ACS Sustainable Chemistry & Engineering
pubs.acs.org/journal/ascecg
Perspective

Sustainable Alternatives to Nondegradable Medical Plastics

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Cite This: *ACS Sustainable Chem. Eng.* 2022, 10, 4792−4806
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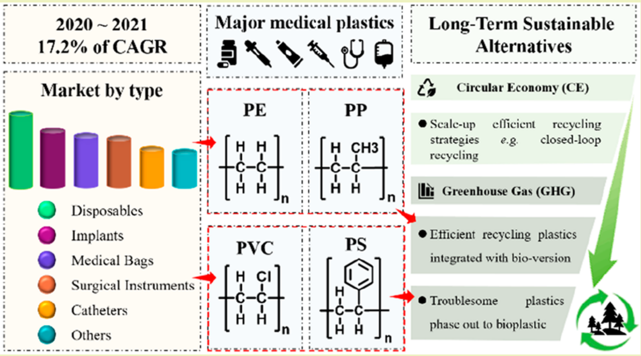


ABSTRACT: In light of the global climate crisis and commitments toward net-zero carbon emissions, this Perspective evaluates the current status of developments in recycling methods and bioplastics to identify long-term sustainable alternatives. The recycling and product application of major medical plastics, including poly(vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP), and polystyrene (PS), are discussed, and their circular potential is evaluated. Researchers are actively investigating bioplastics to solve present concerns and curb the global increase in greenhouse gas (GHG) emissions from petroleum-based plastics. Current recycling methods for PE and PP can be scaled up, and bioversions of plastics, such as bio-PE and bio-PP, can be used as a long-term sustainable solutions to realize their circular potential. As an alternative to PVC and PS, materials with inefficient recycling methods, recent promising bioplastics such as polyurethane (PU) and poly(lactic acid) (PLA) have a competitive performance. Our Perspective recognizes the need for further research on issues such as integrated recycling processes and the possibility of commercializing bioplastics.

KEYWORDS: *Nondegradable plastic, Single-use plastic, Bioplastic, Sustainability, Medical application*

■ INTRODUCTION

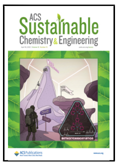
Synthetic plastics have various medical applications due to their good corrosion resistance, good chemical properties, low weight, and most importantly, cost-effectiveness and easy manufacturing.[1−3] They can be processed into any shape to easily impart the desired chemical or physical properties.[4,5] Special plastics are designed for use in medical devices employed in environments with bodily fluids such as blood and urine.[6,7] To reduce the potential risk of transmitting infections with reusable materials, manufacturing of disposable materials has become common in the field of medical plastics.[8,9]

MarketsandMarkets reported that compound annual growth rate (CAGR) of the global market for medical plastics is expected to grow to 17.2% from 2020 to 2021 during the pandemic.[10] Demand for single-use medical plastic items, for instance, syringes, tubes, needle packaging, ventilators, and thermal scanners, increased significantly during this period.[11,12] Consequently, medical plastic waste has also increased greatly. The World Health Organization noted that 89 million masks, 76 million gloves, and 30 million gowns are used monthly during the pandemic.[4] The average waste generated in Wuhan, China (240 tons/day), is estimated to be six times greater than the average generation rate (40 tons/day) of Wuhan before the pandemic.[13] In Hubei Province, China, the estimated hazardous waste volume increased by a record 600%.[14] The total medical waste generated in Asia is approximately 16,659 tons/day.[15] These data clearly indicate the urgent need for alternative solutions for the proper management of medical plastic waste.

Incineration is the commonly adopted method for disposing of medical plastic waste. However, this method causes the formation of toxins such as dioxins and furans.[9,16] These can negatively affect the environment and human health. A reliable disposal method for medical plastic waste is not yet fully realized in spite of the negative hazards and short lifetime of this waste. Many plastics end up in aquatic environments and are detrimental to ecosystems. One study estimated that there is around 269,000 tons of plastic waste in the ocean,[17] and in 2020, the number of pieces of plastic in the ocean exceeded the number of fish. Another study noted that recycling plastics that would otherwise be disposed of in the oceans could save 1 million sea creatures yearly.[4]

The toxicity of plastics and related chemicals in the ocean are now an integral part of the global ecosystem. To deal with this problem, more focus is needed to reduce the dependence on plastic as well as to find methods of promoting sustainability. Toward this end, researchers have pursued

Received: January 8, 2022
Revised: March 19, 2022
Published: April 4, 2022



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https://doi.org/10.1021/acssuschemeng.2c00160

