



Feature article

Recent progress in carbon dioxide (CO₂) as feedstock for sustainable materials development: Co-polymers and polymer blendsRajendran Muthuraj ^a, Tizazu Mekonnen ^{b, *}^a Institute for Materials Research and Innovation, University of Bolton, Bolton, BL3 5AB, UK^b Department of Chemical Engineering, University of Waterloo, Waterloo, ON, N2L 3G1, Canada

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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.

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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 (Fig. 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.

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 (Fig. 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].

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

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