still low.
Biological fixation	- Use CO ₂ as a C ₁ source by microalgae for biofuels (e.g. ethanol) and chemicals (e.g. succinic acid) production	- Gas fermentation technology is still under development. C ₁ feedstock is not energy dense.

2. CO₂ based co-polymers

The development of sustainable and environmentally benign polymers from renewable feedstocks is important to reduce the dependence of most engineering and commodity plastics on fossil-based resources[36–38]. Moreover, the global shift from reusable containment and packaging to single-use contributed to an extraordinary growth in the plastics market [39]. For instance, the global plastic production reached about 407 million tonnes in 2017 [39]. The most extensively produced commodity plastics such as low density poly(ethylene) (LDPE), linear low density poly(ethylene) (LLDPE), high density poly(ethylene) (HDPE), poly(propylene) (PP), poly(ethylene terephthalate)

(PET), poly(styrene) (PS) and poly(vinyl chloride) (PVC) constitute close to 70% of the overall production as shown in Figure 3a [39]. Overall, about 38% of all plastics produced are employed in packaging applications (Figure 3b), mainly because of the appealing cost structure and excellent packaging attributes of plastics [40] over other materials such as metals or glasses.

In addition to their prevalent use, the stable carbon – carbon bond in the backbone of most of these polyolefin and polyolefin derivative plastics that withstand biodegradation, resulted in a tremendous increase in the share of plastics in municipal solid waste. In middle – and high income – countries, plastic waste increase was estimated from less than 1% in 1960 to more than 10% by 2005 [39,41]. The geographic distribution limitation and unstable and unpredictable prices of fossil fuel feedstock for such plastics coupled with the alarming waste accumulation and pollution associated with non-biodegradable plastic caused an increasing research interest in sustainable polymers. In the quest for an alternative raw material to fossil derived resources, agricultural feedstock such as polysaccharides, proteins, chitosan, lignin, algae, glycerol, and lipids are being extensively studied [11,42–45].

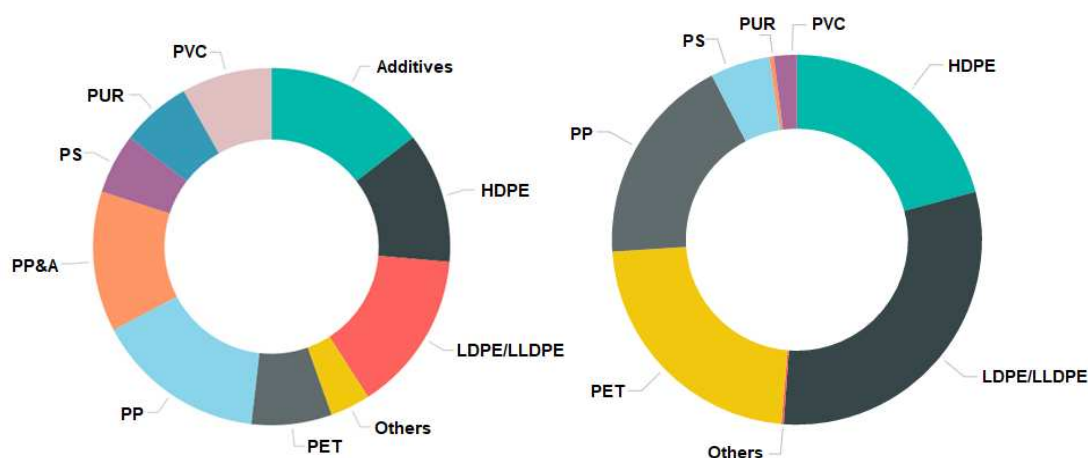


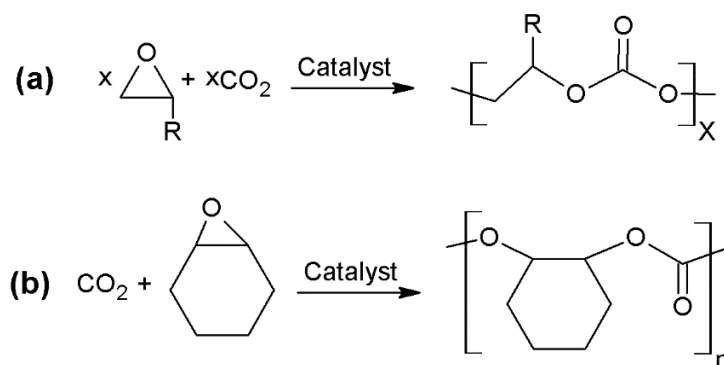
Figure 3. (a) Type of plastics produced worldwide (in percent); and (b) plastic use in the packaging industry in the world in 2015 [40]. Others include thermosets, elastomers, coatings etc. that are not listed here.

2.1. Synthesis of CO₂ polymers

More recently, research and development efforts in catalysis, process development, and polymer science and engineering put a spotlight on CO₂ based polymers. However, the kinetic and thermodynamic stability of CO₂ has limited its extensive utilization as a feedstock for polymers. Many reactions pathways for the conversion of CO₂ into useful polymers involve positive change in enthalpy (ΔH) and thus they are endothermic. Consequently, a substantial input of energy, effective reaction conditions, and often active catalysts, are necessary for such conversions [46]. Despite these challenges, methods to overcome the high energy barriers based on reduction, oxidative coupling with unsaturated compounds on low valent metal complexes, and increasing the electrophilicity of the carbonyl carbon are being developed [23].

CO₂ can be copolymerized with a number of cyclic ethers (e.g. cyclohexene and propylene epoxides, aziridines, episulfides) to produce a range of novel alternating aliphatic polycarbonate co-polymers [47]. Aliphatic polycarbonates refer to thermoplastic polycarbonates with a repeating carbonate [$-\text{O}-\text{C}(\text{O})-\text{O}-$] backbone linkage with no aromatic groups between the carbonate linkages, contrary to the most useful engineering aromatic polycarbonates. Some of the aliphatic polycarbonates produced by the alternating copolymerization of CO₂ with epoxides include poly(ethylene carbonate), poly(propylene carbonate), poly(butylene carbonate), poly(pentene carbonate), poly(hexene carbonate), poly(styrene carbonate), poly(cyclohexene carbonate), poly(cyclopentene carbonate), and poly(cyclohexadiene carbonate) [48–50]. Of these, poly(ethylene carbonate) (PEC), poly(propylene carbonate) (PPC), poly(butylene carbonate) (PBC), and poly(cyclohexene carbonate) (PCHC), as shown in Scheme 2, constitute major industrial CO₂ application potentials [27]. The utilization of the energy rich three-membered oxirane to react with CO₂ and produce alternating CO₂ based aliphatic polycarbonates is gaining

ground as a sustainable alternative to the old technology of ring opening polymerization of (ROP) of cyclic carbonate monomers to produce synthetic aliphatic polycarbonates. The other alternative to produce aliphatic polycarbonates has been the environmentally malign synthesis that involves polycondensation of trans-diols (e.g. bisphenol –A) with toxic phosgenes.

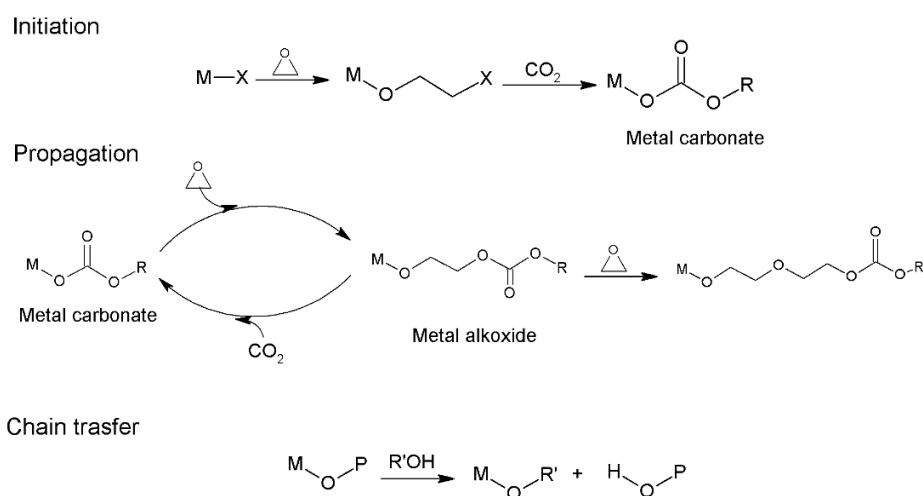


Scheme 2. Copolymerization of epoxides with CO_2 to produce: (a) $\text{R} = \text{H}$, poly (ethylene carbonate) (PEC), and $\text{R} = \text{CH}_3$, Poly (propylene carbonate); (b) poly (cyclohexene carbonate).

As shown in Scheme 2, the co-polymerization of CO_2 with oxirane occurs in the presence of catalysts. The successful copolymerization of CO_2 with styrene oxide, limonene oxide, indene oxide, and epichlorohydrin have also been reported in the literature [51]. Although, the reaction scheme for the synthesis of PEC and PPC aliphatic carbonates were reported in 1969 [52,53], their use has been limited mainly because of limitations in catalysis efficiency and the material performance of the polymers. Thermal properties are among the major challenge of most aliphatic polycarbonates. For instance, the glass transition temperature (T_g) of PEC and PPC is $20\text{ }^\circ\text{C}$, and $35 - 40\text{ }^\circ\text{C}$ (close to human body temperature), respectively [54]. Such T_g ranges indicate that the polymers are too flexible for a rigid engineering plastic applications, and too rigid for a typical industrial elastomeric application, warranting the need for further modification.

Many studies [55–59] demonstrated that the ring-opening co-polymerization of carbon dioxide and epoxides is highly dependent on the selection of catalyst. Recent research effort results

demonstrated that various homogeneous and heterogeneous organometallic catalysts that contain Zn (II), Cr (III), and Co(III) complexes are commonly used [60]. The proposed series of catalytic polymerization reactions are illustrated in Scheme 3. The polymerization reaction initiates when an epoxide molecule displaces a metal bound initiator ligand, and subsequent ring opening by the nucleophilic attack of a carbonate group or ligand to form a metal alkoxide intermediate. Carbon dioxide then gets inserted into the intermediate to form a metal carbonate species, and this carbonate serves as the nucleophile for the succeeding chain propagations. The ring opening continues, and the reaction therefore propagates cycling between metal alkoxide and carbonate intermediates. Changing the reactions conditions or exposure to reagents lead to hydrolysis of the growing chain, and polymerization termination through the formation of a polymer chain end-capped with a hydroxyl group [14,55].



Scheme 3. Catalytic cycle of epoxy – CO₂ copolymerization [14].

In the quest for improved catalysts for CO₂ co-polymerization, research attentions have focused on environmental benign organometallic catalysts. This is to avoid the undesirable consequence of rather toxic metal catalysts that can potentially limit some industrial applications, and to qualify for composting and biodegradation requirements of the polymeric materials. In this contest, metal

center catalysts based on Zn, Mg, Fe, Ti, Al, etc. are being extensively investigated. Catalyst properties such as surface area, amount of crystallinity, size, and morphology can also significantly influence the catalytic activity besides the type of catalyst [61], and as such it is another growing area of research. For instance, due to the excellent catalytic activity, selectivity, low cost, safety, and ease of synthesis, Zinc glutarate appeared to be one of the most effective compounds for commercial use in the copolymerization of CO₂ and propylene oxide [62,63]. Therefore, several studies have focused to enhance the catalytic activity of Zinc glutarate to produce cost competitive PPC [61,64]. However, the currently available best catalyst systems are still one or two orders of magnitude lower in efficiency than the common catalysts used for the synthesis of polyolefins [65]. The inefficiencies are associated with activity, product yield, and purity of the product [60].

Because of the properties and success in catalysis, numerous studies show that PPC is the leading CO₂ based co-polymer in terms of production. For example, a report by Research and Markets [66] show that about 63,000 tonnes of PPC was produced in China alone in 2016, with an ex-works price of about USD 4.02/kg. In the same year, the global market size of PPC was estimated to constitute about \$610 million and is expected to grow at a rate of 6.64% annually. Key industrial players in the PPC market includes Empower materials, SK Energy, Novomer, BASF, Cardia BioplasticsTM, Tianguan, Nantong Huasheng, Bangfeng, Jiangsu Jinlong-CAS Chemical Co., Ltd, etc. Some governments (e.g. China) have started issuing policies to support the development of CO₂ based biodegradable polymers including PPC. Reports on the commercial production of other CO₂ based polymers is rather scarce.

2.2. Mechanical and thermal properties

Aromatic polycarbonates are well-known engineering thermoplastics with a range of applications such as eyewear, medical devices, automotive components, digital discs, lighting fixtures, etc. The success of these aromatic polycarbonates is due to the unique combination of properties: extreme toughness, outstanding optical transparency, high heat distortion resistance, impact resistance, and excellent compatibility with several polymers [67]. On the contrary, aliphatic polycarbonates are largely unexplored commercially until the 2000s despite their synthesis in the 1930s' at Carothers' laboratory of DuPont [68]. This is mainly because of the characteristic low melting point, high susceptibility to hydrolysis, and low molecular weight that result in a rather inferior property compared to many traditional polymers [51].

Recent commercial success stories of aliphatic polycarbonates from CO₂ are mainly as a low molecular weight polycarbonate polyols, to produce polyurethanes for various applications including automotive, coating, adhesive applications. Overall, the use of CO₂ as a feedstock to produce polycarbonate co-polymers, while mitigating CO₂ accumulation in the environment, resulted in a renewed research and commercial interest in aliphatic polycarbonates. Moreover, the quest for biodegradable industrial biopolymers for which the hydrolysis susceptibility of aliphatic polycarbonates that used to be perceived as major limitations turned into their competitive advantages [51,69,70]. This renewed research interest led to an advancement in catalysis and application development efforts of CO₂ co-polymers.

Like other polymers, the properties of the aliphatic polycarbonates depends on the backbone and side chains [71]. For example, Thorat and co-workers [48] reported that PEC in its low T_g range (ca. 10 °C) behaves as an elastomer at room temperature with an elongation at break of over 600% and completely recovers to the initial length after unloading. Conversely, the mechanical properties of PPC are more complicated owing to its amorphous morphology and higher T_g (35–42 °C) compared to PEC. Overall, PPC is brittle at low temperatures (below 20 °C), and

exhibits poor dimensional stability at elevated temperatures. Table 2 presented mechanical properties and thermal degradation temperatures of a few common CO₂ based aliphatic polycarbonates. Comparison of PPCs as a function of molecular number average (M_n) (Table 2) indicates that higher molecular weight improves tensile modulus. However, most commercial PPCs display a wide range of polydispersity index (PDI), and comparisons based on solely M_n would not be accurate. Studies have shown that CO₂ derived aliphatic polycarbonates are completely amorphous [48,60]. Crystallization of PEC and PPC has not been observed, even for a regioregular microstructure.

