STM JOURNALS

Journal of
Polymer & Composites

ISSN: 2321-2810 (Online)
ISSN: 2321-8525 (Print)
Volume 11, Special Issue 3, 2023
DOI (Journal): 10.37591/JoPC

http://engineeringjournals.stmjournals.in/index.php/JoPC/index

Review JoPC

A Smart Investigation on Nanocomposites Composed of Carbon Dioxide-Derived, Repeatable Biological Polymers

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Abstract

In recent years, an increasing number of people have begun to focus their attention on the environmental impacts that are caused by the widespread use of therapeutic polymeric composites that are generated from fossil fuels. Another factor that probably contributes to the short shelf life of biomedical polymer products is the fact that many of them are designed to be used just once before being discarded. When a biomedical polymer product goes over its sell-by date, it must often be burned before being discarded, thus increasing carbon dioxide emissions (CO_2). By ultimately replacing their unsustainable fossil-based equivalents, biomedical goods based on polymers produced from CO_2 fixation would improve CO_2 recycling in this industry and aid in the mitigation of the greenhouse effect. However, the bulk of presently available polymer materials manufactured from renewable raw materials do not satisfy these expectations due to a number of property deficiencies, and the superiority and values for biomedical devices are constantly expanding. The materials do not have the essential characteristics to satisfy the requirements. Many people are trying to apply nanotechnology in this field due to these problems. In addition to discussing replicable CO_2-fixed polymer-based nanocomposites that may be used in biological applications, this work gives a number of suggestions for further research areas in this field.

Keywords: Biopolymers, gelatin, nanocomposites, emission, chitin

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Received Date: January 30, 2023
Accepted Date: February 02, 2023
Published Date: February 14, 2023

Citation: I.S. Chakrapani, M. Rajasekhar, L.V.K.S. Bhaskar, Chandra Mohan, Shalini Sharma, Sumanta Bhattacharya. A Smart Investigation on Nanocomposites Composed of Carbon Dioxide-Derived, Repeatable Biological Polymers. Journal of Polymer & Composites. 2023; 11(Special Issue 3): S1–12p.

INTRODUCTION

Due to rising population and growing economies, there has been a rise in the need for energy and the production of greenhouse gases [1–4]. Since the start of the industrial age in the 17th century, greenhouse gas emissions have increased. The results were a worsening of the greenhouse effect and other problems. The majority of the greenhouse effect is due to carbon dioxide (CO_2), which is produced by burning fossil fuels and its byproducts. Multidisciplinary teams of scientists have worked together to cut down on carbon dioxide production. This action is necessary to forestall further contributions to global warming gases [5–7].

Many biomedical polymer products that we use regularly are blamed by healthcare specialists for contributing to global CO_2 emissions. Biomedical polymers have several applications in the medical field, including in tissue engineering, artificial

organs, medication production, diagnostic devices, consumables, and packaging (Figure 1). Primarily responsible are the advantages and low cost of biomedical polymers [8]. Most of these discarded medications emit CO_2 when burned. More than one hundred biomedical polymer polymers are used in more than 1800 pharmaceutical products [9]. From 2011 to 2019, biomedical polymer material production and distribution rose 5.6%, from 4.391 million metric tons to 6.771 million metric tons. Biomedical polymer waste generates 20 million tons of CO_2. The manufacturing of medical devices adds considerably to CO_2 emissions due to its stringent process limitations and high failure rate. Prioritizing CO_2 recycling of biomedical polymers is important since it lessens the material's effect on the environment.

Biomedical devices designed to prevent epidemics have seen greater usage after the spread of COVID-19. China's production of COVID-19 masks increased by about 100%. Numerous systems for the organization of biological polymers have been proposed [10, 11]. It is possible to find both biodegradable and nonbiodegradable biomedical polymers. Biomedical polymers include thermoplastics, thermosets, and elastomers. Biomedical polymers may either be derived from living sources or from remains. This is supported by the studies. Bio-based polymers, also known as naturally generated polymers, have a lower global warming potential than polymers made from fossil fuels, because the components of bio-based polymers are sustainable [12]. Biomedical polymers are more carbon-efficient than their petrochemical counterparts since they are often produced by plant photosynthesis or other natural CO_2 fixation processes.