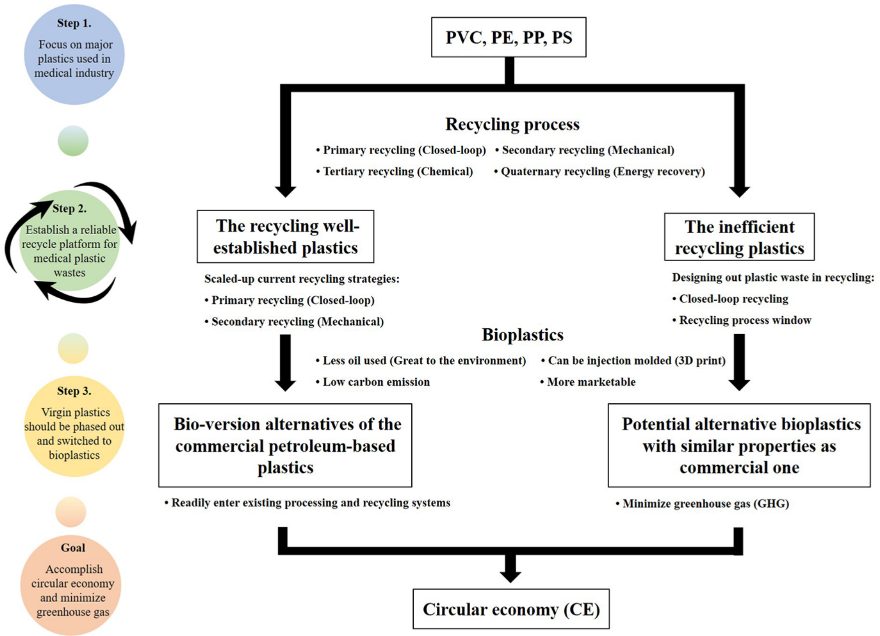

Figure 1. Circularity potential for recycling management and bioplastics.

three main objectives: reducing overreliance on medical plastics, effectively recycling medical plastics, and developing sustainable polymer alternatives to medical plastics.

The reduction of the use of medical plastics and products can mitigate their harmful environmental effects; however, it is not a viable solution. For example, the COVID-19 pandemic has revealed how unforeseen external factors can hinder efforts to reduce plastics. This study comprehensively reviews currently available approaches, including innovative strategies to recycle and produce sustainable bioplastics with comparable properties that can feed into the circular economy (CE). To assess the sustainability of plastics, it is crucial to realize the types of materials used and their respective characteristics because these characteristics determine their potential uses and waste management options such as recycling. This Perspective focuses on poly(vinyl chloride) (PVC), polyethylene (PE), polypropylene (PP), and polystyrene (PS) because these are the major plastics (70% of all plastics) used in the medical industry.[4] Classification, Properties, and Recycling of Medical Plastics discusses the opportunities and challenges of each plastic, and proposed recycling options are discussed to promote sustainable processes. Alternative Bioplastics for Medical Plastics discusses plastics that cannot be recycled efficiently, sustainable alternatives to these plastics, and the feasibility of these alternatives for medical applications (Figure 1).

CLASSIFICATION, PROPERTIES, AND RECYCLING OF MEDICAL PLASTICS

Medical plastics must be biocompatible, resistant to sterilization, and most importantly, robust to surface modification.[18−20] Many medical manufacturers coat plastics with antimicrobial materials[21,22] to repel bacteria, thus reducing the likelihood of infection and preventing cross contamination. Table 1 summarizes currently available plastics, their properties, and their applications.

Normally, plastics can be categorized into petroleum plastics and bioplastics based on their composition. Further, plastics can be biodegradable or nonbiodegradable. Biodegradable plastics can be broken down by microorganisms (e.g., fungi, bacteria) into water (H_2O), carbon dioxide (CO_2), and methane (CH_4) through hydrolysis or microbial degradation in the environment.[23,24] The biodegradability can differ depending on the designed properties of the plastics,[25,26] the properties of the physical environment in which they are used (e.g., wind, rain, or ultraviolet (UV)), and processing settings.[27,28] Nearly all commercially available medical plastics are derived from nonbiodegradable petroleum polymers.[29] The low biodegradability of plastics is a key factor contributing to environmental damage because these plastics are typically disposed of inappropriately by incineration or landfilling. To realize a CE, reliable recycling methods for medical plastic wastes in accordance with their properties and potential hazards must be developed. Effective recycling procedures can reduce plastic waste as well as greenhouse gas (GHG) emissions and energy usage.

Recycling has four main types: primary, secondary, tertiary, and quaternary. Primary recycling (or closed-loop recycling) involves extruding uncontaminated plastic scraps into a new product with equivalent properties. Secondary recycling is also called mechanical recycling, in which the chemical composition of the material remains unchanged and plastics are mechanically reprocessed into a product used for a purpose different than its original one. Currently, secondary recycling is the best-established and preferred method for plastic recycling.[30−33] However, the effectiveness of both primary and secondary recycling is reduced due to plastic instability. As plastics are continually reprocessed, they become prone to thermomechanical degradation.[34] An additional challenge is to achieve an efficient postconsumer recycling process on the basis of current separation techniques, as the plastics are often mixed with highly contaminated waste. Tertiary recycling, also called chemical recycling, involves chemically converting plastic waste into smaller molecules and using those as feedstock for processes that generate value-added commodities (e.g., chemicals or fuels). Typically, these processes include