Thorat *et al.* [48] studied the physical properties of a homologous series of CO₂ based aliphatic polycarbonates with different side chain-lengths and showed that factors such as side chain length, intermolecular dipolar interaction, and stiffness of the backbone chain affect the mechanical, thermal properties and decomposition behavior of CO₂. A notable observation in this study includes polycarbonates derived from long-chain epoxides that exhibit T_g below room temperature. On the contrary, polycarbonates derived from cyclohexene oxide showed a T_g of 105 °C, which is among the highest reported for similar polymers. Koning *et al.* [72] synthesized poly (cyclohexane carbonate) (PCHC) from CO₂ and cyclohexene oxide. The properties of the PCHC showed a high T_g of 135 °C in comparison with both PPC and PEC, and behaves like a brittle polymer with an elongation at break and tensile modulus of 1.7 % and 3600 MPa, respectively. The brittleness of PCHC is thought to be associated with the low chain entanglement density.

Poly(butylene carbonates) (PBC) prepared using melt polycondensation method, exhibited a degree of crystallinity (calculated from wide angle x-ray diffraction), glass transition temperature, melting temperature, and thermal decomposition temperature of 22%, -32 °C, 55.2 °C, and >180 °C, respectively [73]. In an effort to improve the thermal stability of PBC, Cai *et al.* [74] incorporated cyclohexanedimethylene carbonate and prepared a series of poly (butylene-co-1,4-

cyclohexanedimethylene carbonate) (PBCCs) random co-polymers. The glass transition (T_g), melting temperature and thermal decomposition temperature of the PBCC co-polymers exhibited a monotonous increase with an increase in the concentration of the co-polymer component. The increase in T_g ranges from $-32\text{ }^\circ\text{C}$ for the baseline PBC to $47\text{ }^\circ\text{C}$ for PBCC co-polymers that contain 90% cyclohexanedimethyle carbonate. The increase in thermal decomposition temperature ranges from 337 to $373\text{ }^\circ\text{C}$ for the aforementioned samples [74]. Clear changes in tensile properties and crystallinity was also presented as a result of the co-polymerization effort.

Table 2. Mechanical properties and peak degradation temperature (T_{deg}) of CO_2 based poly (alkylene carbonate) polymers.

Polymer	Tensile yield strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)	Tdeg (TGA, $^\circ\text{C}$)	Reference
Poly(ethylene carbonate)	-	3-8	>600	229	[48]
Poly(ethylene carbonate) (M_n 127 kDa, PDI 1.9)	10	88.04	-	-	[75]
Poly(propylene carbonate) (M_n 50kDa, PDI 1)	21.5	830	330	285	[76]
Poly(propylene carbonate) (M_n 260kDa, PDI 4.97)	17	680	255	290	[77]
Poly (propylene carbonate) (M_n 350 kDa, PDI 5)	15	2000	>300	302	[78]
Poly(butylene carbonate) (M_n 70,400, PDI 1.76)	28.1	320	447	337	[74]
Poly(cyclohexane carbonate) (M_n 42 kDa, PDI 6)	43	3600	1.7	-	[72]

As illustrated in Table 2, the peak thermal decomposition temperature of PPC is above $250\text{ }^\circ\text{C}$ from thermogravimetric studies. It is important to point here out that the PPCs are obtained from different companies, and as a result, there is a difference in the catalyst used for production as is in molecular weight. As expected, the thermal degradation temperatures presented here showed a correlation between molecular weight and decomposition temperatures. The higher molecular weight PPC ($M_n = 350\text{ KDa}$), and the lower molecular weight PPC ($M_n = 50\text{ KDa}$) exhibited a

peak decomposition temperature of 302 and 205 °C, respectively. Overall, the thermal decomposition temperature of PPC is in the range of 180 to 260 °C [79–81], depending on the molecular size, catalyst used to prepare the PPC, the co-polymer component (cyclic propylene carbonate used during PPC synthesis), the ambient gas and the heating rate during the measurement. A study by Tao and co-workers [82] showed the improvement in the thermal degradation behavior of PPC with an increase in molecular weight. The employed thermogravimetric study results are shown in Figure 4a. The onset thermal degradation temperature showed an increase by about 37 °C as the molecular weight (M_n) of the PPC increased from 109 to 227 kg/mol. In general, this study showed that increasing the molecular weight *via* terpolymerization or multipolymerization might be an important method to improve the mechanical and thermal properties of PPCs. In a recent study, the effect of molecular weight (2 to 263 kDa) on the thermal stability of PPC has been reported. The 2 kDa molecular weight PPC is a polyol [83]. It is interesting to note that both 2 kDa and 137 kDa molecular weight PPC showed nearly the same onset thermal decomposition temperature with heating rate of 1 °C/min under N₂ atmosphere (Figure 4b). However, the rate of decomposition of 2 kDa PPC is much faster than PPC with 137 kDa molecular weight. Such behavior is expected as low molecular weight polymers with more end groups can undergo faster unzipping mechanism than high molecular weight polymers. In the same study, the effect of ambient gas during the thermal decomposition of PPC is reported (Figure 4c). The PPC appeared to have higher thermal stability under air atmosphere compared to the corresponding samples under nitrogen atmosphere. This could be due to specific intermediate species during the PPC decomposition process react with oxygen to slow the decomposition. Further investigation is worthwhile to better understand the role of oxygen in PPC decomposition phenomenon.

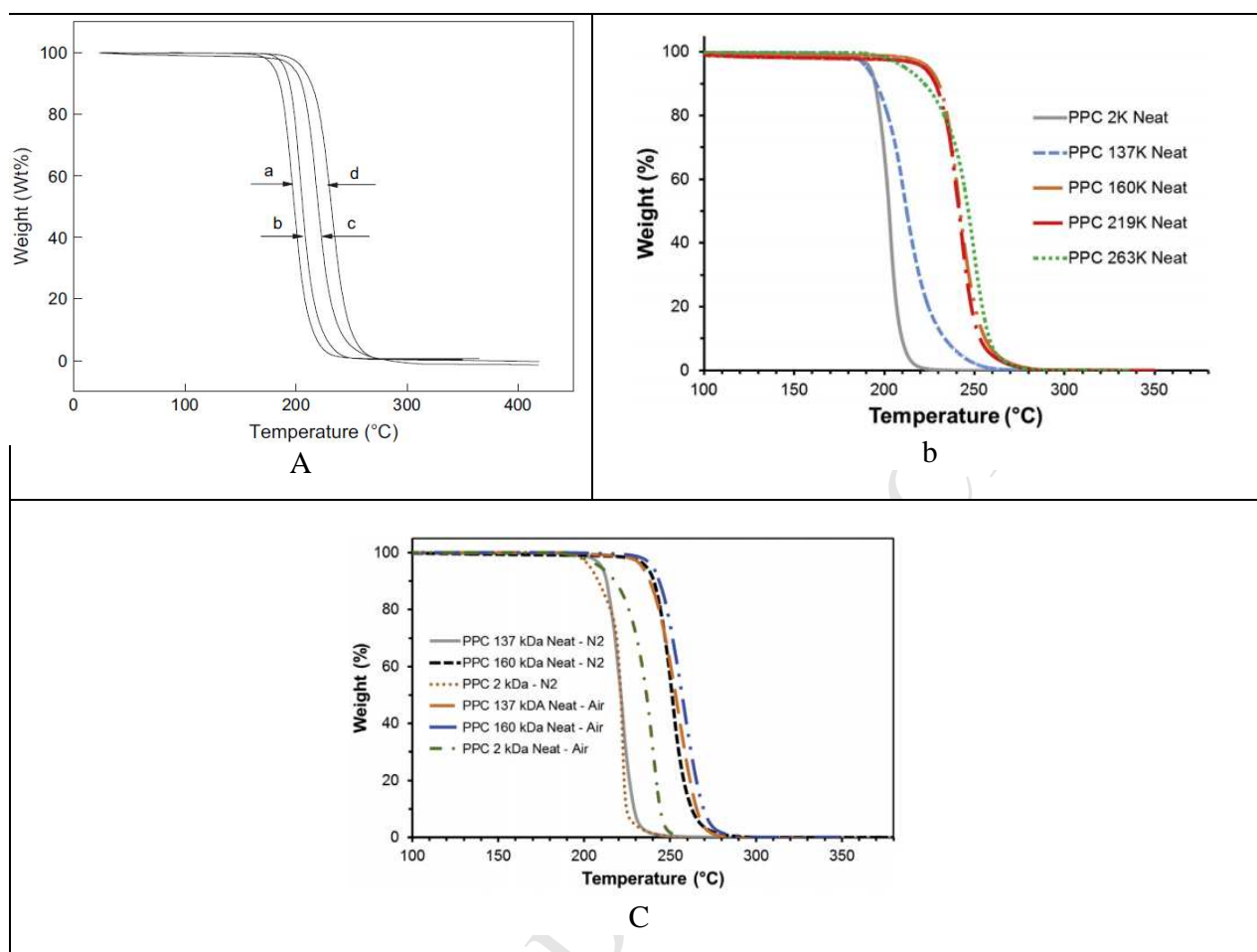
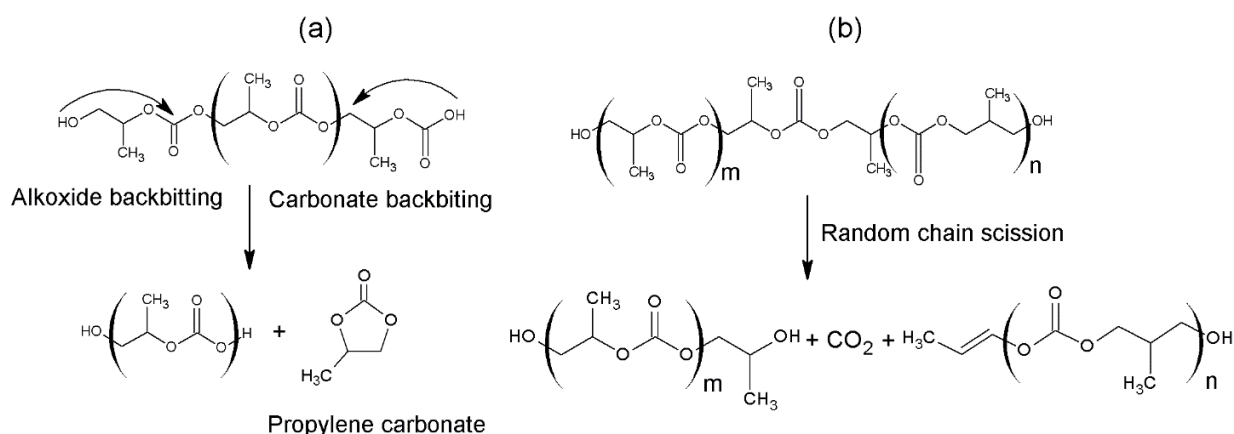


Figure 4. (a) TGA curves of PPC with various molecular weights. (a) $M_n = 109$ kg/mol; (b) $M_n = 132$ kg/mol; (c) $M_n = 156$ kg/mol; (d) 227 kg/mol. Adapted from ref.[82] Springer, copyright ©. (b) Neat Novomer PPC with molecular weights of 2 kDa, 137 kDa, 160 kDa, 219 kDa, and 263 kDa at a ramp rate of 1 °C/min in N₂ atmosphere. Adapted from ref. [81] Elsevier, copyright © 2006. (c) Neat Novomer PPC with molecular weights of 2 kDa, 137 kDa, 160 kDa at a ramp rate of 5 C/min in N₂ and ambient air atmosphere. Adapted from ref. [81] Elsevier, copyright © 2006.

Mechanisms for the thermal decomposition of aliphatic polycarbonates reported in the literature includes: (i) random chain scission (chain scissions occur at random locations), (ii) polymer unzipping/end-chain scission (individual chain ends are stripped successively starting from the end), (iii) chain stripping (side groups are cleaved from the backbone), and (iv) grafting and crosslinking (bonds are created between chains) [60,81,84]. Cyclic propylene carbonate by random chain scission is the typical degradation product generated from thermal decomposition of PPC (Scheme 4) [60,81,85]. Different research teams [86] have studied stabilizing agents and additives

that inhibit polymer chain-end unzipping and random chain scission of PPC, that enhance thermal stability. Maleic anhydride, pyridine, benzoyl chloride, ethyl silicate, acetic anhydride, phosphorus oxychloride, 4-nitrophenyl chloroformate, and vinyl chloroformate have been used to end-cap the PPC and inhibit unzipping reaction during thermal processing [81].



Scheme 4. (a) Chain unzipping reaction in PPC occurring *via* an alkoxide or carbonate backbiting pathway creating the cyclic propylene carbonate as the product. (b) Chain scission reaction in PPC via thermally induced cleavage of C-O bonds creating carbon dioxide as one of the products[81].

Li *et al.* [87] demonstrated that chain unzipping depolymerization dominated the thermal decomposition of PCHC. Separate studies by Bahramian *et al.* [88] and Li *et al.* [87] highlighted the importance of residual metal catalyst system in the thermal decomposition of such polymers. For instance, the onset thermal decomposition temperature of PCHC containing 5 ppm zinc catalyst was 56 °C higher than that of PCHC that contains 4,400 ppm of residual Zinc [87]. For PPC, similar observation of increasing rate of thermal decomposition with an increase in residual catalyst concentration was reported (Figure 5a) [88]. It can be seen from Figure 5a that PPC with 2450 ppm zinc showed two distinct degradation slopes with lower thermal stability compared to PPC with 250 and 1250 ppm Zinc residue. The first change in the slope was attributed to the cyclic propylene carbonate impurity decomposition, which was formed during PPC synthesis. After the purification of the PPC by high-pressure CO_2 /water system, a cyclic propylene carbonate

decomposition was not observed in the PPC, while an improvement in thermal stability was marked. Overall, the thermal stability of the PPC was effectively improved by reducing the residual Zinc catalyst apart from enhancing mechanical properties.

Similarly, Figure 5b presents the thermal degradation of PCHC as a function of various Zinc concentrations from thermogravimetric analysis. The curves showed the increase in the onset and peak degradation temperatures with the reduction in the residual catalyst content. It was also evident that the change in catalyst concentration affected the molecular size of the PCHCs. The number average molecular weight differences among the samples with the three catalyst levels was about 10 kDa among each other, and it can be anticipated that the molecular size variation could also play a role in the observed thermal degradation behaviors. In a broad sense, it appears that PCHC polymers have better thermal stability than PPC and PEC. PEC on the other hand generally exhibits a lower decomposition temperature in comparison with PPC or PCHC [48].