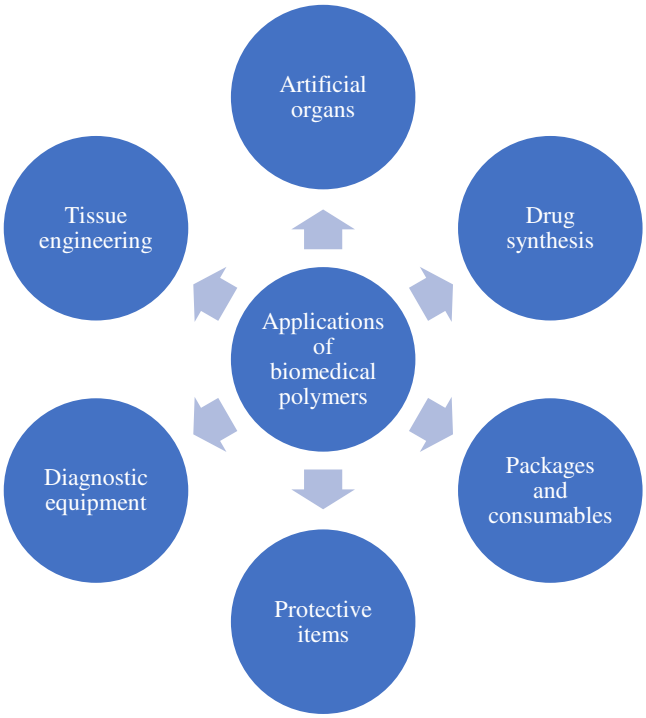

Figure 1. Applications of biomedical polymer products.

There are three repeating polymers that are able to repair CO_2. Examples include polymers generated from natural sources (Figure 2), polymers made from renewable resources, and polymers made from CO_2. The term "synthetic renewable polymers" refers to polymers that are derived from renewable sources such as those that are created by the polymerization of natural subunits. The production of CO_2-based polymers requires polymerizing carbon dioxide gas with chemicals sourced either from biological sources or from fossil fuels [13]. CO_2 fixation is used to create carbon-neutral repeating polymers. To encourage CO_2 recycling and reduce the carbon footprints of medical supplies, petrochemical alternatives must be phased out in favour of biomedical products created from polymers from CO_2

fixation using repeatable sources. The vast majority of polymers produced by CO_2 fixation fall short of achieving the ever-increasing quality and performance demands for biomedical applications. This is true regardless of whether the polymers are based on CO_2 or on renewable resources.