Table 1. Main Types of Petrochemicals and Biobased Plastics Available, Their Circularity Potential, and Their Key Applications

type	property[4,122]	prevalent polymers	circularity potential	main applications in the medical industry[4,8a]
petroleum-based and non-biodegradable	commodity plastics (70% of all plastics in medical devices applications)	polyvinyl chloride (PVC)	nonrenewable	tubing
			recyclable[159] (not easy)	film packaging
		polyethylene (PE)	nonrenewable	connectors
			recyclable[159]	labware
		polypropylene (PP)	nonrenewable	IV bags
			recyclable[159]	face mask
		polystyrene (PS)	nonrenewable	catheters
			recyclable[159] (not easy)	drug-delivery components
				membranes
				sutures
				syringes
				implants (dental or bone)
				surgical trays
	engineering thermoplastics (20% of all plastics in medical devices applications)	polyamide (PA)	nonrenewable	surgical instruments
			recyclable[159]	balloons
		polycarbonate (PC)	nonrenewable	blood set components
			recyclable[159]	blood bowls
		polyoxymethylene (POM)	renewable	blood oxygenators
			recyclable[160]	syringes
		poly(ethylene vinyl-*co*-acetate) (EVA)	nonrenewable	moving parts and components
		polyurethane (PU)	renewable[161]	luers
			recyclable[162]	catheters
				implants (dental or bone)
				tubes
petroleum-based and biodegradable	high-temperature engineering thermoplastics (10% of all plastics in medical devices applications)	polyimide (PI)	renewable	surgical instruments
			recyclable[163]	surgical trays
		polyetherimide (PEI)	nonrenewable	syringes
		polyglycolic acid (PGA)	nonrenewable	high precision parts
		polyphenylene sulfide (PPS)	renewable	electronic components
			recyclable[164]	moving parts and components
				luers
		poly(vinyl alcohol) (PVOH)	nonrenewable	implants (dental or bone)
			recyclable[165]	
biobased and non-biodegradable	bioversion of commercial petroleum-based plastics	biobased polyvinyl chloride (Bio-PVC)	renewable	tubing
			recyclable (not easy)	film packaging
				connectors
				labware
				IV bags
				face mask
		biobased polyethylene (bio-PE)	renewable	catheters
				drug-delivery components
			recyclable	membranes
		biobased polypropylene (bio-PP)	renewable	sutures
				syringes
				implants (dental or bone)
			recyclable	surgical trays
		biobased polystyrene (Bio-PS)	renewable	
			recyclable (not easy)	
biobased and biodegradable	the most commercialized bioplastic in terms of production volumes	poly(lactic acid) (PLA)	renewable	film packaging
			recyclable[159]	catheters
				epidural trays
		thermoplastic starch (TPS)	renewable	heart pump
			recyclable[166]	tendon repair devices
				anticancer agents
				drug-delivery components
				membranes

https://doi.org/10.1021/acssuschemeng.2c00160

Table 1. continued

type	property[4,122]	prevalent polymers	circularity potential	main applications in the medical industry[4,8a]
				sutures
				syringes
				implants (dental or bone)
		polyhydroxyalkanoate (PHA)	renewable	
		polyhydroxybutyrate (PHB)		

[a] In the majority of applications, mixtures of two or more polymers are used by lamination and coextrusion.

gasification, hydrolysis, pyrolysis, depolymerization, and purification of waste plastics. Finally, quaternary recycling involves recovering the energy content of the plastic waste through incineration. This is the most effective method for reducing the volume of medical plastic waste, especially for very poor quality or highly contaminated plastic waste streams. However, this method can have substantial negative effects on the environment (e.g., climate change, soil erosion, poor air quality) and human health (e.g., bronchopulmonary dysplasia, deep venous thrombosis, reduced fertility).

The overall recycling efficiency of medical plastic wastes primarily depends on the sorting and pretreatment processes. Typically, medical plastics are presumed to be infectious and are not classified as common municipal waste. Therefore, different types of plastics should be discussed separately. The properties, common recycling methods and relevant trade-offs, and opportunities and challenges for each type of plastic are summarized below.

Poly(vinyl chloride) (PVC). PVC is widely used in the biomedical field because of its inertness in fluids, chemical resistance, tunable flexibility, and sterilizability. By consumption volume, PVC is the most popular plastic in medical applications.[35] However, the high glass transition temperature (T_g: 60−80 °C) of PVC extends the real-time utilities. Interestingly, the PVC optimized blend ratio of phthalate-based plasticizers remains influential in harvesting better mechanical and processing properties. To date, di-(2-ethylhexyl) phthalate (DEHP) is considered the best plasticizer for PVC because its flexibility grades can be adjusted according to the desired end-user application.[36,37] For example, semirigid PVC is used for drip chambers, blister packaging, and trays, and highly plasticized flexible PVC is used in intravenous bags, tubing for infusion, and respirators.[4] PVC is mainly used to handle human body fluids or tissues due to its stabilizing effect on red blood cells.[36,38] However, DEHP is considered highly toxic because of its related metabolites through peroxisome proliferation.[39−41] Thus far, the usage of DEHP has been somewhat regulated in medical applications; it is not prohibited even though various studies have demonstrated its harmfulness.[42] Because analysis of the PVC life cycle (LCA), including production, usage, and disposition, reveals its negative effects on human health and the environment, its usage has been significantly reduced. Nevertheless, PVC is widely utilized in medical applications due to its cost-efficiency and applicability.