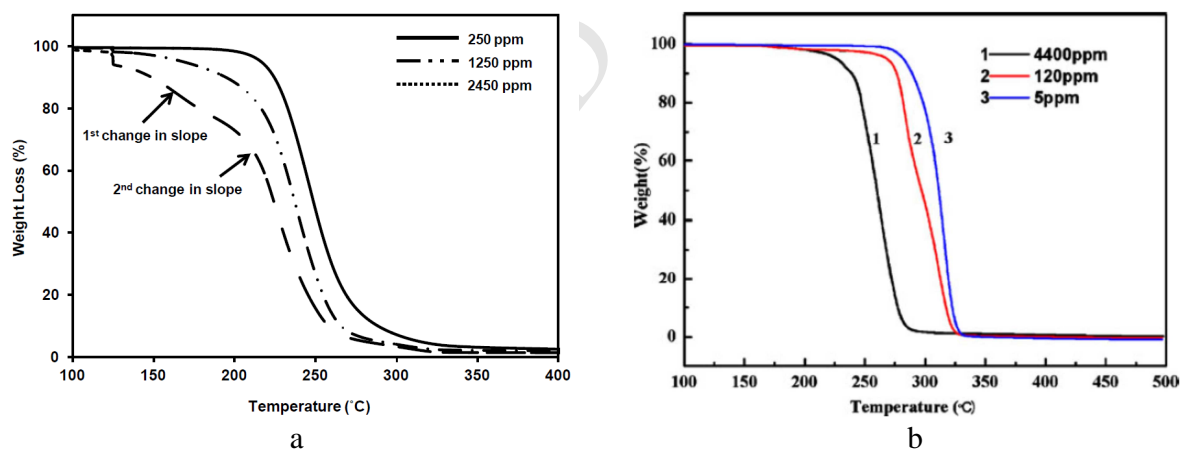


Figure 5. (a) Dynamic TGA curves (N₂- 5 °C/min) for PPC with various zinc contents: (250 ppm Zinc content with Mw of 509,570 and PDI 2.79; 1250 ppm Zinc content with Mw of 508,373 and PDI 2.97; 2450 ppm Zinc content with Mw of 463,746 and PDI 3.26) Adapted from ref.[88] RSC ©. (b) Effect of catalyst residue on thermal stability of PCHC – 1 (Mn = 46.3 KDa, Zn content 4500 ppm), PCHC – 2 (Mn 58.6, Zn content 120 ppm), and PCHC – 3 (Mn 69.6, Zn content 5 ppm). Adapted from ref.[87] Springer, copyright ©.

Tao *et al.*[82] synthesized a range of high molecular weight PPCs by incorporating small quantities of difunctional epoxides to the catalyst system. The variation in molecular weight (M_n) of the PPC resulted in a dramatic impact on both the thermal and mechanical performance of the polymers. Figure 6 presented the dependence of storage modulus (E') as a function of temperature for various molecular weight of PPC from dynamic mechanical analysis studies. This study clearly showed the dependence of storage modulus on molecular weight, specifically near the glass transition temperature (T_g). For instance, below T_g while the storage modulus of the low molecular weight PPC ($M_n = 109$ kg/mol) was 4.3 GPa, the high molecular weight PPC in the study ($M_n = 227$ kg/mol) exhibited a storage modulus of about 6.9 GPa. This is a 60% increase in with approximately double of the molecular weight. In the rubbery zone (above T_g), PPC with M_n of 227 kg/mol displayed a modulus of 38 MPa, whereas PPC with M_n of 109 kg/mol showed a modulus of only 8.6 MPa. This is a 340% difference between the high and low molecular weight PPCs. Furthermore, modest changes in the T_g was observed from the inflection point of the storage modulus (Figure 6). While PPC with M_n of 85 kg/mol showed a T_g of around 43 °C, PPC with M_n of 227 kg/mol showed a T_g of about 51 °C [82].

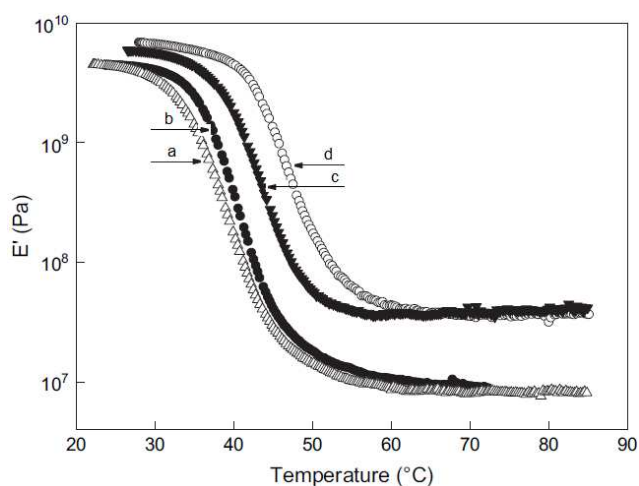


Figure 6. Plots of storage modulus (E') against temperature of PPC with different M_n . (a) $M_n = 85$ kg/mol; (b) $M_n = 109$ kg/mol; (c) $M_n = 156$ kg/mol; (d) $M_n = 227$ kg/mol. Adapted from ref. [82] Elsevier, copyright © 2006

2.3. Physical properties

CO₂ based polymers are generally amorphous resulting in good optical transparency after they are processed *via* melt extrusion, solution casting, injection molding or compression molding. PPC is amorphous in most polymer processing and treatment techniques, including electrospinning that usually aligns and changes crystal morphology. The weak molecular chain interaction, and the presence of many weak polar, flexible C – O – C bonds in the backbone leads to its amorphous state[82,89], which is quite different from many polyolefins that shows various range of crystallization behaviors. However, some CO₂ based aliphatic polycarbonates may crystallize under special treatment. For instance, Takahashi and Kojima [90] demonstrated the crystallization of poly(trimethylene carbonate) under tension, even though the polymer returns to a complete amorphous morphology when the tension is relaxed. PBS also exhibited some crystallinity [74]. Wu and co-workers [91] reported CO₂-based PCHC polymer from the asymmetric alternating copolymerization of CO₂ and cyclohexene oxide with semi-crystalline morphology. This polymer is stereoregular with typical semi-crystalline thermoplastic behavior, which displays a high melting point (T_m) of 215–230 °C and a peak decomposition temperature of 310 °C. Wide angle X-ray diffraction study of PEC polymer by Unger *et al.* [75] showed a wide, amorphous halo morphology, confirming the amorphousness of PEC like PPC.

Solubility of polymers is important not only to prepare solution cast films, but also to conduct characterizations such as molecular size quantification. PPC is soluble in chlorinated hydrocarbons (e.g., chloroform, dichloromethane, benzene, and dichloroethane), tetrahydrofuran (THF), acetone, methyl ethyl ketone, ethyl acetate, etc. [92,93], while insoluble in water, ethylene glycol, ethyl alcohol, methanol, and other aliphatic hydrocarbons. Substituted aromatic compounds are also poor solvents of PPC[60,93], PBC and PCHC are soluble in THF [72,94]. Liu *et al.* [95] conducted detailed investigation on the solubility of PEC by characterizing the physical properties of PEC

solutions in various solvent systems. The study showed that PEC is soluble in chloroform, 1,4-dioxan, N-methylpyrrolidone (NMP), dimethyl sulfoxide, dimethyl formamide, and 2-pyrrolidone, which have a solubility parameter ranging from 9.3 to 14.7 cal^{1/2}cm^{3/2}. The study demonstrated that 1,4-dioxan was the best solvent among the studied systems. Dichloromethane also solubilizes PEC. The lack of functional groups on common aliphatic polycarbonates usually limits modification potential to enhance either their physical or thermal properties. As observed in many polymer systems, the incorporation of functional groups offers an array of further functionalization or modification options to tailor such material properties including hydrophilicity, hydrophobicity, biocompatibility, and biodegradability for various purposes [50,96,97]. Thus, the incorporation of active functional groups in these CO₂ based aliphatic polycarbonates is an expected growth area.

2.4. Processing and applications

The fact that CO₂ based poly(ether carbonates) are made by fixation of CO₂, and their outstanding properties such as relative ease of processability, strength, low density, biodegradability, and good electrical insulation render these materials of high industrial interest for applications in the electronics, industrial packaging, agricultural mulch films, foams, biomedical and health care sectors. Moreover, the recent advances achieved in the catalysis of CO₂ copolymerization makes industrial scale production of aliphatic polycarbonates feasible. The major limitation to the industrial scale thermoplastic processing of some of these common polymers is the low thermal degradation temperature. For instance, most PEC and PPC currently available in the market start to degrade in the vicinity of 150 and 180 °C, respectively. Thus, methods of broadening the properties and processing window to enhance the applicability of aliphatic polycarbonates need to be investigated.

Since poly (ether carbonates) have the propensity to absorb some moisture [78,98], drying is important prior to processing to avoid hydrolysis. However, the low glass transition temperature of some of the common polymers in this group (e.g. PEC, PPC) limits traditional elevated temperature drying. Thus, low temperature vacuum drying, or freeze-drying may be employed to avoid sticking of pellets that otherwise would occur if dried at elevated temperatures. PPC can be processed by all major thermoplastic processing techniques such as injection molding [78], blow molding [99], blown films [100], extrusion film casting [78], compression molding [101], solvent casting for films [98], spin casting [93], and electrospinning [102,103]. It is important to note that solvent casting have possibility to remove the stabilizing agent by dissolution [81]. Consequently, the thermal stability of the PPC could be reduced. PEC can also be processed as a thermoplastic employing extrusion for film casting [104], solution casting for coating and thin films [105], electrospinning into a fiber [106], and spray coating [107]. PCHC can also be processed with various thermoplastic processing methods: extrusion [108], injection molding [108], compression molding [72], and electrospinning [109]. Poly (butylene carbonate) is a new entrant to the family of poly (ether carbonates) and as a result, its processability and applications are not extensively identified in the literature. Some literatures reported that PBC have beneficial properties in tape casting and other applications where flexibility and good green strength are critical [73] could also find biomedical and environmental applications [110].

The increasing environmental concern from plastic waste prompted considerable interest in the preparation of biodegradable materials. Geyer and co-workers [41] analyzed the global mass production of plastics, their use and fate, and presented the lifetime distribution for eight core industrial use (Figure 7). Packaging, that constitute 38 – 41% [39,87] of all plastics produced, has the shortest lifetime. Thus, there is a special interest in replacing stable plastics that have short lifetime applications such as packaging, shopping bags, composting bags, mulch films, and other

consumer uses. CO₂ co-polymers such as PEC and PPC are excellent candidates for use in packaging and other short lifetime plastic applications. The potential of CO₂ co-polymers in packaging is not only because of their biodegradability, but also because of the excellent gas barrier properties. For example, the oxygen permeability of PPC is below 20 cm³/m²/day/atm, this is much better than other biodegradable and compostable polymers, such as poly (lactic acid) (PLA), poly(butylene succinate) and Ecoflex that shown a permeability of 550, 1200, and 1400 cm³/m²/day/atm, respectively [71].

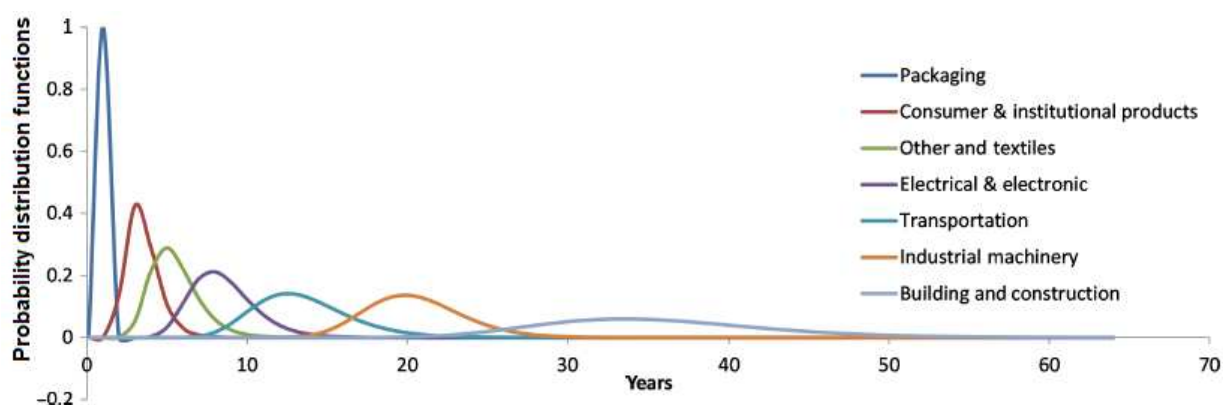
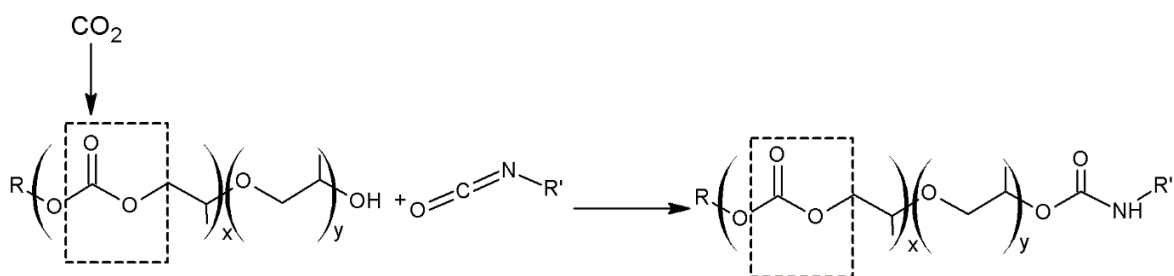


Figure 7. Product lifetime distributions for the eight industrial use sectors plotted as log-normal probability distribution functions (PDF). Adapted from Ref.[39] Science advances, copyright © 2017.

The use of CO₂ based polyether carbonates as the polyol component for polyurethane polymer production is perhaps one of the most advanced application, which is currently pursued at a commercial scale by multinational companies such as Covestro and Aramco. Polyurethanes, with a global production of about 20 metric tonnes in 2014 [111] are among the top six most extensively used polymers for an array of applications (e.g. foams, elastomers, coatings, thermoplastics, sealants, and adhesives). All polyurethanes are built by the polyaddition process of polyols and (poly) isocyanates, with a characteristic chain link of urethane group. This paves the way for an immense quantity of CO₂ co-polymer utilization as a sustainable feedstock of polyurethanes.

Additionally, polyols are important polymer additives for applications as plasticizers, chain extenders, and processing aids [112]. While a diverse variety of polyols exist in the market, polyether polyols, polyester polyol, and polycarbonate polyols constitute the majority of the polyol production.

Conventional polyols are sourced from petroleum feedstock through an energy demanding process that result in a large CO₂ footprint [113]. This has resulted in a significant interest for renewable resourced and eco-friendly process for the development of polyols. A typical example of this effort is the chemical conversion of vegetable oils into polyols. However, the use of edible resources for such industrial products is creating direct competition with food and feed production [114]. On the contrary, CO₂-based co-polymers do not rely on agricultural processes. Thus, the use of CO₂ as a renewable and ubiquitous co-monomer to produce polyether carbonate polyols can provide an eco-balance resulting in enhanced sustainability [113]. Life cycle analysis suggested that oligoethercarbonates with 20 wt.% CO₂ can reduce greenhouse gas emissions by 11–19% while saving 13–16 % of fossil resource [115]. Scheme 5 illustrates the reaction between polyether polyol, derived from CO₂, and isocyanate crosslinking agents for the synthesis of polyurethane. CO₂ based polyurethane foams can be used for many applications because of their properties (mechanical, hydrolysis/oxidation resistance), and are comparable or even better than conventional polyurethanes [116]. This has resulted in an increased industrial activity for the commercial production of CO₂ based polyols. For instance, Huasheng Polymer Co. in Nantong city, Jiangsu province, China has been in progress to produce 10,000 tonnes/year of CO₂-polyols [117]. Covestro (Germany) has also planned to setup a factory, which can produce 5000 tonnes/year of CO₂-polyols [118].



