

CO-POLYMERIZATION OF CARBON DIOXIDE AND EPOXIDES TO CREATE PLASTICS FROM CO₂

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Abstract

As a result of global warming, it is expected that petroleum supplies would run out within the next century at the current rate of consumption. As a result, there is an increasing push to create new chemical processes that use biorenewable sources. A plentiful, affordable, and non-toxic biorenewable source is carbon dioxide. The techniques by which CO₂ can be used are immobilisation by polymerization, reduction by metal catalysed processes, and chemical transformations. In addition to these procedures, copolymerization of epoxies is crucial. When CO₂ and the copolymers cyclohexene oxide and propylene oxide are used to create epoxies, cyclic carbonates are a prominent byproduct. It's crucial to choose a copolymer that has the fewest obstacles, C-O connections, and rivalries. Inoue group (aluminum catalysts) fulfills the basic requirements. Sometimes, salen metal complexes are also used in the formation of epoxies with CO₂. Formation of nano-particles by intermolecular cross linking and high activity Zn (II)-based catalyst can be used for asymmetric CHO-CO₂ copolymerization.

Keywords: Co-polymerization, reduction, chemical transformation, metal complexes and biorenewable.



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Introduction:

The term "global warming" refers to the accelerated warming of the earth's surface as a result of anthropogenic (related to human activity) emissions of greenhouse gases (CO₂, CH₄, N₂O) from industrial activity and deforestation, which causes the sea level to rise and changes the climate. Carbon dioxide is the main gas involved in this process. At the current pace of consumption, petroleum supplies are expected to run out within the next century, hence efforts are being made to create new chemical processes that use renewable bioresources. CO₂ is a plentiful gas found in costly, non-toxic, and renewable biosources. Consequently, it might be a substitute for raw materials.

The amount of carbon dioxide in the atmosphere has been rising recently, which could have a negative impact on the ecosystem in the future. CO₂ is the main cause of the greenhouse effect. Additionally, CO₂ is a very stable, linear molecule in which the carbon is an electrophile and the oxygen atoms are weak lewis bases. The O-C-O bond bends as a result of nucleophilic assaults on the carbon, which dominate reactions involving carbon dioxide. Utilization and immobilisation of CO₂ have grown to be difficult in recent years. At pH range 7, 250°C, and 1 atm pressure, the most frequent reactions of CO₂ in this regard are as follows.

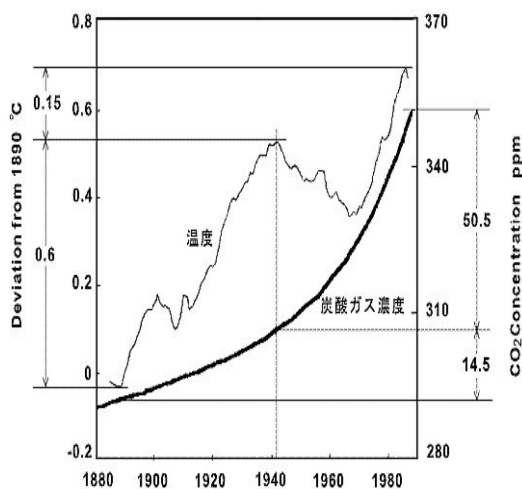
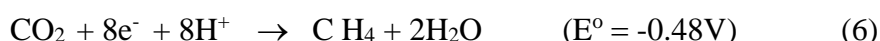
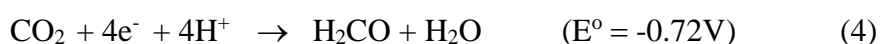
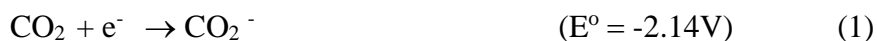