The hazardous plasticizers added to PVC make it difficult to recycle efficiently. PVC that is recycled through mechanical recycling can be converted into products such as bottles, traffic cones, and drainage pipes.[43] Mechanical recycling retains the original composition of PVC; however, PVC products can contain different additives depending on their applications. Even products used for the same application but made by different manufacturers may have different compositions. Because different types of PVC waste are recycled mechanically, the resulting composition of the product is difficult to control; thus, the recycling efficiency is reduced. To overcome this problem, the innovative VinyLoop process has been developed.[44] The VinyLoop process separates PVC from other materials through the dissolution, filtration, and separation of contaminants using an organic solvent, enabling the recycling of PVC waste from other composites. However, this process cannot remove low-molecular weight phthalate plasticizers during recycling. The separation of the plasticizer from PVC remains a major challenge in mechanical recycling.

Chemical recycling is considered complementary to mechanical recycling because it can convert mixed or unsorted PVC waste into valuable materials. In Australia, the Vinyl Council has extensively recycled PVC and produced many new products from PVC medical waste.[45] A novel low-temperature aqueous ammonia process was developed for the sustainable management of DEHP-rich PVC wastes.[46] This process can produce highly concentrated 2-ethyl-1-hexanol (86.12%), a vital chemical feedstock derived from the DEHP decomposition. Additionally, the dechlorination could reach 98.7% at 300 °C. These results indicate that chemical recycling is a promising and highly efficient strategy for sustainable management. However, several studies have shown that chemical recycling incurs a higher cost compared to other recycling processes (e.g., mechanical recycling, incineration), primarily owing to the low value of the recovered products. For example, recycling PVC will generate hydrochloric acid (HCl), and an additional step and cost are required to replace the same.[47] Thus, chemical recycling for PVC might not be a cost-efficient option.

Generally, approximately 70% of PVC waste is treated as general waste and is sent to landfills or incinerators.[48] Because PVC waste can persist for a long period of time owing to its nonbiodegradability, landfilling is not a suitable option. PVC incineration produces dioxins, carbon monoxide (CO), CO_2, and HCl, all of which can affect the respiratory system.[49,50] Landfilling and incineration are considered the least desirable options; however, owing to the inefficiency of recycling processes, they remain the most popular options for dealing with PVC waste. In response to the negative effects on human health and the environment, most studies currently focus on reducing the toxins released by incineration. One strategy is dechlorination of PVC by using a sodium hydroxide base before incineration because HCl can be transformed into a safer compound.[51] Another strategy is to perform hydrothermal carbonization (HTC) with lignocellulose.[52] In combination with a washing process, the dechlorination efficiency can reach 89.5%. In addition, the waste can be converted into biofuel.[53−55] Although many studies have attempted to diminish the toxins released to the environment during PVC incineration, incineration is not considered a sustainable alternative.

PVC postconsumer waste is difficult to recycle due to the need for separation and dechlorination before reprocessing. From a cost-efficiency perspective, it is normally cheaper to manufacture new PVC medical products than to sort and reprocess them; this exacerbates the problem of PVC waste in the environment due to landfilling or incineration. PVC remains difficult to recycle because of the associated risks; for example, it potentially contains toxic chemicals that are dangerous to human health. Thus far, studies of recycling have been unable to effectively differentiate and capture specific materials or to separate PVC from plasticizers.[30,37,56]

Given these limitations, the development of a safe plasticizer and the substitution of PVC with an alternative safer plastic are critical areas of research. For nontoxic plasticizers, studies have investigated citrates,[57,58] carboxylates,[59] phosphates,[60,61] trimellitates,[62,63] and cyclohexane derivatives.[64,65] In particular, studies have focused on biocompatible plasticizers, possibly of a natural origin, to address the concerns regarding PVC. This task remains challenging because recycling PVC still requires an additional step and additional cost for plasticizer separation. Even nonplasticizers require separation because the substantial chloride content makes PVC difficult to recycle.[66,67] In this case, from a long-term perspective, the substitution of PVC with biodegradable polymers is more suitable. The usage of PVC-free medical devices can diminish the negative effects existing in PVC by removing the formation of toxicities, for instance, ethylene dichloride and vinyl chloride monomer formed during the PVC production, and by eradicating HCl and dioxin generated during the incineration. These concerns persist with modern disposal and incineration technologies for PVC waste. Therefore, substitute polymers with satisfactory LCA data are preferable in the future.