Scheme 5. Reaction between CO₂ based polyol and isocyanates for the production of polyurethanes.

2.5. Other uses of CO₂ based aliphatic polycarbonates

The unique combination of biodegradability, renewability and biocompatibility of CO₂ based aliphatic co-polymers have attracted a significant interest for industrial polymers and biomedical applications. The use of CO₂ in polymers is one of the most successful examples of a process that utilizes CO₂ as a feedstock. About 30 – 50% of these polymers mass is derived from carbon dioxide, with the remainder derived from petrochemicals [115,119]. Applications of carbon dioxide polymers in industrial plastics are dependent on molecular weight regimes. The low-molecular-weight hydroxyl end-capped polycarbonates are applied as polyols in the manufacture of polyurethane [120]. The relatively low viscosities and glass transition temperatures of these polymers makes them suitable substitutes for the common petrochemical based polyols that are used to make furniture foams, adhesives, clothing and coatings [121]. Alternatively, the high-molecular weight polycarbonates can be used in rigid plastics, blends with bio-based and petrochemical based polymer, matrices for polymer (nano)composites, etc. [78,122]. Table 3 and Figure 8 summarizes reported possible applications for these polymers.

Table 3. Applications of CO₂ based aliphatic polycarbonates co-polymers.

Aliphatic polycarbonate polymer	Applications
Poly(ethylene carbonate)	- Ion-conductive polymer for flexible solid electrolytes [90,123] - Binder for ceramic powder [124]

	<ul style="list-style-type: none"> - Coatings, pastes and inks [104] - Used to make high purity technical parts [104] - Multi-layer packaging film barrier layer due to its low oxygen barrier feature [125] - Medical applications (e.g. for controlled drug release because of its biodegradability [125]) - Temporary adhesives for wafer-to-wafer bonding [126]
Poly(propylene carbonate)	<ul style="list-style-type: none"> - Reactive hot melt adhesives for plastics (polycarbonates, acrylonitrile butadiene, poly(methyl methacrylate)), metals (metals, steel) [127] - Polyurethane foams for mattresses, automotive seats, armrests, sponges, furniture cushioning, foam sheetings etc. [128] - Waterborne polyurethane emulsions: polypropylene carbonate was used as the soft segment for coating and films applications [94] - Thermoplastic polyurethane adhesives [129] - Biomedical material for tissue scaffolding, drug-delivery carriers, non-woven fabrics etc. [109,119] - Functional biodegradable packaging film (e.g. antimicrobial film) [130] - Electrospun fiber mats for porous materials [102] - Ion-conductive polymer for flexible solid electrolytes [90,123] - Temporary adhesives for wafer-to-wafer bonding [126]
Poly (butylene carbonate)	<ul style="list-style-type: none"> - Tape casting and other applications where flexibility and good green strength are critical [73] - Biomedical and environmental applications [110]
Poly (cyclohexene carbonate)	<ul style="list-style-type: none"> - Temporary adhesives for wafer-to-wafer bonding [126] - Binders, electronics, coating resins, surfactants and foams and others [51] - Hydrogels [94] - Moldable rigid thermoplastics such as toys, utensils, soothing articles etc. [131] - Decomposable channel former [132] - Pore former [132] - Sacrificial placeholder [132]

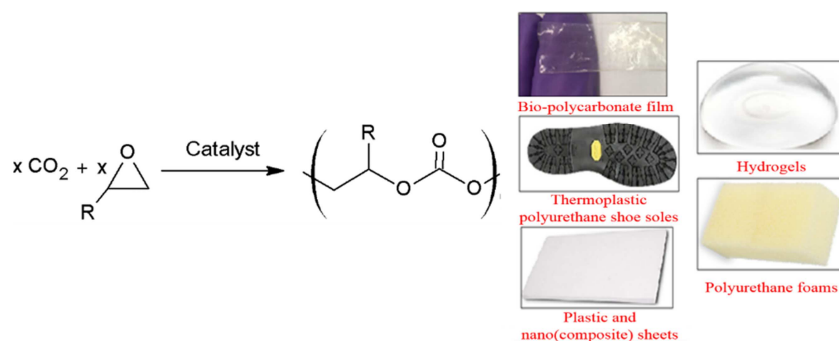


Figure 8. Sustainable polymer applications from CO₂ based aliphatic polycarbonates. PEC, PPC and PCHC can be prepared by copolymerization of CO₂ with oxiranes.

3. Polymer blends from carbon dioxide based polymers and co-polymers

Polypropylene carbonate (PPC) is the most studied polymer in comparison with the other CO₂ derived polymers such as poly (ethylene carbonate) (PEC), poly (butylene carbonate) (PBC), and poly (cyclohexene carbonate) (PCHC). However, the widespread commercial use is still limited because of limitations in processability limitations, performance (e.g. poor thermal stability and mechanical properties) and cost factors. Several research efforts including blending it with other polymers, incorporation of additives, and incorporation of fillers are currently in progress to mitigate these shortcomings. The following section reviews the key understanding achieved in the use of PPC as a co-blend of various polymer formulation systems, including biodegradable and non-biodegradable polymers. Process technology, compatibilization chemistries and their impact on the phase morphology and performance attributes of the blend are also reviewed.

3.1. PPC based polymer blends

In order to improve processability and/or cost structure of PPC, melt blending is one of the most cost-effective and technically less challenging method to prepare polymeric materials with desirable features, and as such, it is crucial to the plastic industry[133]. Many commercially successful blends are made through traditional melt blending processes (e.g. extrusion). For

instance, super tough nylon (Zytel ST801), is an engineering thermoplastic made by melt compounding of nylon 6,6 with functionalized rubber. Interactions, miscibility, compatibility, composition, and individual component properties are some of the crucial parameters that determine polymer blend properties [134]. The interactions between polymers can be characterized by the Flory–Huggins thermodynamic interaction parameter, which in heterogeneous blends can be related to the size of the dispersed particles [135]. Depending on the component polymer – polymer interactions, polymer blends can be categorized as (i) miscible; forming a single phase, (ii) immiscible; forming two phases while remaining compatible, and (iii) incompatible with high interfacial tension [136,137]. Miscible blends can be produced when the polymer blend possesses single-phase morphology at the microscopic level. On the other hand, the morphological features of immiscible blends exhibit phase separation at the microscopic level. In general, most polymer pairs are not miscible because of low entropy of mixing and high enthalpy besides difference in the solubility parameter of the blended components. When immiscible polymer blends show improvements in their mechanical performance, they could be considered as compatible blends or partially miscible blends [134].

Thermal, mechanical, and thermomechanical properties are typically used to identify the individual polymers miscibility and compatibility within the blend at the molecular scale [138]. For example, miscibility of polymers in a blend system can be recognized through glass transition temperature (T_g) measurements. This is because miscible blends show single T_g while immiscible blends show multiple T_g . Understanding of the phase morphology and compatibility of immiscible polymer blends is crucial because these features substantially influence the performances of the final blend material. The phase morphology of polymer blends itself depends on the blended polymers viscosity, processing parameters, blend composition, and compatibility.

Compatibilization is an effective strategy to improve the performances of the immiscible polymer blends by enhancing the compatibility between the blended components. The compatibility of the blends can be enhanced by the incorporation of additives such as compatibilizers [139–141]. A compatibilizer improves the interfacial adhesion or reduces the surface tension between two polymer phases via intermolecular bonding and chain entanglements, thereby enhancing the mechanical properties of the blends [134]. Thus, the formation of miscible and compatible blends is essential to achieve enhanced properties as compared to their individual counterparts. The first patent on compatibilization of binary polymer blends was published in the 1950s. From 1960s onwards, the compatibilization of different binary polymer blends such as poly(vinyl chloride) (PVC)/polyolefin [142], PVC/elastomer [143], PVC/polybutadiene [144], poly(vinylidene fluoride) (PVDF)/poly(methyl methacrylate) (PMMA) [145], and polystyrene (PS)/poly(vinyl methyl ether) [146] have been investigated in both academia and industries. The first reviews on the compatibilization and interfacial properties of polymer blend systems were published in the 1970's by Yu [147], Gaylord [148], Lipatov [149], and Paul [150,151]. In recent reviews, Muthuraj *et al.* [134], and Imre and Pukánszky [135] comprehensively reviewed the compatibilization of various biodegradable polymer blends. These review articles pointed out that the compatibility of polymer blends could be enhanced by adding reactive or non-reactive compatibilizers. Among the compatibilizers, block copolymers, graft copolymers, targeted fillers, impact modifiers, and γ -irradiation or electron beam (combined with or without a co-agent) are widely used to enhance the compatibility of polymer blends.

3.2. PPC blends with biodegradable polymers

CO₂ co-polymers, such as poly(propylene carbonate), in their current development stage will not fulfil most performance requirements for commercial applications as a polymer. This is because such polymers have high susceptibility to hydrolysis and low molecular weight, resulting in

relatively poor mechanical properties, and rather low melting temperature as discussed in section 3.1. Consequently, blending of such polymers with other polymers to improve both their performance and cost structure have been of much interest, in line with the concept of sustainability and eco-friendliness (Figure 9). In other cases, PPC have been used as an “additive” to improve the performance or environmental sustainability of other polymers. In this section, various blends of CO₂ co-polymers, with a focus on PPC, with biodegradable and non-biodegradable polymers are discussed (Table 4).

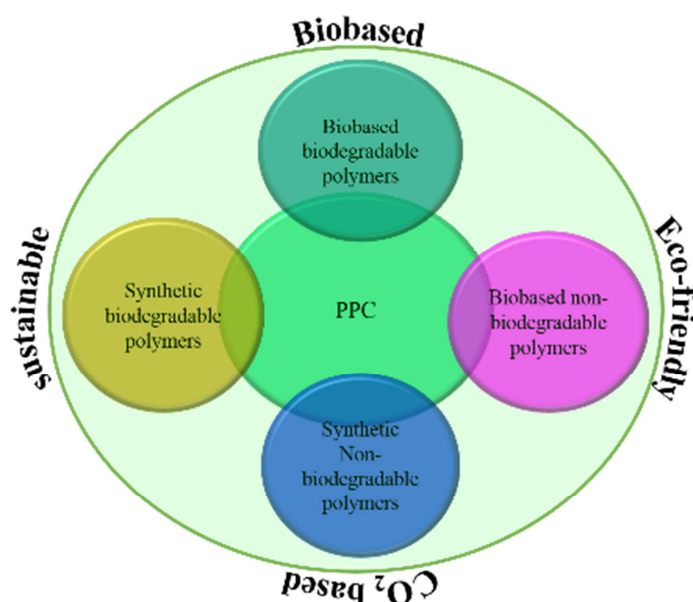


Figure 9. PPC blended with different biodegradable and non-biodegradable polymers.

3.2.1. PPC/PLA blends

Poly (lactic acid) (PLA) is among the most promising polymers in the emerging bioplastics market due to its availability and attractive cost structure. This polymer is a biocompostable thermoplastic with good transparency that can be derived from fully renewable monomer, *i.e.* lactic acid [60]. The lactide monomer can form two stereoisomers because lactic acid contains two chiral carbon centers. Therefore, the performance of PLA is strongly dependent on its stereochemical monomer

compositions [134]. PLA can be used for many applications including packaging, textiles, three dimensional (3D) printing, electronic components, cosmetics, biomedical (e.g., biocompatible sutures, implants, biologically active controlled release devices), etc. Because of its renewability and compostability, PLA is widely considered as a very promising material to produce bio-based, biocompostable and in some cases, biodegradable polymer blend materials with other biopolymers pairs. Blending of PLA with other polymers usually target improving its performance properties (e.g., brittleness), cost structure, and biodegradability. Ma *et al.* [152] studied the effect of melt blending PLA with PPC at 110-120 °C. Two independent glass transition temperatures assigned to PLA and PPC, respectively were observed. It was reported that the T_g of PPC phase increased from 22 to 34 °C with increasing PLA component in the blend, whereas the T_g of PLA phase decreased slightly (by 3 °C) as the PPC concentration increased in the blend. The changes in the T_g of both polymers indicated the partial miscibility between PLA and PPC [152]. It was also mentioned that the thermal stability of PPC was improved in the blends compared to neat PPC.

Due to the inherently higher tensile strength and Young's modulus of PLA, the PPC/PLA blend's tensile yield strength and modulus increased with increasing PLA content. The experimental tensile yield strength and Young's modulus values of the PPC/PLA blend with up to 60 wt. % PLA were superior to theoretically predicted values. On the contrary, lower experimental tensile yield strength and Young's modulus were observed compared to theoretically calculated tensile yield strength and Young's modulus values when the PPC/PLA blends prepared with higher than 60 wt.% PLA. Such a negative deviation of PPC/PLA blends with higher than 60 wt. % PLA was due to the poor interfacial interaction between the components. The toughness of the PPC/PLA blends increased with increasing PLA content up to 50 wt. %. However, the toughness of the PPC/PLA blends has reduced when the PLA content increased to 50-70 wt. %. The observed toughness reduction was attributed to a phase inversion. However, another study [60] on a PLA/PPC blends

gave different experimental data and conclusions from the study mentioned above. In this study, the blend of PPC and PLA was also prepared through extrusion blending, but at a temperature of 170 °C [60]. There were no changes observed in the T_g of the two polymer phases. Moreover, it was reported that a good dispersion of the components in the matrix was detected, illustrating a good compatibility. The Young's modulus ranged from 600 to 3800 MPa, and the yield strength linearly changed from 4 to 80 MPa with increasing PLA content in the PPC matrix [60].

A similar observation was reported in an injection moulded PPC/PLA blends [78]. The injection moulded PPC/PLA (60/40) blends was considered as an optimal blend because it provided a substantial increase in elongation without too much compromise in tensile strength. Therefore, the PPC/PLA (60/40) blend was selected by Sun *et al.* [78] and compatibilized with different concentration (0.2, 0.5 and 1 phr) of epoxy chain extender (Joncryl ADR 4368-C). Chain extenders are normally low molecular weight multifunctional compounds with desirable thermal stability. Melt processing of polymer blends in the presence of such chain extenders can cause long chain branch structures, crosslinking structures, block or graft copolymer structure formations via covalent bonding [153]. Such covalently linked block, graft or crosslinked copolymer structures enhance the compatibility between the component blend polymers. As a result of the covalent bond, such chain extender compatibilized polymer blends exhibit much higher mechanical properties as compared to their corresponding blends prepared without chain extender. For example, the PPC/PLA (60/40) blend prepared with 0.5 phr chain extender showed a dramatic increase in elongation (1940%), tensile strength (37%), and secant modulus (16%) compared to the baseline PPC/PLA (60/40) blend without compatibilizer. These improvements suggest that PPC-Joncryl-PLA co-polymer formation improved the compatibility between the PPC and PLA in the presence of Joncryl. In the same study, it was also noted that the water vapor permeability (WVP) of the base PPC was reduced after blending with PLA due to the high crystallinity of the PLA. The

oxygen permeability (OP) of the PPC/PLA blends were much lower than both PPC and PLA. Such permeability improvements are very desirable attributes for packaging applications. However, the use of Joncryl compatibilizer did not positively influence the WVP and OP of the PPC/PLA blends compared to PPC/PLA blend without Joncryl. Overall, an optimal Joncryl concentration could be a potential chain extender and compatibilizer for PPC/PLA blend systems [78].