Fig1 The major reason of global
Warning

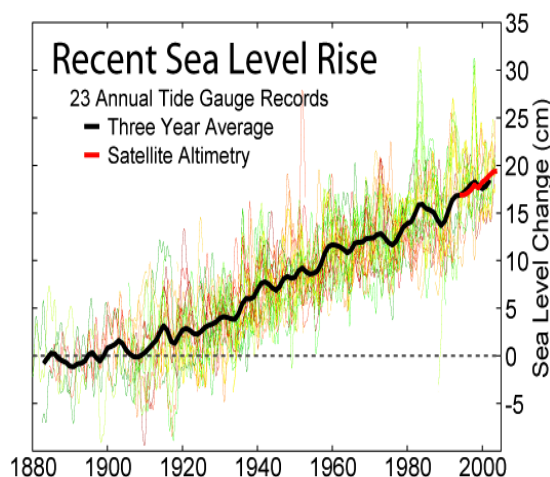


Fig2 Sea-level rise caused by
global warming

The main reaction compounds are formic acid, methanol, hydrocarbons and oxalic acid. This electro-reduction of CO₂ is of interest as a potential component of a carbon energy cycle i.e. CO₂ + energy → methane → CO₂ + energy. The synthesis of CO₂ is a complex multi-step reaction with adsorbed intermediates, most notably adsorbed CO. the possible pathways to obtain chemicals from CO₂ and illustrated in figure3.

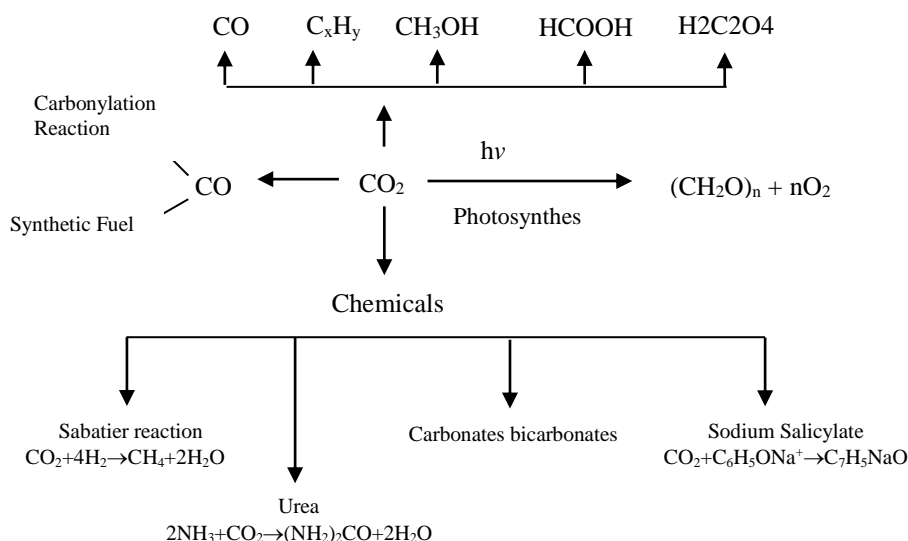


Fig3 Possible pathways to obtain chemicals from CO₂

Three of the most efficient processes for the processing and recovery of the air carbon based sources appear to be photosynthesis, photo catalysis, and electrochemical reduction of CO₂ [1, 2]. In order to break the C-O bond in CO₂ and help turn it into useful chemicals, various energies are required. Due to the stability and chemical inertness of CO₂, it is important to take into account the thermodynamic requirements for different CO₂ reduction reactions. The energy required to transport our CO₂ recovery of the air carbon based sources can be produced by high temperatures, extremely reactive reagents, electricity, or photon energy.

CO₂ polymerization is one of the most effective ways to immobilise CO₂. In recent years, there has been an increase in interest in using carbon dioxide as an industrial solvent. The characteristics [3] of CO₂ make it more environmentally friendly than many organic solvents that are frequently employed in industry (naturally occurring, renewable supply that is safe to handle, non-toxic, and non-flammable). Supercritical CO₂ is easy to obtain due to the low critical temperature and pressure of CO₂ (31.170C, 73.8 bar), which is another benefit

for industrial use [4]. CO₂ can be employed as a solvent in oxidations, biocatalysis, hydrogenations, and polymerizations as well as a raw ingredient in industrial processes [5]. The main limitation is the use of supercritical CO₂ in industry is its weak solvent power, in industry materials that exhibit solubility in supercritical CO₂ at moderate temperature and pressure (T<100⁰C, P<200 bar) need to be synthesized.