Polyethylene (PE). Polyethylene (PE) is an inert and hydrophobic material that does not degrade in vivo.[68] PE can have different molecular weights and crystallinities. The two most common types of PE are low-density polyethylene (LDPE) and high-density polyethylene (HDPE). LDPE is a low-cost plastic noted for its flexibility, toughness, and lightweight. It is commonly used in injection-molded parts, sterile blister packs, and tubing for injections[69] because it does not contain components harmful to the human body.[68] Compared to LDPE, HDPE is translucent and has a better stiffness and chemical resistance owing to its higher crystallinity. It is widely used in surgical and medical instruments or in sliding surfaces like artificial joints due to its easy moldability and low cost, which makes it a competitor to PVC. PE can undergo oxidation and gamma sterilization to increase its hydrophilicity, cause recrystallization, and increase its brittleness.[70,71] Both LDPE and HDPE are recyclable;[72−74] however, they must be recycled separately.

The recycling of PE is one of the most successful examples of the CE concept for plastics. Most current recycling methods can be applied to PE. Recycled PE can be made into bins, pipes, films, and nonfood bottles.[75] Although most PE recycling processes are well-established and considered promising to overcome the problem of PE waste, the deterioration of PE in terms of material performance (mechanical recycling)[76,77] and cost (chemical recycling)[78,79] is a major limitation.

To address this deterioration, studies have suggested recycling PE waste using blending techniques.[80,81] For example, recycled HDPE with wood flour as a filler showed better dimensional stability for composite panels compared to those without.[82] Moreover, the composite with additional 3−5 wt % maleated polypropylene (MAPP) can further improve the mechanical properties. Oladele et al. found that incorporating natural fibers and dust-6063 aluminum alloy particles in recycled PE enhanced its tensile strength by approximately 39%.[83] The exploitation of waste and additives could overcome the drawbacks of mechanical recycling.

Regarding chemical recycling, it is not possible to successfully depolymerize PE to a single monomer due to its random chain scission of carbon−carbon covalent bonds. PE can be degraded into a series of products used in the petroleum industry for combustible gases. Therefore, most studies mainly focus on different types of pyrolysis (e.g., thermal, catalytic) to produce shorter-chain molecules that eventually can be utilized for fuel.[84−86] Compared to thermal pyrolysis, catalytic pyrolysis is currently considered preferable because it requires a lower temperature and reaction time and therefore has improved economic feasibility and selectivity. Notable advances in the catalytic pyrolysis of PE have been recently achieved, resulting in increased yields and lowered reaction times and temperatures.[85,87] Although most approaches for depolymerizing PE have focused on yielding hydrocarbons for fuel or energy, pyrolysis products can be used as raw materials to produce other materials. Recently, Bäckström et al. noted that HDPE waste can be synthesized into a mixture of succinic, glutaric, and adipic acids.[88] These products were used as plasticizers for the formulation of poly(lactic acid) (PLA). When these plasticizers are added during PLA formulation, the strain at break can be improved from 6% to 144%. Although these studies have suggested novel approaches for exploiting PE waste with the enhanced performance of sustainable sources, high energy consumption and cost remain problematic.

Recently, Mecking and co-workers reported that renewable PE-like materials derived from common biobased feedstocks (plant or microalgae oils) can be recycled by solvolysis with an overall recycling rate exceeding 96%.[89] The processing is performed by common injection molding (e.g., 3D printing), and the materials are suitable for additive manufacturing. The authors demonstrated a promising way to use fully recyclable PE-like materials for high-performance applications, which would enable the closed-loop recycling of PE-like materials. This research provides new insights into PE recycling; however, data about the recycling rates in the practical waste stream are limited. Further studies are necessary to obtain information regarding the PE recycling ratio under working conditions, especially through closed-loop recycling.

Polypropylene (PP). The properties of PP are similar to those of PE; however, the additional methyl group side chain significantly affects its properties. PP is inert, hydrophobic, strong, and translucent; however, it is heavier and stronger than PE.[90] Depending on the specific configuration, PP is categorized into three types: isotactic, syndiotactic, and atactic.[91] The crystallinity can differ greatly based on the type and affects the physical and mechanical properties. For example, the melting point (T_m) of highly isotactic PP (~60% crystallinity) is 171 °C,[92] whereas that of syndiotactic PP (~30% crystallinity) is 130 °C.[90] PP is considered safe from an occupational health and safety perspective because it does not have any chemically toxic effects.[68] PP is versatile in the medical industry, for instance, being used in medicine packaging,[93] sutures,[94] meshes,[95] and syringes,[96] mainly due to its excellent chemical and bacterial resistance and resistance to steam sterilization. However, its applications are limited by its poor resistance to UV light, chlorinated solvents, and aromatics and its low brittleness temperature (90−120 °C).

Products made of PP require 20−30 years to completely decompose because PP is nonbiodegradable. Currently, it is not as cost-efficient to recycle PP as it is to recycle other plastics, especially PE. A negligible amount of PP is recycled because it is generally found in mixed waste streams as a component of electronics, rugs, and other products. In these streams, PP is not the only plastic present, and the necessity of washing and separating are main barriers to recycling.[97] In cases where separation is feasible, recycled PP can be turned into dishware, fiber, and food containers.