Yao *et al.* [154] improved the compatibility of the PPC/PLA blend with the help of maleic anhydride (MAH). The MAH concentration was varied from 0.15 to 1.5 wt. % to enhance the compatibility and miscibility of the PPC/PLA blends. The PPC/PLA blend prepared with 0.3 wt.% MAH exhibited an optimal improvement in compatibility based on the reduction of inclusion phase size. When the PPC/PLA blends are prepared with higher than 0.3 wt.% MAH, the compatibility between the blends was reduced, which is in agreement with their earlier study [80]. The ductility of the PPC/PLA blend was improved in the presence of MAH compared to the PPC/PLA blend without MAH. The enhanced ductility of the PPC/PLA was attributed to the plasticization effect of the MAH. In the PPC/PLA blend, the PLA content was varied while keeping constant ratio (0.3 wt.%) of MAH. While the PPC/PLA blends tensile strength has reduced up to 30 wt.% PLA incorporation, an increase was observed when the incorporated PLA was beyond 30 wt.%.

Influence of polyvinyl acetate (PVAc) on the MAH end-capped PPC (MAH-PPC)/PLA blends compatibility was explored by Gao *et al.* [155]. A uniform dispersion of MAH-PPC was obtained in the MAH-PPC/PLA blends when 10 wt.% PVAc was added into the MAH-PLA blends. The PVAc was located at the interface of the MAH-PPC/PLA blends to bridge the MAH-PPC and PLA. The formed bridges led to an increase in the compatibility between PLA and MAH-PPC irrespective of the blend composition in the resulting blends. The improved interfacial adhesion between PPC and PLA resulted in finer phase morphology which was far more favorable in

triggering large-scale shear yielding compared to the coarse phase morphology observed in the PPC/PLA blend without compatibilizer [156]. It was observed that the PPC/PLA blends with PPC as a major phase showed tensile strength (28.5 MPa) and Young's modulus (1.4 GPa) values comparable to commodity polymers such as polypropylene [157].

The elongation at break of the MAH-PPC/PLA blends was effectively improved with the help of tetrabutyl titanate ($\text{Ti}(\text{OBU})_4$) transesterification catalyst [158]. During this reactive process, oligomers of MAH-PPC, MAH-PLA and MAH-PPC-b-PLA co-polymer were generated by direct ester-carbonate exchange, alcoholysis, and acidolysis reactions. The produced block co-polymer was located at the interface to compatibilize the MAH-PPC/PLA blend while the formed oligomers plasticized the MAH-PPC/PLA blend. Due to this plasticization effect, the elongation of the MAH-PPC/PLA blends have increased with plastic deformation whereas tensile strength has decreased compared to the baseline pristine blend. Among the produced blends, a maximum elongation (~400%) was observed in the MAH-PPC/PLA/ $\text{Ti}(\text{OBU})_4$ (70/30/1 phr) blend with a tensile strength of ~ 29 MPa. However, the impact resistance of the MAH-PPC/PLA blend did not show significant improvement after compatibilization. This could be attributed to a lack of elastomeric or rubber structure formation to spread deformation energy to large parts of the matrix.

However, the impact strength/toughness of the PLA was substantially improved by mechanical blending with commercially available thermoplastic PPC polyurethane (PPCU) [159]. The improved toughness of the PLA was due to the shear yielding that occurred in the PLA matrix by the cavitation of PPCU particles. The PPCU/PLA (50/50) blend showed impact strength of 102.8 kJ/m^2 with an elongation at break of 457.9% [159]. In another study, PPC-b-PLA co-polymer was formed in PPC/PLA blends during reactive blending with $\text{Ti}(\text{OBU})_4$ catalyst (0.5 and 1 wt.%) by transesterification (Figure 10) [160]. The formed PPC-b-PLA copolymer improved the miscibility and compatibility of the resulting blend. In addition to an increase in compatibility/adhesion

between PPC and PLA phase, the PPC-b-PLA co-polymer can also form block co-polymer micelles in the matrix, which decreases the coarsening rate in the morphology development as shown in Figure 10b. The elongation at break of PPC/PLA (60/40) blend with optimal catalyst concentration (0.5 wt.%) exhibited a nearly two-fold increase compared to the uncompatibilized PPC/PLA (60/40) blend. Hwang *et al.* [161] improved the compatibility between PLA and PPC blend with MAH and Luperox 101 initiator by reactive processing. The oxygen barrier properties of the blends slightly increased compared to neat PLA because of the increased crystallinity.

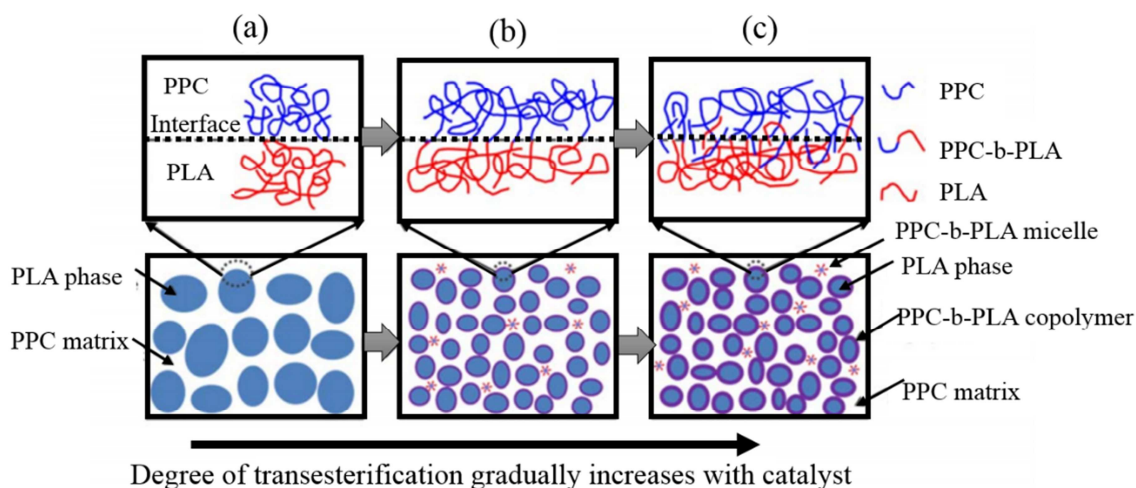


Figure 10. Schematic representation of the compatibilization of PLA/PPC blends with the transesterification reaction. Adapted from ref. [160] copyright © 2018

In another study, the miscibility of blown film PPC/PLA blend was improved with the help of 9 wt.% biodegradable plasticizer *i.e.*, poly(1,2-propylene glycol adipate) (PPA) [162]. Due to the high transparency of PLA, the clarity of the PPC/PLA/PPA blend was higher when the blend was prepared with higher PLA content. A similar trend was observed in the haze values. Depending on the PPC/PLA compositions, the machine direction and transverse direction tear strength of the resulting blend films varied between 100.6-131.8 kN/m and 112.8-143.4 kN/m, respectively. These tear strength values are much higher than polyethylene film (73.3 kN/m in the machine direction

and 83.3 kN/m in the transverse direction) that was processed similarly [162]. In summary, several studies have demonstrated that the blending of PLA with PPC, together with coupling agents can improve key performance features (e.g. mechanical, thermal properties), and processability of PPC polymers.

3.2.2. PPC/PHBV blends

Microbial – produced poly (hydroxy butyrate-co-valerate) (PHBV) is fully biodegradable biopolyester polymer, which has potential application in a wide range of application platforms, including the packaging and biomedical fields[163]. PHBV, produced by a variety of microorganisms as an internal carbon storage, is an optically active and biocompatible thermoplastic amenable to melt-processing. The relatively high cost, brittleness and narrow melt-processing window constitutes major limitations of PHBV [60,163]. With the intention of utilizing the ductile PPC to modify the brittleness of PHBV while maintaining the biodegradability, Corre *et al.* [164] prepared a blend of PPC and PHBV through extrusion blending at 170 °C. The study showed that the rather fragile mechanical behavior of PHBV was improved in the presence of PPC, as observed from the improved elongation at break. The impact strength of the blends was also significantly enhanced compared to the neat PHBV, which is a significant improvement concerning its potential utilization for film development. Moreover, the barrier properties of PPC (for both oxygen and water) were improved due to the high crystallinity of PHBV. This study demonstrated that blending PHBV and PPC could be a practical and feasible way to extend their application field as bioplastics, especially in the packaging platform.

Injection molded PPC/PHBV blends with different concentrations of PHBV were prepared by Enriquez *et al.* [165] and Corre *et al.* [164]. Owing to the high strength and stiffness of PHBV, the tensile yield strength, Young's modulus, and heat deflection temperature of the PPC all increased

with increasing PHBV content in the resulting PPC/PHBV blends. In these samples, the toughness of the PPC reduced with increasing PHBV due to the inherent rigidity of the PHBV. Furthermore, it was observed that the PPC shrinkage could be entirely eliminated with the addition of 30 wt.% PHBV [165]. Corre *et al.* [164] used melt blended PPC/PHBV films (100 and 150 μm) to study the oxygen permeability (OP) and water vapor permeability (WVP) at 23 $^{\circ}\text{C}$ and 50% RH [164]. The PHBV had lower WVP and OP compared to neat PPC because of the crystallinity of PHBV. The lower oxygen and water permeability of the PHBV assisted in the reduction of the OP and WVP of the PPC/PHBV blends compared to neat PPC. The reduced OP and WVP from neat PPC down to neat PHBV were not linear. It was found that the PPC/PHBV (50/50) blend has lower OP and WVP than other prepared blends. This phenomenon could have come from the thinner morphology of the blend, leading to a longer torturous pathway [164].

Melt compounding of PLA/PHBV/PPC ternary blends were prepared to study their compatibility and mechanical performances [166]. The produced ternary blends were not miscible. Despite their immiscibility, the ternary blends showed superior toughness compared to binary blends of PPC with either PLA or PPC. The improved toughness was mainly due to the synergistic effect of the dispersed components [166]. Similarly, the performances of a solution blended PPC/PHBV with different blend compositions were investigated by Peng *et al.* [167] and Tao *et al.* [168]. The PPC/PHBV blends showed complete immiscibility because of their difference in crystallinity. The crystallization rate difference between PPC and PHBV hindered the reactivity between the molecules to enhance miscibility.

Reactive compatibilization is expected to improve the interfacial interaction between PPC and PHBV, thereby enhancing the performances of the resulting blends. For example, Li *et al.* [169,170] conducted reactive compatibilization of a PPC/PHBV blend with 0.2 wt.% dicumyl peroxide (DCP) and 1 wt.% glycidyl methacrylate (GMA). During reactive processing, PHBV

graft PPC co-polymer was formed by a transesterification reaction. The formed copolymers improved the compatibility with small and uniform droplets of PHBV inclusion phase. Furthermore, the compatibilized PPC/PHBV blend showed about 12.3% reduction in crystallinity. The mechanical performances of the reactive compatibilized PPC/PHBV blends were compared with mechanically blended PPC/PHBV blends [170]. The impact energy and elongation at break of the reactive compatibilized PPC/PHBV blends were 10 and 18 times higher than the mechanically blended corresponding blends, respectively. As explained earlier, the observed improvements in the mechanical properties were due to the enhanced miscibility with the help of reactive processing.

3.2.3. PPC/PHB blends

Poly (3-hydroxybutyrate) (PHB) is another promising biodegradable thermoplastic polyester. It possesses superior biodegradability and biocompatibility that makes it a favorable material in the face of global concern associated with plastic waste pollution and non-renewable fossil feedstock utilization. Additionally, PHB has very similar properties to conventional polypropylene and polyethylene, which are among the most extensively utilized petroleum-based commodity plastics [134,171]. Nonetheless, the brittleness and high-cost structure of PHB has limited its commercial success in many applications [134,172]. Since PPC is a ductile polymer with high elongation at break, it was hypothesized that blending of PPC with PHB could be an appropriate route to produce polymer blends with improved and optimized properties.

For instance, Yang and Hu [172], investigated a solution blend of PHB and PPC using chloroform as a common solvent. Two distinct observations were made here depending on the concentrations of the PPC and PHB component regimes. When higher loadings of PHB were used (>30 wt. %), two distinct T_g values were observed, indicating the immiscibility between PPC and PHB. The

crystallization behavior of PHB did not show any significant changes as PPC was added into the system. The morphological study of the blends showed clear phase separations between the PPC and PHB phases in these composition ranges. The observations here demonstrated that there was no miscibility between the two polymers as the PHB concentration in the blend increased beyond 30wt. %. However, the elongation at break of PHB was significantly enhanced with a slight decrease in the tensile strength, which was indicative of an improvement in the toughness of the blends. This suggests that PPC could be acting as a plasticizer of the PHB in these concentration ranges. The same study [172] reported that the solution blending of PPC with PHB exhibited enhanced miscibility when the blends were prepared with <30 wt.% PHB concentration. In another study, solution casting (chloroform as solvent) of PPC/PHB blend was performed. Results demonstrated that these blends are immiscible in most compositions and only miscible when the PHB content is 10 wt.% or lower [173]. Yang and Hu [172] observed that the addition of PHB enhanced the strength of PPC, but reduced its ductility tremendously. In fact, the ductility decreased from 1090 to 2.7 % with the addition of 40 wt. % PHB, due to the crystallization of PHB within the blend.

More recently, researchers are working on modifying and improving the miscibility of PPC/PHB blends so that a new green material with tailored properties can be obtained. For example, electrospinning of PPC/PHB blends with acetyl triethyl citrate (ATEC) plasticizer and polyvinyl acetate (PVAc) compatibilizer was prepared by using a solvent mixture of 90% chloroform and 10% dichloromethane [174]. With the incorporation of these additives into the PPC/PHB blend, the miscibility of the blends was greatly improved via hydrogen bonding interaction (Figure 11). It could be seen that the blend in the absence of additives exhibited complete immiscibility with a big inclusion domain size. On the contrary, the inclusion domain size was reduced considerably with uniform dispersion and an enhanced embedment of PPC in the PHB matrix when the blend was

prepared with higher additive loading (Figure 11 d and d'). This phenomenon was ascribed to the fact that the additives aimed at dispersing the PPC into small domains in the PHB matrix, leading to interactions between PPC and PHB. As a result, the electrospun PPC/PHB/PVAc/ATEC (25/43/12/20) blend (prepared with 25% solvent concentration) fibres showed a maximum elongation at break of 475% and a maximum tensile strength of 22 MPa. The fibres developed as such could be used in air and water filters, absorbent pads in diapers, wound dressings, surgical sutures, and drug delivery applications.