Propylene oxide and carbon dioxide can be used to create the poly (propylene carbonate) polymers [6]. CaH₂ was used to dry the propylene oxide, and it was subsequently separated by distillation and stored under nitrogen. Reactions were place under intense pressure. The catalyst was added to the reactor (0.05 mole percent) and dried under vacuum. Propylene glycol, the initiator poly, was vacuum-dried before being fed into the reactor. Dry propylene oxide was then injected after that. The reactor was then half-pressurized with gaseous CO₂ while still at room temperature. The reactor was fully fueled after being heated to the reaction temperature. The reactor was depressurized and the polymer was dissolved in toluene following a 4 to 5 hour reaction period. An isolation funnel was used to separate the polymer. It was washed in a solution of saturated NaCl and ammonium hydroxide in water.

In addition, cyclohexene [7] oxide (CHO), which forms cycli carbonates as a significant byproduct and is thermodynamically more stable than polycarbonates, can be used to co-polymerize epoxides and CO₂

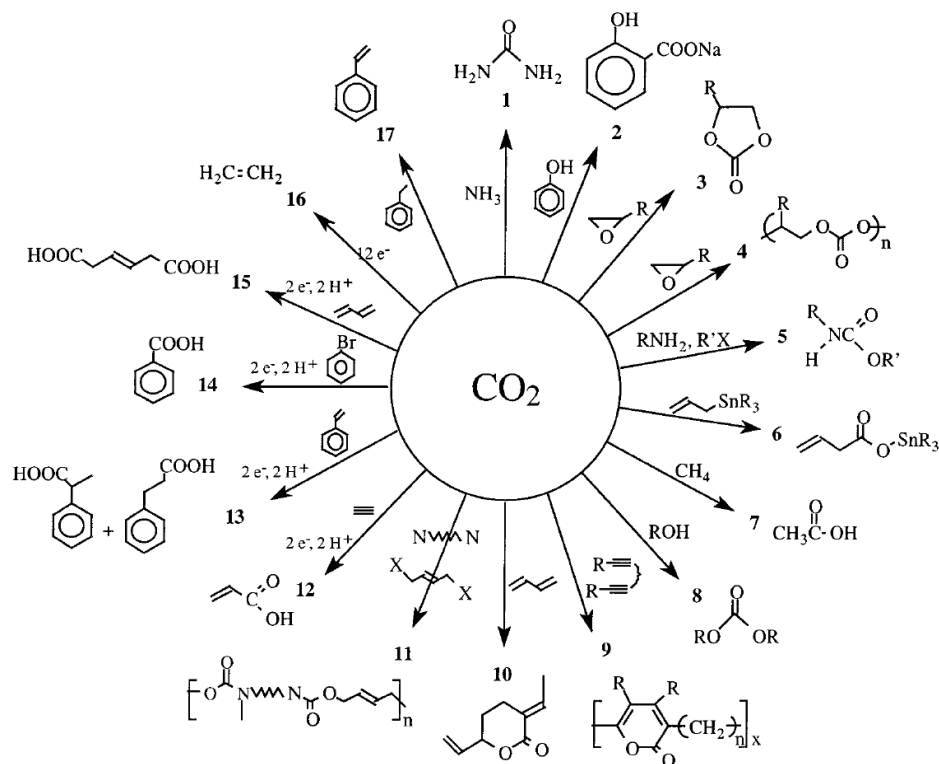
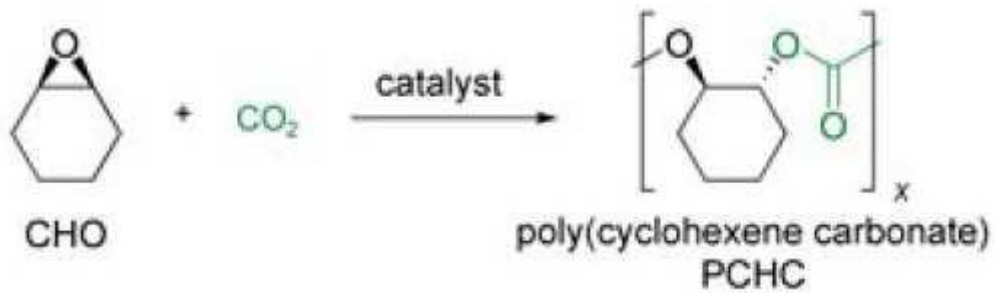
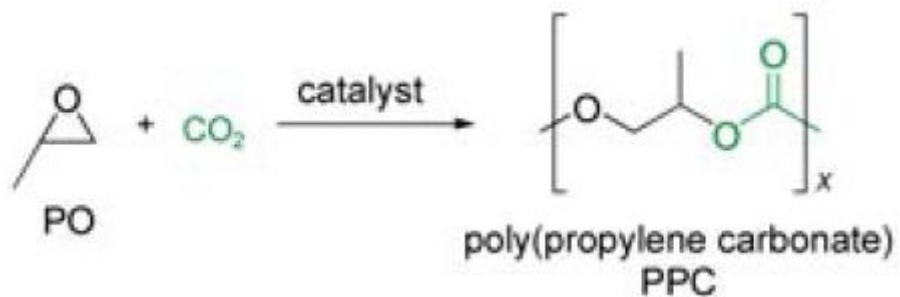