PP gradually undergoes thermal degradation that compromises the structural integrity by weakening the carbon−hydrogen bonds. Therefore, the performance of recycled PP products deteriorates with the number of mechanical recycling cycles performed. For instance, the elongation at break of virgin PP decreased from 65% to 45% after 10 cycles of recycling.[98] Some PP plastics contain a stabilizer to avoid thermal degradation. The stabilizer alleviates the deterioration of the PP properties but particularly hampers the mechanical recycling efficiency due to the difficulty of segregating PP and the stabilizer. To overcome this problem, recycled PP can be added to 50% of virgin PP to manufacture new products.[99] This new product has mechanical properties competitive with commercial PP. Recently, a preliminary study showed that the recycled PP from surgical face mask waste could be converted into porous sound absorbers.[100] The sound absorption performance was comparable to that of commercial products. The demand for surgical masks has greatly increased during the pandemic; thus, the methods in this study could have a substantial benefit for recycling PP. Li and co-workers studied a similar concept by using disposable PP face masks to enhance the toughness of concrete.[101] The demonstrated increase in toughness can be ascribed to the denser spacing of the fibers.

For PP that can no longer be recycled by mechanical processes, some strategies of turning PP into value-added feedstocks have been identified. Guddeti et al.[102] reported the depolymerization of PP into propylene by using an induction-coupled plasma reactor. Through this process, PP can be converted into gaseous products (up to 78 wt %); 94% of these products are propylene. Supercritical water is another medium used for recycling PP. She et al. have utilized supercritical water to turn PP into oil.[103] The results showed high conversion (~91 wt % of PP turned into oil) under 425 °C for 2−4 h or 450 °C for 0.5−1 h. The oil comprised olefins, paraffins, cycloalkanes, and aromatics that had properties similar to those of naphtha, and it could be further extracted to produce gasoline. The depolymerized PP through supercritical water is considered a major sustainable alternative toward upgrading PP waste into value-added feedstocks. According to difficulties in obtaining pure PP from waste streams, PP mixed with other materials for recycling has recently attracted great interest. Generally, the pyrolysis of biomass waste produces low-value products. Interestingly, the pyrolysis of biomass waste with PP has been reported to have final products with enhanced properties. For instance, mixed bamboo with PP can yield bio-oils during pyrolysis; these can potentially be used as fuel. Additionally, the oil production can be upped to 62 wt % with a bamboo/PP ratio of 2:1.[104]

Although most recycling strategies are considered sustainable, their large-scale applications have not yet been demonstrated. Because substantial PP waste is produced every day, the economic feasibility of recycling methods must be tested by scaling-up volumes and evaluating costs relative to the feedstock price. To reduce the production of petroleum-based plastics, it is unsustainable to mix recycled PP with virgin PP because new PP is still used in the recycling process. The addition of waste biobased materials instead of using virgin PP to prevent deterioration is advisable in the future.

Polystyrene (PS). Polystyrene (PS) has many attractive properties for medical applications, such as low-cost, transparency, and adaptability to radiation sterilization; however, it is not resistant to organic solvents (e.g., aromatic, aliphatic, chlorinated). Medical PS typically comes in two forms: crystal PS and high-impact PS (HIPS).[105,106] Crystal PS products include labware, for example, Petri dishes and tissue culture trays.[107] For high-strength products, HIPS is competitive with PVC and PP; it is typically used in thermoformed products, for instance, catheters, heart pumps, and epidural trays. Both crystal PS and HIPS can be used in respirators, health care equipment, syringe hubs, and suction canisters. Studies have demonstrated that carcinogenic symptoms could be caused in the human body by long-term exposure to a small quantity of styrene.[66] Therefore, PS is commonly not used if biocompatibility is a requirement.

Similar to other types of plastics, PS recycling has numerous difficulties including eco-efficiency, separation availability, and product quality. Typically, PS can be recycled to produce planters and desk items, for instance, pencils, doors, and window frames. Due to the difficulties of separating PS from the plastic waste stream, most studies have focused on enhancing selective and efficient separation/segregation techniques.[108−110] Froth flotation is a possible and common separation process used by the mineral industry owing to its efficient separation of hydrophobic and hydrophilic materials.[111,112] However, most plastics are naturally hydrophobic; therefore, the plastic surface must be selectively modified before plastic flotation. For example, a mixture of acrylonitrile−butadiene−styrene (ABS) and HIPS can be successfully separated by coating with zinc oxide and performing microwave treatment before froth flotation.[111] Thus, PS-based plastics can be differentiated through froth flotation. Because PS can be separated, it can be reprocessed from the suspension after precipitation. By using this method, used medical PS could be economically viable for the first time. However, froth flotation can only differentiate mixtures that do not contain highly complex plastics. In practice, the plastic waste stream contains more than ten types of plastics, increasing the difficulty of using this technique.