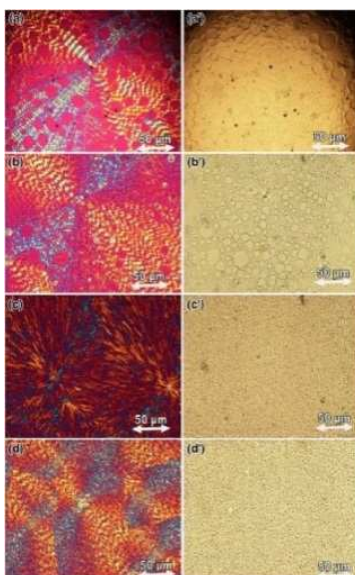


Figure 11. Optical micrographs of the PHB/PPC/PVAc/ATBC blends with and without polarized (a, a') 75/25/00/00, (b, b') 47/25/08/20, (c, c') 45/25/10/20 and (d, d') 43/25/12/20. Adapted from reference¹⁶⁸ copyright © 2017.

Propylene carbonate (PC) was shown to be an effective plasticizer for PPC. For example, Zhou *et al.* [175], investigated MAH end-capped PPC/PHB blends plasticized with different concentrations (0-15 wt.%) of PC to study the brittle-ductile transition of the resulting blends. In this study, the brittle-ductile transition of the PPC/PHB (50/50) blend had reduced from 60 to 10 °C after the addition of 12.5 wt.% of PC. As expected, the modulus of the plasticized PPC/PHB blend had diminished with increasing PC content. The PPC domain size in the plasticized PPC/PHB blend

became uniform and smaller. This phenomenon was demonstrated to be beneficial in improving the toughness and reducing the brittle-ductile transition of the resulting blends.

3.2.4. PPC/PBS blends

Poly (butylene succinate) (PBS) is an aliphatic biodegradable polyester that can be produced from poly-condensation of succinic acid and 1,4-butandiol[176–179]. Recent efforts demonstrated the production of succinic anhydride building block via fermentation of polysaccharides, and as such PBS can be partially biobased [134,180]. There is also an intense research activity to produce 1, 4-butandiol from renewable feedstock, and as such it is more than likely that PBS can be completely bio-resourced in the next few years. PBS as a material is a semi-crystalline, biodegradable and compostable polymer with excellent thermal stability (wide processing window) that offers outstanding material properties comparable to conventional polymers such as polyethylene and polypropylene [134]. Therefore, PBS is an interesting candidate to produce fully biodegradable polymer blends with PPC. Melt blended PPC/PBS binary blends were investigated by Zhang *et al.* [181], Pang *et al.* [182], Chen *et al.* [183], and Henke *et al.* [184]. Zhang *et al.* [181] observed the partial miscibility of PPC/PBS blends that was prepared with 10 wt.% PBS. When the PBS content increased above 10 wt. %, the resulting blends exhibited complete immiscibility due to the onset of crystallization, which led to phase separation. It was also observed that the PPC/PBS blend with 10 wt. % PBS showed minimal increment in the impact strength compared to neat PPC. The impact strength of the PPC/PBS blends was negatively affected when the PBS content was increased above 10 wt. % in the resulting blends. In contrast, the ductility of the PPC/PBS blends has gradually reduced up to 20 wt. % PBS incorporation, while further addition of PBS resulted in an exponential deterioration resulting in a brittle polymeric blend. Optimum properties were obtained in the PPC/PBS (90/10 wt. %) blends with considerable miscibility.

Unlike the observation by Zhang *et al.* [181], Pang *et al.* [182] noted the enhanced miscibility with increasing PBS content in PPC/PBS blends. This study claims that the enhanced miscibility was attributed to the reduced viscosity of these blends. The viscosity reduction had resulted from the higher processing temperatures and processing times. Due to the orientation-strengthening effect of PBS, both the yield strength and strength at break of PPC/PBS blends were enhanced with increasing PBS content. Furthermore, the yield strength of the blends exhibited a marked improvement in the PPC-rich regimes. Henke *et al.* [184] prepared a series of PPC/PBS blends without any compatibilizer and found that almost all mechanical and thermal properties deteriorated, indicating that PPC has a detrimental effect on neat PBS and *vice versa*. The impact toughness of the PPC/PBS blend could be improved by the addition of <10 wt.% of PBS. The shrinkage of the PPC was entirely eliminated by blending it with 50 wt.% PBS.

The performances of the PPC/PBS blend could be effectively improved with the incorporation of suitable additives like compatibilizers or coupling agents. Chen *et al.* [183] selected triphenylmethane triisocyanate (TTI) (0–0.54 wt.%) as a reactive compatibilizer to compatibilize a PPC/PBS blend film by a calendaring process. Both tensile strength and ductility of the blends increased with increasing TTI up to 0.36%, above which it deteriorated significantly. In this study, processing parameters such as die temperature (160–210 °C) and calendaring roller speed (15–35 rpm) were optimized to enhance the performances of the resulting blends. The blends prepared with a die temperature of 200 °C showed optimal mechanical properties. Due to the orientation of the crystalline phase toward machine direction (MD), the mechanical properties of the blend films were superior in MD as compared to transverse direction (TD). Similarly, calendar roller speed enhanced the properties in MD while it deteriorated in TD.

In another study, PPC was modified with L-Aspartic acid (Asp) to improve its melt processability [86]. It can be seen from the Figure 12 that the PPC processed without Asp at 120 °C (Figure 12A)

and 150 °C (Figure 12C) showed lower viscosity because of the molecular weight reductions. On the other hand, PPC modified with Asp exhibited no significant reduction in the average molecular weight indicating good thermal stability at 120 °C (Figure 12B) and 150 °C (Figure 12D). The compatibilizing effect of the Asp in the PPC/PBS blends was investigated with 2 wt.% of Asp. The resulting PPC/PBS/Asp blends exhibited remarkably improved flexibility, yield strength, and Young's modulus compared to similar blends prepared without Asp. The observed improvement in the properties was attributed to the enhanced interfacial compatibility between PPC and PBS with the help of Asp.

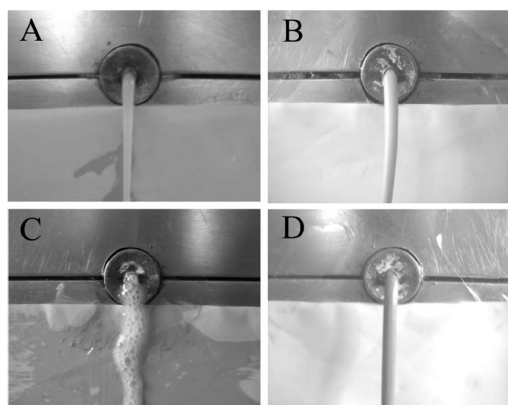


Figure 12. The extrusion photographs of (A) extruded neat PPC at 120°C, (B) extruded PPC with 2% Asp at 120 °C, and (C) extruded neat PPC at 150 °C, (D) extruded PPC with 2% Asp at 150 °C. Adapted from ref. [86] copyright © 2016.

3.2.5. PPC/Starch blends

Starch is a renewable, biodegradable, natural polysaccharide polymer. It has attracted significant attention as a co-blend component of various biodegradable and non-biodegradable polymers to produce sustainable materials due to its film-forming properties, melt processability after plasticization, renewability, biodegradability, modifiability, low cost, and abundance [185,186]. In this sense, the inherent properties of starch derived from various resources were exploited as a co-blend of CO₂ based co-polymers, specifically PPC in the last two decades. Several of these studies

have focused on optimizing the processing method (e.g. melt blending, reactive blending, etc.), and the material performance of starch–PPC blend. For instance, Ge *et al.* [187] conducted melt compounding of PPC with corn starch (CS) at 150 °C.

The performances of PPC/CS blend systems were investigated by Peng *et al.* [188], Ge *et al.* [187], Zeng *et al.* [189], and Ma *et al.* [190]. Peng *et al.* [188] prepared PPC/CS blends from 100/0 to 60/40 ratios and found that the resulting blends exhibited good compatibility due to hydrogen bonding interaction between the hydroxyl groups of CS and carbonyl groups of PPC. Quantum mechanical modelling, based on density functional theory (DFT), has been used to confirm hydrogen bonding interactions between the PPC and starch [191]. It was predicted that two hydrogen bonds with -11 kJ/mol average binding energy per hydrogen bonding could form between the monomer of amylose and one monomer of PPC. The computationally predicted hydrogen bonding distance between the amylose and PPC can be seen in Figure 13.

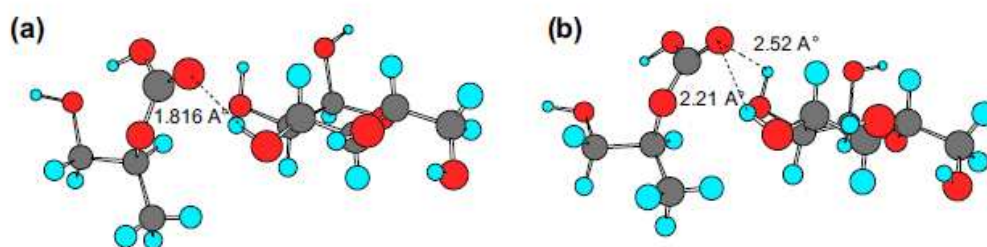


Figure 13. Geometrically optimized structures of one amylose monomer with one PPC monomer complexes at (a) quantum mechanical calculation based on DFT and (b) Semi-empirical method based calculation. Adapted from ref. [191] copyright © 2007.

In another study [187], PPC/CS blend ratios of 65/35 to 30/70 were prepared. The Young's modulus of the PPC was enhanced with the addition of starch [187,188], irrespective of the concentration. The experimental Young's modulus values of the PPC/starch blends were found to be higher than the theoretical values of the blends. The higher experimental Young's modulus was due to the excellent interaction between the PPC and starch. On the other hand, the percent

elongation at break of PPC had drastically reduced from 641 to 1.87% when PPC/starch blends were prepared with 35 wt.% starch. The reduced elongation at break was in agreement with the observed Young's modulus improvements of the blends [187]. It was observed that the PPC blend with higher amount of CS content showed voids and gaps between the PPC matrix and CS particles. The observed voids and gaps between the PPC and CS were attributed to the incompatibility and poor interfacial adhesion between the blended components [187], at higher loading of starch

Chemical modification of starch is one way to improve the compatibility of starch with PPC. As an illustration of this, Zeng *et al.* [189] modified starch via acetylation to enhance the hydrophobicity of the resulting starch. As expected, the hydrophobicity of the modified starch was dependant on the degree of substitution of the acetyl groups. Unlike lower degree of acetyl group substitution (≤ 0.51), the higher degree of acetyl group substitution showed a single-phase microstructure. The acetylated starch/starch acetate with PPC blends showed improved compatibility and strong interfacial adhesion between the blend phases. Zeng *et al.* [189] also studied the mechanical properties of the PPC/starch acetate blends. They found that the tensile strength increased with increasing starch content while the impact strength was decreased. The degree of acetyl group substitution (DS) on the starch controlled the mechanical properties of the PPC/starch acetate blends. For instance, a maximum strength was observed in the PPC/starch acetate blend prepared with 0.51 DS starch. Due to the good dispersion of starch acetate in the PPC matrix, the continuity of the ductile PPC phase was interrupted when the blends were prepared with a higher DS starch content. Consequently, the toughness of the resulting blend was reduced. Overall, the PPC/starch acetate blends exhibited enhanced strength and ductility compared to that of the neat PPC.

Similar to melt blended PPC/acetylated starch, the tensile properties of the PPC/S-g-PMA blends were investigated by Ge *et al.* [192] through melt blending PPC/polymethylacrylate grafted starch

(PMA-g-S). This blend showed dramatic improvement in the interfacial adhesion and compatibility between the PPC and starch [192]. The PPC/PMA-g-S blends showed an almost linear tensile strength increment up to 35 wt.% S-g-PMA loading. There was no change in tensile strength when S-g-PMA was incorporated beyond 35 wt.% compared to the neat PPC. The toughness of the PPC was also enhanced with the addition of S-g-PMA due to the secondary bonding interaction between the components. Due to the stiffening effect of modified starch, the modulus of the PPC was improved with the addition of up to 10 wt.% starch, while the further addition of S-g-PMA resulted in saturation.

In a separate study, 1 wt.% succinic anhydride (SA) was used to compatibilize PPC/starch blend as reported by Ma *et al.* [190]. When the PPC/starch blends were prepared with SA, a better interfacial interaction between the PPC and starch was observed compared to uncompatibilized blend. Besides, morphological analysis revealed that the starch particles were very smooth in the uncompatibilized blend while coarse starch particles (black arrow in Figure 14C) were formed in the compatibilized blend (Figure 14c). This morphological observation suggests that the compatibility between the PPC and starch was improved in the presence of SA. The improved compatibility between the PPC and starch with SA can be explained as follows: SA can end-cap with PPC and starch during melt processing. When SA end-capped PPC and starch were located in the same vicinity to interact with PPC and starch, the interfacial tension could reduce, resulting in the improvement of compatibility. The enhanced compatibility between the PPC and starch with SA increased the mechanical properties (e.g., break stress, break strain, and Young's modulus) compared to similar blends without SA (Figure 14a and 14b).

Since the components are bio-based and biodegradable, the PPC/starch blends are also bio-based and expected to be fully biodegradable, which gives it an added advantage of being environmental friendly. In addition, the relatively low cost of starch drives the overall cost of the PPC/starch

blend besides the observed improvements in mechanical and thermal properties of such PPC – PPC blends. Thus, a blend of PPC with starch have great potential to be utilized in various applications that benefit from biodegradability and improved cost structure.