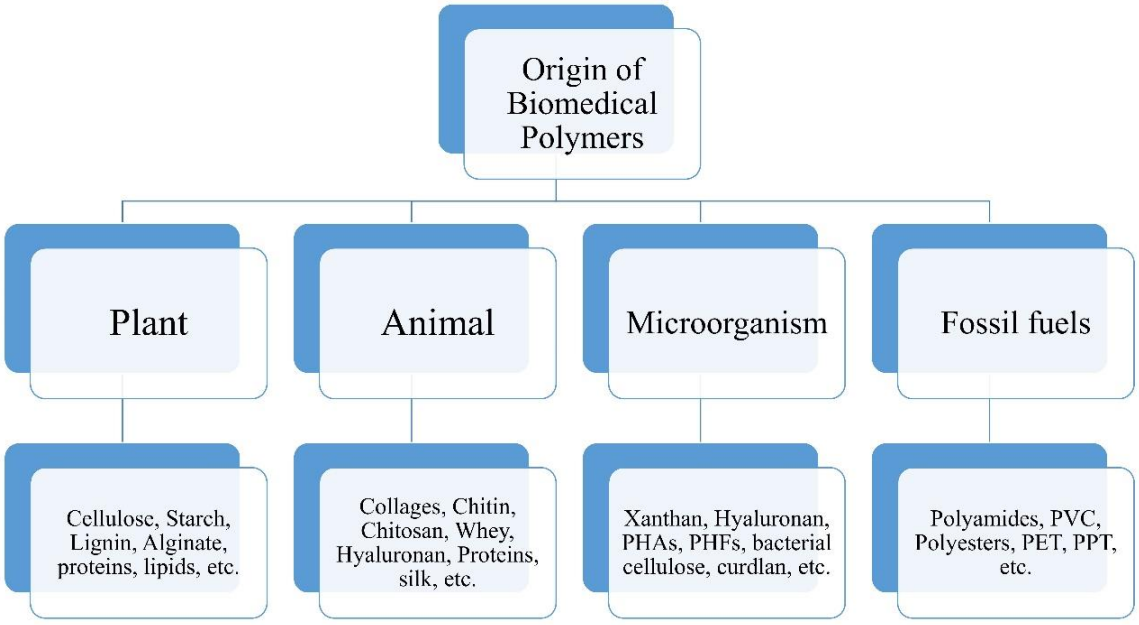

Figure 2. Biomedical polymer materials from different origins.

Over the past several decades, advancements in nanotechnology have allowed for significant upgrades to previously used materials. Many scientists have been modifying carbon dioxide polymers by mixing in nanoparticles in an effort to make environmentally acceptable medicinal polymers (CO_2). Both organic and synthetic polymers may be generated by the process of CO_2 fixation. These repeatable polymers derived from CO_2 fixation are increasingly being used as nanocomposites to enhance the performance of applications. There is a lot of hope for eco-friendly biomedical polymer goods when these nanocomposites are used. CO_2 fixation may produce biological polymers with a high degree of reproducibility, however after their useful life or death, most of these nanocomposites would be incinerated. Combustion-derived CO_2 gas may be utilized by creating repeatable polymers [14].

NATURALLY DERIVED POLYMERS

Natural polymers (Figure 3) have been used for a very long time in the field of biomedical research. Around the year 3500 BC, the Egyptians were the first known people to utilize cotton or horsehair to stitch up wounds. Skulls from the same time period that were found in Mexico may have had wood chips glued on them. Since the 1950s, synthetic polymers have gained a significant advantage over their naturally occurring counterparts. The fact that polymers generated from natural sources are both biocompatible and biodegradable ensures that they will continue to play a significant role in the area of biomedical applications. The development of biomedical products often involves the use of biomaterials that are based on polysaccharides [15–18]. These biomaterials may be represented by things like cellulose, chitin/chitosan, starch, alginate, and derivatives of hyaluronic acid, as few examples. In this part, we will talk about the biological uses of nanocomposites that are made from regular polymers that are derived from natural sources. These nanocomposites are created in a laboratory.

Collagen

Collagens are a kind of protein having molecular weights (MW) below 300,000. Skin and skeletal muscle rely on it because of its large concentration in the body [19–21]. Although more than 20 forms of collagen exist in the body, types I through IV account for the vast majority. Collagen molecules are biomedical nanoparticles because their chain lengths are on the order of micrometers. The amino acids

in collagen may be broken down by enzymes. Collagen has been investigated for potential medicinal uses because of its interesting combination of physicochemical, mechanical, biological, enzymatic degradation, biocompatibility, and osteoconductivity features [22]. Collagen degradation might be stopped by cross-linking polymer chains or treating them with enzymes beforehand.