A reduction in molecular weight and elongation at break is also observed in PS via mechanical recycling. Recycled PS is mostly downcycled into disposable products.[111] Remili et al. reported that the molecular weight of PS decreased by nearly 50% after the tenth reprocessing cycle.[113] Chain scission leads to reprocessing by both molecular weight and rheological measurements. Both chain scission and cross-linking compete in HIPS reprocessing.[114,115] At higher temperatures or cycles, chain scission begins to dominate over cross-linking, and the elongation at break of HIPS decreases. Vilaplana et al. reported

Table 2. Advantages, Drawbacks, and Future Perspectives of Alternative Bioplastics for the Substitution of Petroleum-Based Plastics in Medical Applications

alternative bioplastics	substitute for	advantages	drawbacks	perspectives
biopolyethylene (bio-PE)	PE	readily enter existing processing and recycling systems	insufficient supply chain (bio-PE: 3; bio-PP: 1)[122]	bioplastic versions derived from green resources represent reliable alternatives to solve the energy challenges
biopolypropylene (bio-PP)	PP	potentially available from renewable resources	expensive (∼2 times of the commercial petroleum-based one)[122]	
		effective in reducing greenhouse gas (GHG)	narrow processing window of the production in bioversion monomer	
polyurethane (PU)	PVC	effective in reducing the use of toxic plasticizers	high cost	if the plasticizer concern was overcome, it would confirm PU as a bioplastic of election for medical devices
		more favorable environmental impact	lacking data of long-term effects on human	opportunity to minimize the impact on the environment during production and disposal of PVC
			inefficient recycling process	
poly(lactic acid) (PLA)	PS	inertness	costly in the overall production due to impurities in the processing of LA	alternative to match the all-around PS performance needs critical improvements
		more favorable environmental impact	relatively low glass transition temperature makes it fairly for high temperature applications	competitive scalable costs will promote applications
		potentially available from renewable resources		

that the elongation at break of HIPS decreased by 38% after nine reprocessing cycles.[115] Thus, mechanical recycling of PS has several limitations.

The use of chemical recycling to recover styrene monomer through pyrolysis has received extensive attention because PS waste can be converted into biodegradable polyhydroxyalkanoates (PHAs).[116,117] However, the presence of aromatic compounds in this fraction could act as chain transfer agents that reduce the T_g and eventually result in a polymer with inferior properties. The yield of biodegradable PHA is only 10%. Therefore, studies have focused on reducing energy consumption and creating high-value fuel feedstocks through catalytic pyrolysis. Metal, as a catalyst for the degradation of polystyrene, was decorated with montmorillonite.[118] The liquid yield was 89.20 wt % with 5% aluminum (Al) in montmorillonite and 88.87 wt % with 20% iron (Fe) in montmorillonite. Subsequently, the multiphase metal catalytic process produced oil of enhanced quality that was suitable for integrated circuit engines and generator set applications. The maximum liquid yield of 88.05 wt % was achieved by the liquid phase of the metal catalyst. Similar to PVC recycling, PS recycling is less common compared to recycling of other polymers due to process costs. Therefore, chemical recycling is considered unsuitable for treating PS waste.

From an economic perspective, chemical recycling is unsuitable for recycling PS because its feedstocks are cheaper than the recycling process. Mechanical recycling is optimal for the reuse of plastic waste. Currently, the difficulty of separating specific plastics from the waste stream is a major contributor to the inefficiency of PS recycling. No data are available regarding the efficiency of waste plastic separation, highlighting the urgent need for research and development in this area. Considering the above findings, competitive cost, and sustainability of PS recycling methods, the development of closed-loop recycling within a CE could be a promising research direction.

Currently, the most common methods for disposing of medical plastics are incineration and landfilling; however, these can cause harmful effects on human health and the environment. Most medical plastics can potentially be recycled back into a feedstock for new products or refined fuels. The use and study of plastic products should be switched to recycled or biobased content. The production of bioplastics is considered more sustainable than that of petroleum-based plastics primarily due to their reduced net carbon footprint.[119,120] Therefore, research on suitable bioplastics to replace current petroleum-based plastics is urgently needed, as discussed and evaluated in Alternative Bioplastics for Medical Plastics.

■ ALTERNATIVE BIOPLASTICS FOR MEDICAL PLASTICS

A bioplastic can be classified as biobased, biodegradable, or a combination of both. A bioplastic is derived from biomass sources, for example, sugar can, cellulose, or corn starch. The bioplastics investigated thus far are categorized into three primary groups:[121] (1) bioplastics that are made from biodegradable and renewable sources, for instance, starch, cellulose, protein, lignin, and chitosan (this group includes plastics such as PLA, bio-PVC, bio-PE, bio-PP, and bio-PS; the starting monomers of these plastics are obtained from biological sources); (2) bioplastics that are based on completely biodegradable petroleum sources such as polycaprolactone (PCL), polybutylene succinate (PBS), and polybutylene adipate (PBA); (3) bioplastics that are obtained by using monomers from a mixture of biotic and petroleum resources, like polyurethane (PU) and polybutylene terephthalate (PBT).