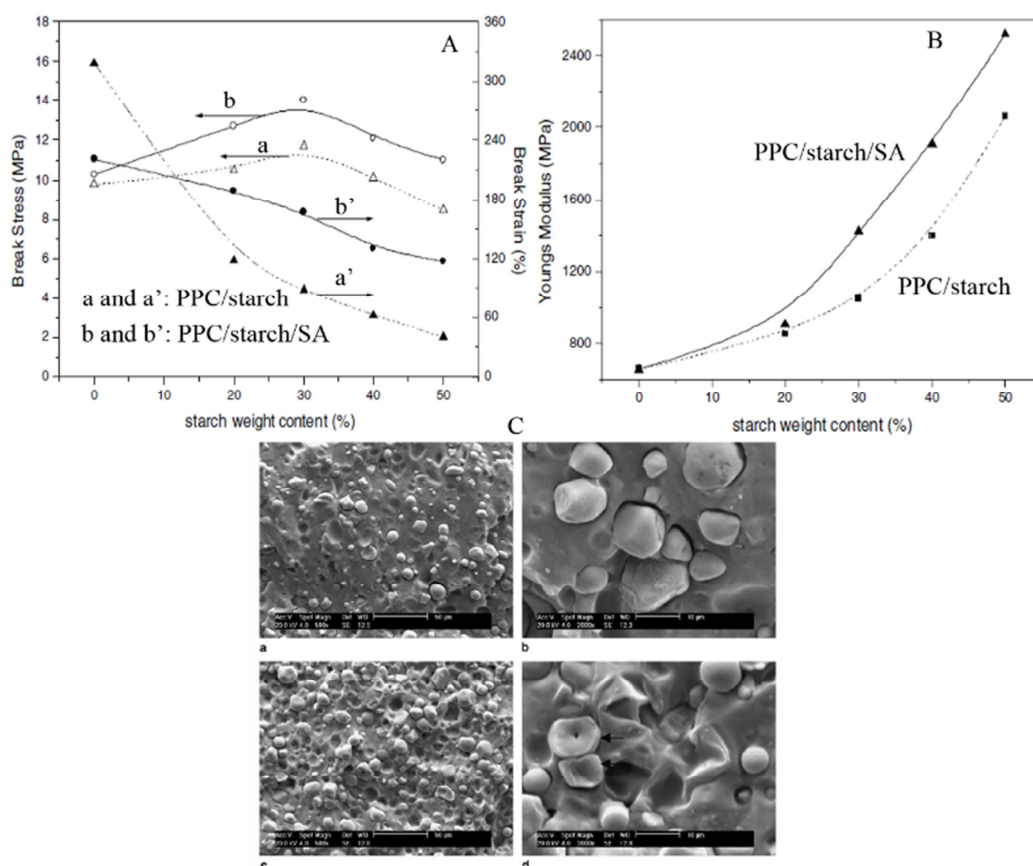


Figure 14. The effect of starch contents on mechanical properties (a and b) of PPC/starch composites with and without SA; (c) surface morphology of PPC/starch (70/30) blend (a and b) and PPC/starch/SA blend (c and d). Adapted from ref. [190] Elsevier © 2017.

3.2.6. PPC/EVOH blends

Poly(ethylene-co-vinyl alcohol) (EVOH) is a biodegradable, semi-crystalline thermoplastic with excellent processability, transparency, chemical resistance and gas barrier properties [193]. Studies have explored the performance improvement of PPC through blending with EVOH. In order to investigate the advantages of EVOH blending with PPC, Wang *et al.* [194] prepared PPC/EVOH blends with different compositions by melt blending. They have found that PPC/EVOH blends

were not miscible when the blend was prepared with low EVOH (<40 wt. %) content. However, when the PPC/EVOH blends were made with higher than 40 wt.% EVOH, the resulting blends showed better miscibility due to molecular interaction between the PPC and EVOH. There was no change in the tensile strength with up to 30 wt. % of EVOH incorporation to the PPC. Owing to the rigidity of EVOH, the ductility of the PPC blends were deteriorated with the incorporation of EVOH up to 30 wt. %. A further increase in EVOH content, up to 60 wt. %, showed the tensile strength of the blend increasing without any change in ductility. The increased strength with increasing EVOH content (40-60 wt. %) was due to the enhanced miscibility via intermolecular interaction between the EVOH and PPC. The EVOH and PPC have contributed synergistically to provide rigidity and ductility to the PPC/EVOH blends, respectively. It was concluded that the best performances were obtained in the PPC/EVOH blends with EVOH content between 40-60 wt. %.

After obtaining a proper compatibility between an optimized polyvinyl alcohol (PVA) and EVOH binary (70 wt. % PVA – 30 wt. % EVA) blend, Chen *et al.* [195] prepared ternary blends of PVA, EVOH, and ultrahigh molecular weight ($M_n = 250$ KDa) poly(propylene carbonate) (UHMW-PPC). The UHMW-PPC content was varied from 50 to 100 wt. % in the ternary blend. Good compatibility across various phases was observed in the resulting ternary blends because of the reaction between the hydroxyl groups and carbonyl groups of the PVA/EVOH blend and UHMW-PPC, respectively. As a result, a considerable increase in tensile strength of the PPC matrix was observed due to the reinforcing effect of PVA/EVOH. However, the elongation at break of neat PPC (350 %) was significantly reduced (~5%) after the incorporation of 10 wt. % PVA/EVOH. There was no further reduction in the elongation at break with increasing PVA/EVOH content in PPC.

3.2.7. PPC blends with other biodegradable polymers

In addition to PLA, PHB, PHBV, PBS, starch, and EVOH, some other biodegradable polymers have also been blended with PPC to produce PPC based sustainable materials. For example, PBAT is a semi-aromatic, biodegradable polymer that is produced by polycondensation reaction between 1,4-butanediol, terephthalic acid, and adipic acid [134,176,178,179,196]. It has mechanical properties similar to that of low-density polyethylene (LDPE), while the oxygen barrier property of the PBAT is 50% lower than LDPE [134] limiting its application in high barrier packaging. The PBAT properties can be tailored through blending with PPC to extend its application range. For example, various ratios of PPC/PBAT blend blown film were investigated by Pan *et al.* [197]. In this study, the T_g and crystallite dimension of the PBAT was reduced in the presence of amorphous PPC. The tensile strength and tear strength of the PPC/PBAT blend films were much higher than the neat PBAT. Specifically, the tear strength of the PPC/PBAT (50/50) blends showed 166 kN/m (transverse direction, TD) and 175 kN/m (machine direction, MD). This value was significantly higher than that of the neat PBAT tear strength (e.g. 74 kN/m (MD) and 42 kN/m (TD)). The CO_2 , N_2 and O_2 permeability coefficient of the neat PBAT also reduced from 7.12 to 2.61 barrer, from 0.59 to 0.087 barrer, and from 0.73 to 0.17 barrer after blending it with 50 wt. % PPC, respectively. CO_2 has better solubility in PPC, because PPC itself is synthesized from carbon dioxide and propylene oxide by co-polymerization. Moreover, owing to the excellent flexibility and amorphous character, the PPC can intercalate into the amorphous region of the PBAT, thereby restricting the movement of small molecules through the polymeric chains. The reduction in permeability of the PPC/PBAT blend towards O_2 and N_2 was due to the reduced availability of active sites in the PPC matrix to form physical interaction with oxygen and nitrogen molecules.

In the study of Xing *et al.* [198], PPC was blended with different ratios of cellulose acetate butyrate (CAB) (100/0 to 0/100) via melt processing. Even though these blends were thermodynamically immiscible, they exhibited partial miscibility due to hydrogen bond

interactions. Both tensile strength and elastic modulus of PPC/CAB blends were significantly improved with increasing CAB content [198]. For example, the PPC/CAB (50/50) blend exhibited 21 times higher tensile strength than the neat PPC. These improvements were attributed to the strengthening effect of CAB in the PPC. Owing to the compatibility between PPC and CAB, the PPC/CAB blend had some level of ductility while increasing the CAB content. Zhang *et al.* [199] also prepared a blend of maleic anhydride end capped PPC (MAH-PPC) with thermoplastic liquid crystalline ethyl cellulose (EC) by solution casting. While the study did not include methods for analyzing compatibility and miscibility of these blends, it clearly demonstrated the enhancement in thermal stability of PPC because of the EC blending.

Polyvinyl alcohol (PVA) is a biodegradable synthetic polymer with excellent flexibility, chemical resistance, high oxygen and aroma barrier properties because of its semi-crystalline structure, and comparatively high glass transition temperature (T_g) [100,200]. These features are beneficial to improve PPC's properties in a blend system. In one study, a melt blend of PPC/PVA showed good compatibility as a result of hydrogen bonding between the PPC and PVA, thereby producing a fine dispersion of inclusion phase [201]. Hydrogen bonding interaction between the carbonyl groups and terminal hydroxyl groups of PPC and hydroxyl groups of PVA was schematically represented in (a) and (b), respectively in Figure 15 [201]. The PVA can produce carbonyl groups after partial alcoholysis, which can form hydrogen bonding (Figure 15a') with the terminal hydroxyl groups of PPC, thus establishing a physical cross-linked network structure at a microscopic level. These network structures localized at the PPC/PVA interface provide good compatibility between PPC and PVA at a macroscopic level. Due to the good compatibility, the T_g of the PPC was increased from 34.1 to 44.0 °C when 30 wt. % PVA was added into the PPC. Such a blend also improved the tensile strength and Young's modulus of the PPC from 10.5 to 39.7 MPa and from 146.5 to above 700 MPa, respectively. When the PPC/PVA blends were prepared with

over 50 wt.% of PVA, the exposure of PPC carbonyl group during melt process was limited because of the accrued high viscosity. Consequently, weak interaction between the PPC and PVA was observed with two relaxation (T_g) peaks. In another investigation, benzenesulfonyl end-capped PPC (BC-PPC)/PVA blends were prepared by solution blending [202]. Before making the blends, the benzenesulfonyl end capping was employed in PPC to improve the thermal stability of the PPC. It was found that the BC-PPC/PVA blends were miscible in the PVA rich composition range whereas BC-PPC/PVA blends were immiscible in the PPC rich composition range. The observed immiscibility of the BC-PPC/PVA blends were attributed to the presence of end-capped benzenesulfonyl, which exhibited repulsive effect due to sulfonyl group and the spatial impact due to benzene ring.

In another study [100], miscible PPC based ternary blends were prepared with PVA and polyester based thermoplastic polyurethane (TPU) in a blown film process. The effects of different concentrations of a binary blend of PVA and TPU (50%/50%) in PPC matrix were investigated. The PPC/(50% PVA/50% TPU) blends did not show phase separation which suggested that the blended components were miscible at a microscopic level. In addition, the miscibility was validated with a single T_g observation. As a result, the mechanical properties (tensile strength, elongation at break, and tear strength) of the PPC/(50% PVA/50% TPU) blend blown films were found to be superior to the neat PPC at 0 °C. At room temperature, the tear strength and elongation at break of these PPC/(50% PVA/50% TPU) blown films increased remarkably with the addition of 30% (50% PVA/50% TPU) blend. Overall, the PPC/(50% PVA/50% TPU) blown film performances were comparable with commercial polyethylene. These observations could widen the PPC based material applications in the area of blown film platforms. In another study, Zhang *et al.*[203] demonstrated that the entire composition of PPC/poly(p-vinylphenol) (PVPh) blends are miscible with a single T_g . The miscibility of the resulting blends was attributed to the formation of

strong hydrogen bonds between hydroxyl groups and the oxygen functional groups of PVPh and PPC, respectively.

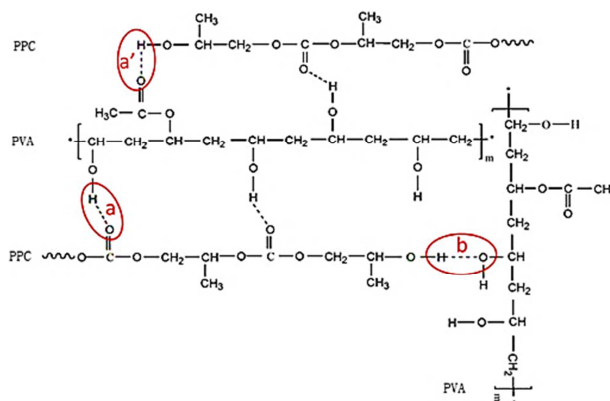


Figure 15. Hydrogen bonding interaction between PPC and PVA [201].

Chen *et al.*[204] have produced PPC based blends with hyper-branched poly (ester-amide) (HBP) by melt blending. These blends showed particle miscibility via hydrogen bond formation between PPC and HBP. In order to observe the phase morphology of the blends, the HBP phase was selectively removed from the PPC/HBP blend by using methanol. The PPC/HBP blend with 2.5 wt. % of HBP showed uniform dispersion of the inclusion phase. However, the HBP domain size increased with increasing HBP content up to 5 wt. %. The increased HBP domain size was attributed to the domination of intramolecular interaction between the functional groups of HBP compared to intermolecular interaction between the PPC and HBP. The maximum tensile strength and elongation at break of the PPC/HBP blends were observed with 0.5 wt.% and 2.5 wt.% HBP concentration, respectively. The observed improvements in the properties were due to the enhanced interfacial interaction between the PPC and HBP through hydrogen bonding. However, both tensile strength and elongation at break were detrimentally affected when the HBP content was above 5 wt.%. These reductions were attributed to the phase separation of HBP by agglomeration in the PPC phase.

Wu *et al.* [110] modified PPC properties by melt blending with different concentrations of poly(butylene carbonate) (PBC). The Pukanszky model suggested the existence of some extent of interfacial adhesion between the PPC and PBC, although the PPC was found to be immiscible with PBC. In this study, both tensile toughness and impact toughness of PPC/PBC blends were much higher than the neat PPC. The marked impact toughness improvement was mainly attributed to cavitation and shear yielding mechanisms. Furthermore, the PPC/PBC blends with 20 to 30 wt.% of PBC showed brittle to ductile transition. Unlike tensile strength, the elongation at break of the PPC/PBC blend increased with increasing PBC content up to 50 wt.%. The enhanced toughness of the PPC after blending with PBC could extend the application for PPC.

3.3. PPC blends with non-biodegradable polymers

In addition to PPC blends with biodegradable polymer, there are few studies conducted on PPC blends with non-biodegradable polymers (Table 4). For example, poly (methyl methacrylate) (PMMA) [205–207], poly(ethylene-co-vinyl acetate) (EVA) [208], polystyrene (PS) [209], urethanes [210], epoxy [112], polypropylene (PP) [211], and bisphenol A (BPA) [212]. The goal of blending PPC with non-biodegradable polymers is to tailor the properties of PPC (e.g., processability, mechanical, thermal). In other cases, PPC can be utilized as an additive (e.g., plasticizer, impact modifier) to other polymers. More recently, there is an interest to reduce the carbon footprint of synthetic polymers via incorporation of renewable polymers. PPC and other CO₂ based co-polymers are among the candidates that are being extensively researched for such purposes.

3.3.1. PPC/PMMA blends

Poly(methyl methacrylate) (PMMA) can be used to improve the performances of the PPC because it has excellent mechanical properties with a high T_g. PPC/PMMA blends are thermodynamically

immiscible [205]; thus there is a need for compatibilization. For example, Li and Shimizu [205] investigated the compatibilization of PPC/PMMA blend with PVAc. In this study, the compatibilizer used in PPC/PMMA blends enhanced the dispersion of PMMA phase in PPC by changing the phase morphology from sea-island to co-continuous morphology. As a result, the PPC/PMMA blends showed increments in both tensile strength and modulus with increasing PVAc content up to 5 phr. Beyond 5 phr, the PPC/PMMA blends did not exhibit any change in strength while the modulus deteriorated. However, the percent elongation at break of all the studied PPC/PMMA/PVAc blend ranges were very high (400%) due to the enhanced compatibility between PPC and PMMA. The PPC/PMMA blends produced as such have a lot of potential in various application platforms including those that currently rely on polyethylene, PP, and PS [205].