Fig 4 Chemical transformations of CO₂



CHO: cyclohexene oxide



PO: propylene oxide

Fig.5 Copolymerization of epoxides and CO₂

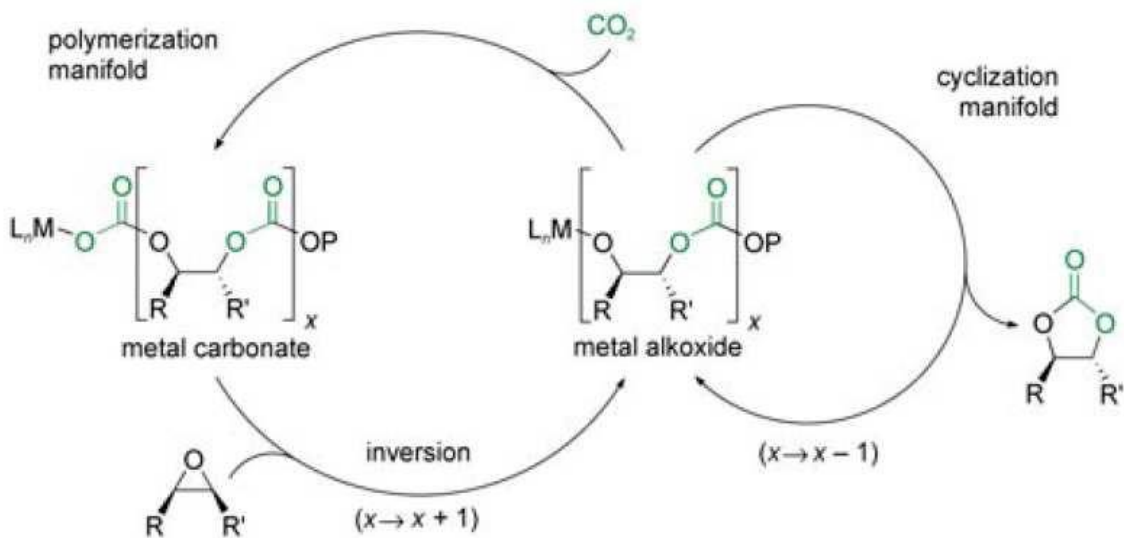
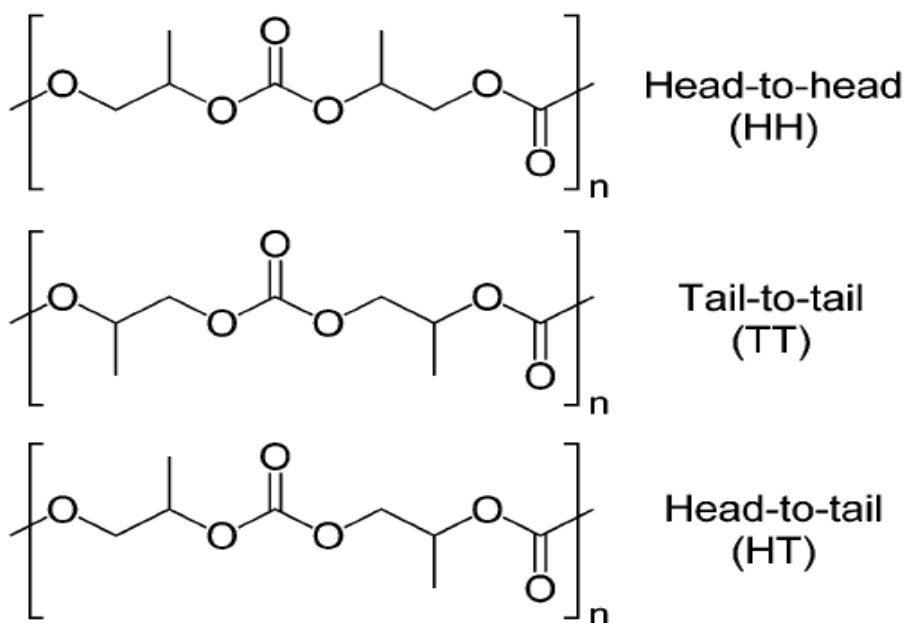
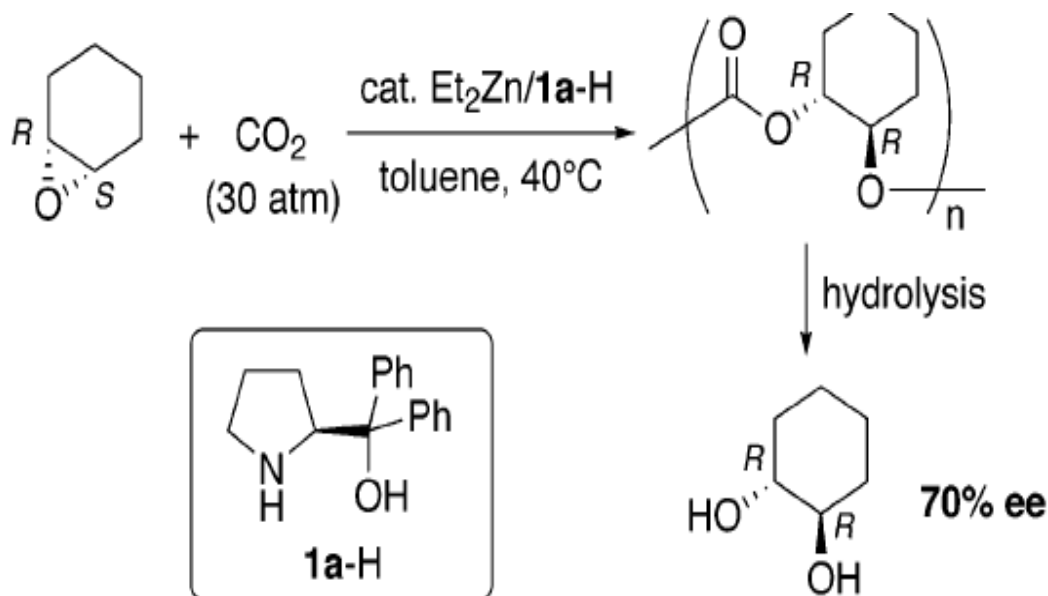