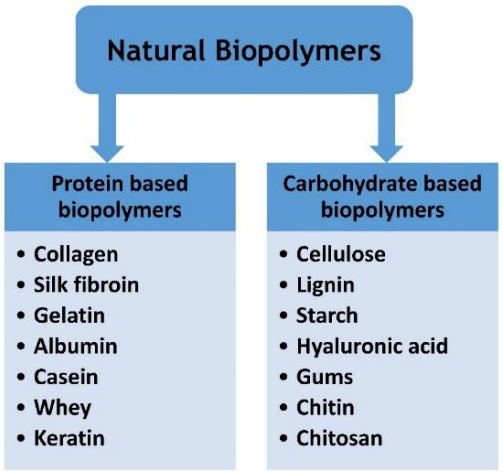

Figure 3. Naturally derived polymer materials.

Nanocomposites made of collagen and calcium phosphate have been the focus of a significant amount of study over the past few years [23, 24]. This is due to the considerable potential that these nanocomposites offer for usage as bionic materials for the replacement and regeneration of bone. Bone transplants made of collagen-hydroxyapatite nanocomposites are becoming more popular owing to the compositional and structural similarity of these nanocomposites to native bone, as well as their innovative functional properties and increased mechanical strength. Nanocomposites containing collagen may improve cell-recognition sites, which in turn accelerates bone regeneration [25]. Collagen-hydroxyapatite nanocomposites rapidly stimulate cell mineralization even in the absence of an osteogenic additive in the culture medium.

There is a wide range of potential uses for commercially available collagen-hydroxyapatite nanocomposites. A Food and Drug Administration (FDA)-approved synthetic bone transplant, Collagraft® is constructed of fibrous collagen, hydroxyapatite, and tricalcium phosphate. The thrombogenic characteristics of collagen are used in the hemostatic product Floseal®, a high-viscosity gel. For repairs to the dura, or inner lining of the eye, doctors recommend using Duragen® suture-free sutures. Collagen's clinical research use is shown by products like the bandages Biobrane®, Sulmycin®-Implan, and the three-dimensional collagen matrix grafts.

Fibrin

The clotting enzyme thrombin converts the protein fibrinogen into the biopolymer fibrin. The paring off of two polypeptide chains causes fibrin to have a molecular weight of about 360 kDa. Its four structural domains consist of the core fibrin peptide E, two pairs of fibrin peptides A and B, and two domains of fibrin peptide D. Fibrin was one of the first biopolymers used in medicine because of its desirable properties such as bioactivity, renewability, injectability, and the ability to promote cell growth and adhesion. Fibrin and its involvement in wound healing have come under considerable scrutiny in recent years [26–28]. This is likely due to the fibrous network properties that are inherent in blood production. Bioseed®, a commercial product, combines keratin-forming cells with fibrin to speed up the healing of chronic wounds. Using the patient's own plasma, Cryoseal® may be utilized to manufacture hemostatic tissue sealants for use in the treatment of burn injuries (Thermogenesis, United States). Cell adhesion, proliferation, and encapsulation are all facilitated by fibrin networks, which are used as a sealer on the surface of fibrin scaffolds or gels. Although fibrin is mechanically unstable and

is rapidly hydrolyzed by hydrolases, it may be improved by complexing it with other polymers, hence increasing its resistance to hydrolysis [29].

Gelatin

When collagen in animal tissues is hydrolyzed, gelatin is the byproduct. Therefore, the kind of collagen employed in the transformation and the method used impact the machine-driven, enlargement, and other physicochemical characteristics of gelatin. Gelatin, like many other naturally derived polymers, is non-toxic, biodegradable, and has a low immunogenicity. Natural and affordable polymer gelatin has several uses in medicine and pharmaceuticals [30, 31]. Many vaccinations and capsules taken orally are stabilized with gelatin. Gelatin may be shaped into a variety of drug delivery vehicles, including hydrogels, microspheres, nanoparticles, and nanofibers. For administration into the brain, nothing beats gelatin nanoparticles. Gelatin nanocomposites including various compounds existence are explored due to their prospective in tissue engineering. Middle-membrane vascular grafts constructed from synthetic tissue [24].