In another study by Yoo *et al.* [206], PPC/PMMA blends were compatibilized with three different compatibilizers *i.e.* poly(ethylene-co-glycidyl methacrylate) (EGMA), poly(styrene-g-acrylonitrile)-maleic anhydride (SAN-g-MAH), and maleic anhydride (MAH). The effects of these compatibilizers were investigated by varying their concentrations in a PPC/PMMA (70/30) blend. It was found that the PMMA inclusion phase size significantly reduced from 3.4 to 0.9 μm with the addition of these compatibilizers, which was attributed to the enhanced interaction between the PPC and PMMA phase. The enhanced compatibility was by the virtue of the combined effect of the polar-polar interaction between PPC and MAH along with the intermolecular forces between acrylonitrile of SAN and PMMA. Similar to SAN-g-MAH compatibilized PPC/PMMA blend, EGMA compatibilized (5 phr) PPC/PMMA blend showed strength improvement. In the case of MAH compatibilizer, the PPC/PMMA blend yielded maximum strength with the addition of 0.5 phr MAH. Due to the plasticization effect of the compatibilizer, the tensile strength of the PPC/PMMA blend was reduced when the compatibilizer content increased above 5 phr. Among

the selected three compatibilizers, the SAN-g-MAH compatibilizer was more effective because of the enhanced miscibility between the blended components. Yang *et al.* [207] used supercritical CO₂ as a solvent to conduct *in situ* synthesis modification of PPC/PMMA blends. The modified PPC/PPMA blends showed enhanced properties because of the improved compatibility and fine dispersion of PMMA in the PPC. The PPC/PMMA blend with 5 wt.% of PMMA resulted in a fourfold increase in tensile strength [207]. The yield strength of the PPC increased by 180% with a small amount (3.5 wt. %) of PMMA addition into the PPC. Significant improvement in properties with the small amount of PMMA addition was due to the fine (nanosize) dispersion of PMMA in the PPC matrix. The observed improvements in the tensile strength are comparable with the PPC/PMMA (70/30) blends prepared by other techniques.

3.3.2. PPC blends with other non-biodegradable polymers

Fei *et al.* [212] prepared PPC/Bisphenol A (BPA) blend using solution blending. The PPC/BPA blend with lower BPA concentration (e.g. <30 wt. %) demonstrated miscibility due to the hydrogen bonding interaction between the PPC and BPA. When the BPA content was increased beyond 30 wt. %, the resulting PPC/BPA blend showed immiscibility due to BPA crystallization. The mechanical properties of PPC and low molecular weight urethanes such as 1,6-bis(hydroxyethyl urethane)hexane (BEU), 1,6-bis (hydroxyisopropyl urethane) hexane (BPU), and 1,6-bis(methyl urethane)hexane (HDU) blends were studied by Chen *et al.* [210]. When 1 wt.% of BEU was added to PPC, significant strengthening effects were observed in the resulting blend, with a 37% increase in strength. With a further increase in BEU, strength decreased while elongation at break increased. However, the strength was still superior to that of pure PPC until the addition of 10 wt.% BEU. The PPC/BPU blend with 5 wt.% BPU showed a two-fold increase in elongation at break compared to neat PPC, while its tensile strength was 50 MPa. This indicates the simultaneous toughening and the reinforcing effects, providing further confirmation of the

importance of hydrogen-bond interactions in the miscibility and compatibility of the blends. However, when the BPU content was increased beyond 10 wt.%, the strength was inferior to that of neat PPC.

Distinct yielding and stable neck growth through cold drawing were observed when the HDU content was varied over the range of 5–10 wt.%. Although HDU had a lower Young's modulus compared to BPU and BEU, transition had occurred from brittle to ductile for the blend. PPC/HDU blend with 10 wt.% of HDU exhibited a remarkable elongation at break, 53 times higher in comparison to neat PPC, while its tensile strength (30 MPa) was comparable to that of the LDPE. The molecular-level miscibility between HDU and PPC, combined with the decrease in T_g values for the blends, were considered as the principal causes for the satisfactory plasticization of the blend. Due to enhancement in mobility of the chain segment, the plasticizer was observed to behave like a lubricant that has been mixed with polymers, thereby reducing cohesion of the molecular chains. During tensile testing, the molecular chains were observed to gradually entangle and get oriented. This, in turn, dispersed the fracture energy more effectively, and thereby delayed the final rupturing of the material. The toughening of PPC by HDU was not accompanied by any drastic reduction in the mechanical stress of the blend. However, an increase in HDU content beyond 10 wt. % led to the domination of hydrogen bonding and crystallinity over the dilution effect of plasticization. This led to a reduction in the elongation at break and an increase in tensile strength.

PPC was also used as an additive to improve the flexibility and drawability of isotactic polypropylene (iPP) by melt blending [211]. Higher yield stress and Young's modulus were observed when 3 wt.% PPC was added to iPP. Unlike iPP, PPC/iPP blend samples were broken in ductile fashion during high elongation speed. The observed high ductility of PPC/iPP blends during high stretching rate can be explained as follows (Figure 16): the stress concentration of the

PPC domain surface boundary creates voids, which subsequently produces a sizeable amount of craze perpendicular to the stretching direction. The crazes dissipate the mechanical energy while preventing the cavitation development towards the longitudinal direction. Combination of voids in the crazes can form micro-cracks opposite to the stretching direction.

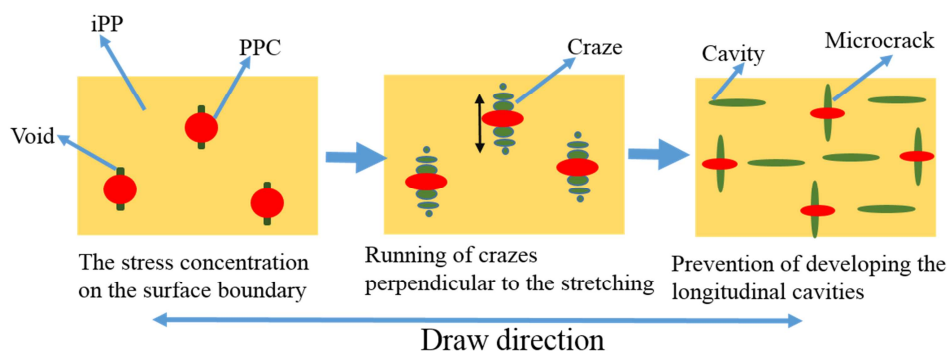


Figure 16. Failure mechanism of iPP/PPC at a high elongation speed (redraw from reference [211] Wiley © 2017. The black arrow indicates the running direction of crazes.

Various compositions of PPC/EVA blends were prepared via melt blending as reported by Wu *et al.* [208]. It was observed that the PPC and EVA were partially miscible with good interfacial interaction between them. The T_g value of the PPC increased with increasing EVA content, indicating the improvement in compatibility between the PPC and EVA. Similar to T_g increase, the tensile strength, Young's modulus and thermal stability of the PPC increased with increasing EVA content in the resulting blends. Due to the partial miscibility between the PPC and PS, the PPC/PS blend prepared with 40 wt.% PS showed a three-fold increase in tensile strength compared to neat PPC [209]. Calderón and co-workers [213] found good interfacial interaction between the PPC and polyoxymethylene due to dipole–dipole interactions. Meanwhile, a drastic reduction in the percent elongation at break of PPC was observed when 40 wt.% of PS was added into PPC [209]. Likewise, Huang *et al.* [214] found partial miscibility between PPC and epoxy. The tensile toughness and impact toughness of the hot pressed bio-based epoxy/poly(furfuryl alcohol) (PFA)

blend were significantly improved with the addition of PPC polyol (10, 20, and 30 phr) [112]. Besides nanoscale size dispersion of PPC polyol in the epoxy/PFA, the marked toughness improvement was attributed to the interpenetrating polymer network (IPN) formation between the blended components. Chen *et al.* [215] prepared a PPC based triblock copolymer, *i.e.* PCL-PPC-PCL to improve the toughness of epoxy. The epoxy with 30 wt.% of PCL-PPC-PCL block copolymer showed 320% increase in elongation at break and 180% increase in toughness compared to neat epoxy, indicating that this strategy can improve the toughness of epoxies.

In summary, many PPC based blends have been studied by various researchers to understand the compatibility, miscibility and their mechanical performances. It was found that the majority of the PPC blends showed immiscibility or partial miscibility behaviour. The observed partial miscibility and compatibility in the PPC blends were due to the hydrogen bonding interaction between the blended components. The observed immiscibility of the PPC blends was due to the difference in glass transition temperature of the constituents. Mechanical properties of the PPC blends were dictated by the blend components concentration, compatibility, and miscibility with the blended components.

Table 4. PPC based blends with biodegradable and non-biodegradable polymers.

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Blends	Preparation method	Compatibility/ Miscibility	Compatibilizer/ Plasticizer	Enhanced performances	References
PPC/PLA	Melt blending	Partial miscible and compatible	-	Thermal stability, Yield strength, and Young's modulus	[152], [60]
PPC/PLA	Melt blending	Compatible	Joncryl ADR 4368-C	Elongation, tensile strength, secant modulus, water vapor barrier, and oxygen barrier	[78]
PPC/PLA	Melt blending	Compatible	Maleic anhydride	Ductility	[154], [80]
MAH-PPC/PLA	Melt blending	Compatible	Polyvinyl acetate	Interfacial adhesion	[155]
MAH-PPC/PLA	Melt blending	Compatible	Tetrabutyl titanate	Elongation	[158], [160]
PPC polyurethane/PLA	Melt blending	-	-	Elongation and impact strength	[159]
PPC/PLA	Melt blending	Compatible	Maleic anhydride and luperox 101 initiator	Oxygen barrier	[161]
PPC/PLA	Melt blending	Compatible	Poly(1,2-propylene glycol adipate)	Transparency, haze, and tear strength	[162]
PPC/PHBV	Melt blending	-	-	Water vapor barrier, and oxygen barrier	[164], [165]
PLA/PHBV/PPC	Melt blending	Immiscible	-	Toughness, less shrinkage	[166]
PPC/PHBV	Solution blending	Immiscible	-	-	[167], [168]
PPC/PHBV	Melt blending	Compatible	Dicumyl peroxide and glycidyl methacrylate	Impact energy and elongation	[169,170]
PPC/PHB	Solution blending	Miscible	-		[172], [173]
PPC/PHB	Electrospinning	Miscible	Polyvinyl acetate and acetyl triethyl citrate	Elongation and tensile strength	[174]
PPC/PHB	Melt blending		Propylene carbonate	Impact toughness	[175]
PPC/PBS	Melt blending	Partial miscible	-	Ductility Elimination of shrinkage	[181], [182], [184]
PPC/PBS	Melt blending	Compatible	Triphenylmethane triisocyanate	Tensile strength and ductility	[183]
PPC/PBS	Melt blending	Compatible	L-Aspartic acid	Flexibility, yield strength and Young's modulus	[86]
PPC/Starch	Melt blending	Compatible	-	Young's modulus	[187,188]

PPC/Starch	Melt blending	Compatible	Acetylated starch	Strength and ductility	[189]
PPC/Starch	Melt blending	Compatible	Polymethylacrylate grafted starch	Toughness	[192]
PPC/Starch	Melt blending	Compatible	Succinic anhydride	stress, strain and Young's modulus	[190]
PPC/EVOH	Melt blending	Compatible	-	Tensile strength	[194]
UHMW-PPC/EVOH	Melt blending	Compatible	-	Tensile strength	[195]
PPC/PBAT	Melt blending	-	-	Tear strength and gas barrier properties	[197]
PPC/CAB	Melt blending	Partial miscibility	-	Tensile strength and elastic modulus	[198]
MAH-PPC/liquid crystalline ethyl cellulose	Solution blending	-	-	-	[199]
Benzenesulfonyl end-capped PPC/PVA	Solution blending	Immiscible	-	-	[202]
PPC/PVA	Melt blending	Compatible	-	Tensile strength and Young's modulus	[201]
PPC/PVA/TPU	Melt blending	Miscible	-	Tensile strength, elongation at break, and tear strength	[100]
PPC/ poly(p-vinylphenol)	Solution blending	Miscible	-	-	[203]
PPC/ hyperbranched poly(ester-amide)	Melt blending	Compatible	-	Tensile strength and elongation at break	[204]
PPC/PBC	Melt blending	Immiscible	-	Tensile toughness and impact toughness	[110]
PPC/PMMA	Melt blending	Compatible	Polyvinyl acetate	Tensile strength and modulus	[205]

PPC/PMMA	Melt blending	Compatible	Poly(ethylene-coglycidyl methacrylate), poly(styrene-g-acrylonitrile)-maleic anhydride, and maleic anhydride	Tensile strength	[206]
PPC/PMMA	Supercritical CO ₂ based <i>in situ</i> synthesis	Compatible	-	Tensile strength	[207]
PPC/Bisphenol A	Solution blending	Miscible	-	-	[212]
PPC/bis(hydroxyethyl urethane)hexane, PPC/1,6-bis(hydroxyisopropyl urethane) hexane, and PPC/1,6-bis(methyl urethane)hexane	Melt blending	Compatible	-	Toughness and strength	[210]
PPC/iPP	Melt blending	-	-	Ductility	[211]
PPC/EVA	Melt blending	Compatible	-	Tensile strength, Young's modulus and thermal stability	[208]
PPC/polyoxymethylene	Melt blending	Compatible	-	-	[213]
PCL-PPC-PCL/epoxy	Melt blending	Compatible	-	Elongation and toughness	[215]

4. Concluding remarks

The use of CO₂ as a feedstock in sustainable polymer development is a feasible approach that can significantly contribute towards the reduction of its accumulation in the atmosphere. Moreover, the use of CO₂ as a building block reduces the reliance on non-renewable, and less environmental-friendly fossil resources for the production of plastics. Typical CO₂ co-polymers are attractive polymers because not only are they derived by fixation of up to 50% of their mass with CO₂, but also the polymers made are biodegradable and biocompatible. The most studied CO₂ derived aliphatic polycarbonate, PPC, can be processed with regular thermoplastic processing equipment such as extrusion, injection molding, blow molding into a variety of forms, and exhibit similar characteristics as many thermoplastics. Many application development technologies on PPC polymer focus on its use in the packaging industry. The less studied PEC on the other hand, exhibits superior oxygen barrier performance compared to many traditional packaging plastics including polyethylene, and polypropylene. Thus, it can play a significant role in reducing food spoilage caused by oxidation in multilayer plastic food packaging, barrier coatings, or in biomedical materials and other niche applications where oxygen barrier is important.

The manufacturing technology, catalysis, polymer processing, and application development of many of these aliphatic polycarbonate polymers are still at a relatively early stage. As a result, their full potential as a material is yet to be explored. The low glass transition temperature, and rather insufficient strength constitutes the major performance limitations of CO₂ co-polymers. Moreover, since many polymers used for packaging applications are highly commoditized, their acceptability is driven by cost than performance. Thus, cost reduction in addition to performance improvement of CO₂ co-polymers are the grand challenges that need to be addressed for their

extensive utilization. In an effort to enhance the cost – and performance – competitiveness and expand the application range of these polymers, numerous studies have focused on blending them with other polymers. Some of the advances achieved in such multiphase polymeric materials demonstrated excellent performance with a clear potential to substitute conventional non-biodegradable polymers. The global drive to reduce plastic waste accumulation that prompted interest in sustainable materials could provide further motivations for innovations in CO₂ co-polymers.

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