Fig.6 The basic mechanism of epoxide and CO₂ copolymerization and the formation of cycli carbonates



Regiochemistry of PPC



Asymmetric Copolymerization of CHO and CO₂

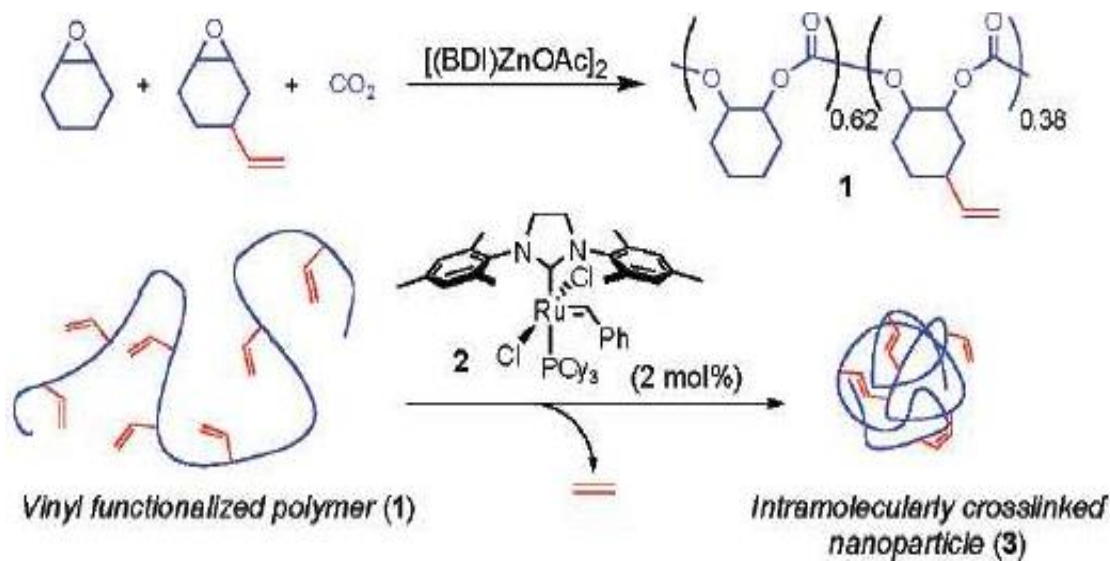


Fig.7 Synthesis of alkene crossing- linked polycarbonate nano-particles

Poly (propylene carbonate) is used as an adhesive and to make epoxy resin more durable. It can be utilised as a plastic material for oxygen diffusion since it is an inadequate oxygen barrier. Getting rid of plastics is really challenging. Burning them can release harmful substances like dioxins, and sustainably collecting and recycling them is challenging due to the wide variety of types and the fact that each must go through a unique process is complex. Plastics would not be so awful if we only used a modest bit of them, but we use astonishing volumes of them. Literally, we are drowning in plastic that we are unable to dispose of. and the most of it is produced using oil, a non-renewable resource that is getting more and more expensive. It's been estimated that 200,000 barrels of oil are used each day to make plastic pac. Broadly speaking, so-called "environmentally friendly" plastics fall into three types:

- **Bioplastics** made from natural materials such as corn starch
- **Biodegradable plastics** made from traditional petrochemicals, which are engineered to break down more quickly
- **Eco/recycled plastics**, which are simply plastics made from recycled plastic materials rather than raw petrochemicals.

The idea behind bio-plastics is straightforward: if we could create plastics from less harmful chemicals at the outset, they would decompose more rapidly and readily after being discarded. The most well-known bio-plastics are those that are offered under the brands EverCorn™ and NatureWorks and are manufactured from organic components like corn