Chitin/Chitosan

Biodegradable chitin and chitosan may be produced indefinitely. Due to their cell attachment and growth characteristics, they are utilized in the production of biomedical scaffolds, gels, particles, films, and more [5, 18, 32]. A greater number of negatively charged cells were attracted to positively charged chitosan. Chitosan dressings prevent bleeding and fight infection. Skeletal substitutes made from chitosan are used in tissue engineering regenerative scaffolding. By fusing with neighboring muscle and maintaining automatic strength on par with innate tissue, filamentous protein/chitosan scaffolds were able to address myofascial anomalies in the abdominal wall. It has been proposed that chitosan colloidal particles might encapsulate a wide range of biological molecules, providing new avenues for medication administration. Rabbit eyes were injected with vancomycin by Duan R et al., who used chitosan as a delivery vehicle. Chitosan is not bone tissue-friendly on its own [33]. Membrane swelling, protein adsorption, and roughness were all enhanced in diatomaceous earth-doped chitosan composite membranes. Saos-2 cell proliferation and alkaline phosphatase activity were both boosted by the use of biocompatible composite membranes.

Starch

Starch is found in the endosperm and tubers of several plants [15, 34]. Starch nanocrystals are frequently employed in biomedicine because they are cheap, biocompatible, and biodegradable. Osteointegration, thermal-mechanical characteristics, and cell adhesion might all be enhanced with the use of starch-hydroxyapatite in tissue engineering. Nanocomposites using a combination of nanoscale magnesium olivine, poly(vinyl alcohol) (PVA), thermoplastic starch, and vitamin E showed superior biological and mechanical characteristics, breakdown, and secondary osteoblast development compared to starch-PVA. It is also possible to use starch that has been chemically modified to deliver drugs. Due to its nonionic nature, starch is an effective co-blendant for polymers, allowing them to better absorb water and expand their pore structure [35]. Hydrogels degraded when treated with or without ketoprofen, and gellan gum and starch were involved in both instances. Starch hydrogel characteristics were modulated by the concentrations of polymer and cross-linker. Hydrogels' malleability made them excellent candidates as medicine delivery vehicles for a wide range of medical conditions. The shear and heat resistance of SPCL, which is made from starch (S) and biodegradable polycaprolactone (PCL), is higher than that of starch alone (PCL). PCL lowered the stiffness and water sensitivity of the starch, which enhanced the SPCL's capacity to be processed, degraded, have better mechanical characteristics, and promote cell proliferation [36]. Starch has the potential to reduce manufacturing costs and boost PCL's biodegradability.

Cellulose

Cellulose is the most valuable renewable biological resource [9, 11, 37] due to its high economic value and abundance as the most common natural polymer. Cellulose is a straight-chain polymer

composed of -D-glucopyranose disaccharides linked together through glycosidic-(1, 4). The cellulose in plants forms nanofibrillar networks between 20 and 100 nm in size. Nanofibrils of bacterial cellulose have a size of 20 to 50 nm. Bacterial cellulose may be able to hold more water than plant cellulose because it is less crystallin. The glycan polymers found in plant cellulose are resistant to biotransformation, limiting its use [7, 26, 38]. Efforts are being made to study bacterial cellulose. Bacterial cellulose might be used in drug delivery methods. Silver bacillus coagulans, often known as Ag-BC, is a powerful antibacterial agent that can kill off any kind of bacterium, including Gram-positive and -negative strains. Specialties such as orthopedics, ophthalmology, urology, neurology, and otolaryngology are included. Scaffolds made from bacterial cellulose are often used for tissue repair [39].