starch, with an emphasis on their environmental credentials. Some bioplastics resemble conventional petrochemical plastics so closely that it's difficult to tell them apart. Food containers are increasingly frequently made with polylactide acid (PLA), which resembles polyethylene and polypropylene in appearance and behaviour. Making PLA, according to NatureWorks, requires only one-third of the energy needed to produce conventional plastics. Bioplastics [8–10] often degrade without adding significantly more carbon dioxide to the atmosphere than conventional plastics or biodegradable plastics (because the plants that were used to make them absorbed the same amount of carbon dioxide to begin with). When PLA breaks down in landfills, for instance, it emits roughly 70% fewer greenhouse emissions. Another benefit of bio-plastics is that they may be composted, decomposing into organic substances that mix naturally with soil. In a few of weeks, some bio-plastics can degrade. They contain cornstarch molecules, which slowly absorb water and expand, disintegrating into smaller pieces that the bacteria can consume more easily. These biodegradable polymers, as their name implies, contain additives that hasten their decomposition in the presence of light and oxygen (moisture and heat help too). Biodegradable plastics, in contrast to bio-plastics, are made of regular (petrochemical) plastics and can leave behind a hazardous residue, making them generally (but not always) unsuitable for composting. Anything that assists humanity in finding a solution to the plastics problem must be beneficial, right? Unfortunately, environmental problems are rarely so straightforward. Even actions that seem to benefit the world in blatant ways may have significant downsides and can cause harm in other ways. Understanding whether "environmentally friendly" practises are actually doing more harm than good requires taking a holistic approach to the situation. Some biodegradable polymers release methane gas when they break down in landfills. This potent greenhouse gas makes the issue of global warming worse.

- Bioplastics and biodegradable plastics don't always break down easily. Some require relatively high temperatures to break down, and in some circumstances, they can still take several years. Even then, they can leave behind hazardous waste.

- Since bio-plastics are produced using plants like corn and maize rather than petroleum, land that could be utilised to grow food for the entire world is now being used to "grow plastic." By 2014, it's anticipated that over a quarter of US grain production will go toward the creation of biofuels and bioplastics, which might result in a large increase in food prices.

- Genetically altered corn is used to make some bio-plastics, including PLA. Genetically modified (GM) crops are typically viewed as being intrinsically bad for the environment. Bio-plastics and biodegradable plastics cannot be easily recycled.

- Although PET (polyethylene terephthalate) and PLA appear extremely similar to most people, mixing the two makes it hard to recycle the entire batch. There are worries that growing PLA use could sabotage current plastic recycling efforts.

Nowadays, crude oil is mostly used in the production of plastics. The plastics sector is seeing a rise in the viability and promise of renewable resources in this situation. Burning petroleum-based plastics releases the carbon dioxide that is found in the fuel into the atmosphere, causing global warming. Utilizing bioplastics has a lot of advantages for the environment and the economy. Bioplastics are a type of plastic made from plant materials such as maize starch, hemp oil, sugarcane, hemp, and sugar. Bioplastics are more environmentally friendly than standard plastics because less carbon dioxide is released during production, which is regarded to be a contributing factor to global warming. They are also biodegradable, which means that after being buried in the earth, the substance returns to its original state. Starch in plants is broken down by enzymes into glucose, which is fermented and converted to lactic acid. After being heated and moulded, the polymerized lactic acid is transformed into polylactic acid, a material that can be employed in the production of goods. Bioplastics can also be broken down naturally. Microorganisms will degrade bioplastic into carbon dioxide and water if it is buried in the ground. The materials also have an increasing variety of other uses, such as artificial fibres, medical items, and construction materials. Bioplastic bags can be discarded and buried with other biodegradable trash. Melt compounding was used to create poly(propylene carbonate)/starch (PPC/starch) composites with varying starch concentrations. By burying the composites in soil for six months, the biodegradability of the materials was examined. Thermal analysis, FTIR analysis, and morphological observation all made it evident how the buried specimens had changed. A three-stage biodegradation, corresponding to the growth of microbes, the degradation of starch, and the degradation of PPC, was demonstrated by the weight loss curves and molecular weight changes of the specimens. According to the experimental findings, adding starch sped up PPC deterioration. Greater weight loss in the second stage and lesser weight loss in the third stage were seen in specimens with higher starch contents.

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