Hyaluronic Acid

Meyer and Palmer achieved their goal of successfully isolating hyaluronic acid (HA) from vitreous fluid in 1934. The backbone of HA, an abundant anionic linear polymer, is formed by the combination of D-glucuronic acid and *N*-acetyl-D-glucosamine. In the field of tissue engineering, natural polymers such as HA are often used because of the biocompatibility and biodegradability of these materials. Scientists just recently realized that HA might be used in tissue engineering scaffolds to regulate cell mobility and adhesion, speed up the healing process, and distribute medications. This discovery was made over twenty years ago. Motor receptors such as CD44 bind HA as part of a pathway that is mediated by HA (RHAMM). When cancer cells take up CD44-HA, the expression of CD44 is lowered, which makes it possible for anticancer drugs to penetrate the cells with greater efficiency [40]. Esterified HA derivatives, such as ethyl/benzyl esters (HYAFF®), and cross-linked HA gels, both of which have been extensively researched as wound dressings, are just two examples of the many biomedical products that are based on HA derivatives. HA derivatives are also used in a wide variety of other applications. Mucoadhesive HA solutions, such as SYNVISC® and ORTHOVISC®, may reduce pain and restore mobility in arthritic joints by acting as synovial fluid replacement therapies for osteoarthritis patients. AMVISC® vitreous fluid replacement made from HA assures the safety of delicate eye tissue when it is put to use during ocular surgery. Using Hyalomatrix® (Anika treatment) as a dermal replacement for major surgical wounds has been hypothesized to have the potential to promote capillary development, fibroblast attraction, and wound healing [13, 41].

Alginate

Alginate is a kind of anionic polymer that may be found naturally occurring in the cellular walls and intercellular gaps of some types of algae. It is also known by the name sodium alginate. Non-Newtonian aqueous solutions are characteristic of glycosaminoglycans and also of alginate, a block copolymer of two glycuronates. Because of its low cost, low toxicity, biocompatibility, lack of immunogenicity, ease of gelation, and regulated biodegradability, alginate has several potential applications in the biomedical industry. Soft alginate gels may encapsulate chemicals or even living beings without damaging them. The implantation of alginate capsules containing pancreatic cells into people first occurred in the 1980s. Two examples of alginate derivatives that are used in the therapy of infected wounds, allograft wound dressings, and pressure injuries are called Kaltostat® and AlgiSite® respectively [41–43]. Bioactive substances and cells may be transported through alginate hydrogels, making them a promising scaffold for tissue regeneration. Proteins and bioactive chemicals are more easily targeted by alginate gels, making them a promising therapeutic option.

Synthetic Renewable Polymers

It is possible to create renewable synthetic polymers using biological or chemical processes [44]. Natural chemicals or macromolecules are used to create the monomers for this polymer (such as sugar, starch, cellulose, proteins, etc.). Their carbon footprints are less than those of polymers made from fossil fuels since they are produced via photosynthesis or microbial CO_2 fixing. In order for a substance to significantly add to the greenhouse effect, it must see widespread use. The possibility for decarbonization has attracted the greatest attention and research into synthetic renewable polymers like polyhydroxyalkanoates and poly(lactic acid)-related polymers.

Polyhydroxylalkanoates

Bacterial polyhydroxyalkanoates (PHAs), a kind of intracellular polyester (Figure 4), have evolved into a biosynthetic renewable polymer in recent decades. PHAs are the biggest class of biopolymers, and they are biosynthesized by genetically engineered bacteria. PHAs are capable of being biosynthesized by live cells from a wide range of various nutrients, such as sucrose generated from sugar cane or sugar beets, glucose derived from maize starch, vegetable fats (such as beans, palms, grain, etc.), and bovine fats. It has been shown that the presence of PHAs in surgical sutures, drug administration systems, substrates, and transplants encourages the growth of stem cells [1, 22, 45] due to their biocompatibility, biodegradability, and availability.

Poly(Lactic Acid)

Biomedical applications of poly(lactic acid) (PLA), a synthetic renewable polymer (Figure 5), are many. Carbohydrates like maltose, sucrose, lactose, etc. are fermented to produce PLA. The structure of stereoisomeric PLA has an effect on its performance. Different from the amorphous poly(D,L lactic acid) (PDLLA) and meso-PLA, the semi-crystalline PDLA and PLLA are a useful material [46].

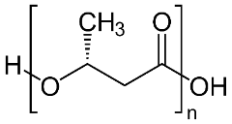

Figure 4. Molecular form of polyhydroxyalkanoates (PHAs).

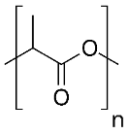

Figure 5. Molecular form of poly(lactic acids) (PLAs).

Despite its intricate molecular stereo structure, PLA has excellent chemical, mechanical, biocompatibility, and biodegradability properties. Surgical clips, sutures, adhesives for wound closure, bone staples and plates, regenerative scaffolds, drug delivery systems, medical equipment, packaging, and more are just few examples of the wide range of biomedical items that may be manufactured from PLA. PDLLA is great for coatings in orthopedic biomedical applications since it is both biocompatible and mechanically stable. Antibiotics and other medications with a low molecular weight may be localized using PDLLA. PLLA's safety, biocompatibility, and biodegradability make it an attractive candidate for use in cardiac tissue [16, 25, 47, 48].

CO_2-Based Polymers

Polymers that can repair CO_2 are quite promising. Using catalysts for ring-opening copolymerization (ROCP), polymers may be synthesized from CO_2 [33]. This procedure generates mostly aliphatic polycarbonates, which have the potential to replace petroleum plastics in applications such as medical and food packaging, agricultural films, trash bags, etc. Poly(ether carbonate) polyols might be made from CO_2-based polymers with a low molecular weight. Using bio-based monomers from poly(ether carbonate) polyols in polyurethane manufacture would reduce emissions by 20%. Every year, 3 to 4 Mt of polyols are required for polyurethane manufacture. Poly(ether carbonate) polyols of CO_2-based polymers are a potential replacement for polyether polyols in the context of decarbonization [49].

Polypropylene Carbonate

Alternating CO_2 and propylene oxide copolymerization produces polypropylene carbonate (PPC) (Figure 6). Cheap propylene oxide and CO_2 make PPC one of the most promising eco-friendly synthetic polymers. Biomedical product-friendly PPC is non-toxic, non-polluting, transparent, renewable, degradable, barrier, flexible, and electrically conductive. PPC's dimensional instability and low glass transition temperature restrict its employment in high-temperature applications (Tg). Water and CO_2, PPC breakdown products in vivo, decrease inflammation and protect PLA and PLGA. PPC scaffold tissue engineering advantages. Another experiment developed PLA-TCP (tricalcium phosphate)-PPC elastic polymer scaffold (PPTE). PPTE composite-inoculated mouse osteoblasts adhered, proliferated, and calcified. Bone healing was regulated by PPTE composites [46, 47]. PPC delays and transports

medicines [22, 34]. PPC's strong water barrier and low gas permeability boost antibacterial action. PPC helps medical packaging, dressings, and devices. Bone fixation, surgical sutures, and polymer "additives" may use PPC [48]. PPC and its nanocomposites—the best CO_2-based polymers for biological applications—need additional study.

Polycyclohexene Carbonate

Another CO_2-based polymer that has received a lot of attention is polycyclohexene carbonate (PCHC) (Figure 7). The six-member ring structure of PCHC makes it more efficient at retaining heat than PPC. It has a Tg that is higher than 100°C. A novel epoxide/CO_2 copolymer that can withstand extreme heat. The biodegradability of PCHC molecules is diminished due to the presence of hydrophobic cyclohexane groups throughout the molecular chain. Incorporating PCHC becomes more challenging due to these characteristics. PCHC composites have been the subject of substantial research for their potential use in drug-loaded nanoparticles, hydrogels, pore-forming chemicals, biodegradable surfactants, and regenerative scaffolds [29, 48].

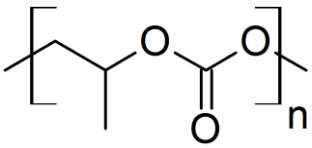

Figure 6. Molecular form of polypropylene carbonates.

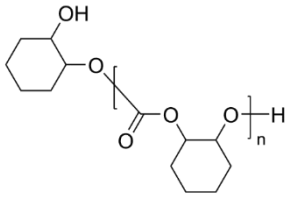

Figure 7. Molecular form of polycyclohexene carbonate.

Polyethylene Carbonate

The well-studied fatty acid polycarbonate polyethylene carbonate (PEC) (Figure 8) is produced via reductive organic carbonation polymerization (ROCP) of ethylene oxide and carbon dioxide, and its surface erodes in vitro and in vivo. Thus, PEC-based delivery systems' drug-release behavior is intimately linked with polymer mass loss, enhancing predictability. PEC is easily degraded by cells and enzymes. If successful, this strategy might enhance medicine delivery in the body. Microorganism growth was suppressed by rifampicin released by PLA microparticles. In vitro, macrophages caused degradation of PEC surfaces. Surface degradation caused by macrophages reduced the breakdown of 41-kDa PEC. Methods based on PECs disperse medicines that stimulate macrophages [12]. Long-term medication administration is not feasible since PEC degrades in 2 to 4 weeks [50]. Degradation of PECs led to the development of controlled-release, extended-release medication delivery devices.

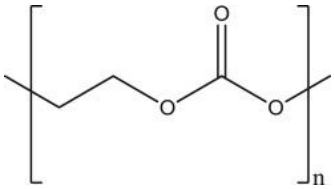

Figure 8. Molecular form of poly ethylene carbonate.

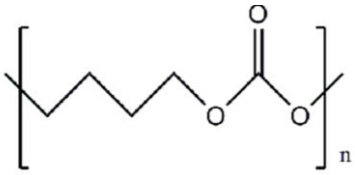

Figure 9. Molecular form of Polybutyl carbonate.

Polybutyl Carbonate

The combination of epoxy butane with CO_2 monomers gives polybutyl carbonate (PBC) remarkable elasticity, tensile strength, elongation at break of more than 400%, and a glass transition temperature (Tg) of 32°C. Despite being biocompatible, PBC (Figure 9) is very unstable and melts at about 55°C. Potentially higher grade compounds may be made from PBC by blending polymers [51–53]. Breakdown of PBC nanofiber membranes. Hydrophilic, antibacterial, and mechanical PBC/PLA/chitosan nanofiber membranes produced by electrostatic spinning. Axial electrostatic

spinning was used to create core-shell PVA/PBC nanofibers for doxorubicin administration (DOX). The results that DOX-loaded PVA/PBC core-shell nanofibers suppressed SKOV3 ovarian cell adhesion and proliferation have implications for tissue engineering and chemotherapeutic applications. PBC has the potential to affect drug development. By combining PBC, PLA, and graphene oxide (GO), Gu et al. created nanofibers with anti-tumor properties. The use of a PBC/PLA/GO nanofiber matrix for cell imaging and drug transfer was successful, demonstrating the matrix's biological potential. Incorporating PBC into biodegradable polymers improves their mechanical and chemical properties [54–56]. Biodegradable polycarbonate PBC needs further research and implementation.

CONCLUSION

This investigation explores state-of-the-art CO_2-fixing polymer nanocomposites, which might be used to minimize the environmental effect of biomedical polymers. CO_2 fixing results in the creation of polymers, which may be found in nature or engineered in a laboratory. Biomaterials – non-cytotoxic, recyclable, and environmentally beneficial, nanomaterials of renewable polymers – created by CO_2 fixation are used by numerous researchers to build novel biomedical materials. Research in this area focuses mostly on tissue engineering, medication delivery, cancer treatment, and organ transplantation. These businesses have a smaller carbon impact since they seldom employ biological resources. Researchers have overlooked the fact that many disposable biomedical items are constructed from petroleum-based polymers. The single-use items pollute biopolymers. Therefore, it is critical to develop CO_2-fixation-based repeating polymers for usage in short-term medical devices.

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