The most commercialized bioplastics in terms of production volumes are PLA and starch-based plastics.[122] However, recycling technologies are still being developed, and only a few studies of LCA have been conducted using laboratory data.[123,124] The use of the bioversions of conventional monomers to replace the petroleum-based plastics is advisable in the future, because these bioplastics can readily enter existing processing and recycling systems. Specifically, bio-PE and bio-PP are among the most promising alternatives to petroleum-based plastics.

Despite the promise of bio-PE and bio-PP, these bioplastics still have inefficient recycling processes and carcinogenic contents (e.g., PVC: vinyl chloride; PS: styrene). Substitutes for PVC and PS must eliminate these concerns to effectively minimize the global carbon footprint and realize sustainable development. Any potential alternative polymers must have a comparable performance and total cost.

The possibility of using plasticizer-free polymers is a promising approach to overcome the concerns regarding PVC in medical applications. Poly(ethylene vinyl-*co*-acetate) (EVA),[37,125] polysilicon,[126,127] and PUs[128,129] function as potential substitutes for PVC polymers. In particular, PU is currently the most thoroughly tested and used bioplastic because of its good sterilizability[130] (e.g., ethylene oxide and γ-irradiation) and thrombogenicity. In addition, PU can be prepared through a simple process, and its mechanical properties, for instance, durability, elasticity, and bodily tolerance while healing, are controlled by fine-tuning the chemical structures. Besides, the modification of the bulk and surface by combining anticoagulants, biorecognizable groups, or hydrophilic/hydrophobic groups brings the chemical moieties into the functional PU structure. Optimized modifications elevate the acceptance of implants into the human body. Overall, PU is the best candidate for a PVC replacement in high-performance systems.

Among alternatives to PS, poly(vinyl alcohol) (PVOH),[131,132] thermoplastic starch (TPS),[133,134] and PLA[135,136] are popular. In particular, PLA has developed as an important biopolymer for medical applications due to its better biocompatibility, biodegradability, and mechanical properties and easy processability. Most importantly, lactic acid (LA) can be obtained by the fermentation of sugars derived from renewable resources, for instance, corn and sugar cane, and thus, it is an ecofriendly and nontoxic material that can be used in the human body. PLA is a Food and Drug Administration-approved biocompatible plastic and is extensively used in numerous medical applications. PLA could be considered as a potential alternative to PS in medical applications because of its similar or better mechanical and barrier properties.[137,138]

Different bioplastics have currently been developed as alternatives to conventional petroleum-based bioplastics. Table 2 lists the major bioplastics.

Bio-PE and Bio-PP. Bio-PE and bio-PP could be obtained from glucose by the dehydration of ethylene and butylene, respectively. Glucose can be extracted from different biological feedstocks, such as sugar cane, sugar beet, starch obtained from grains, and lignocellulosic materials.[121] The polymerization of bio-PE and bio-PP is the same when using a monomer derived from petroleum, and the chemical, physical, and mechanical properties of the corresponding bioplastics are identical with those of petroleum-based ones.

The bioversions of the existing monomers have become more popular than other bioplastics in part because the management of bioplastics requires major changes to and investments in waste management infrastructure. Prominent companies (e.g., Lego, Nestle, Borealis, DOW) have already announced that they will introduce bio-PE and bio-PP in their products to mitigate environmental impacts. Although the bioversions are favorable replacements for current medical plastics such as PE and PP, their prices are much higher than those of the dominant conventional substitutes. Thus far, the bioversions of PE and PP lag in the establishment of commercialized market products, ascribed to their material costs and narrow processing window.[121,122] For example, the first and the most important step of bio-PE and bio-PP production is the conversion of bioethanol to biomonomer by dehydration. To date, numerous investigations are going on with bio-Pe and bio-PP production by utilizing different catalysts.[139,140] Further studies are on demand to extract information regarding the manufacturing process and to extrapolate the developed bioversions of plastics in their working conditions.

Polyurethane (PU). PUs are synthetic polymers that can be synthesized by the polyaddition reaction between diisocyanate and diol monomers under catalytic and other additive conditions. Tuning the two monomeric components results in PU with different structural features and ultimate mechanical properties ranging from being stiff to flexible. In recent years, PUs have been successfully employed as durable artificial implants because of their mechanical robustness and biocompatibility. Besides, PUs can be 3D printed as biological artificial implants and prosthetics with excellent tailorable aspects in achieving the anatomical, mechanical, and biological requirements for life-saving medical applications.

When flexible synthesis approaches are used, the mechanical and chemical properties of PUs can surpass those of PVC; thus, they are well-suited substitutes to PVC for the durability enabled medical implants, such as percutaneous endoscopy gastronomy tubes (PEG tubes).[141,142] Numerous studies have compared the PVC and PU derived PEG tubes and have pronounced the PU derived PEG tubes to have better durable operational stability than their conventional PVC counterparts. Further, owing to PU's minimal thrombogenicity degree, ease of sterilization via ethylene and γ-irradiation, and sterilization cycle stability,[130] it serves as an impactful substitute for PVC blood bags.

In contrast, polymeric-based 3D scaffolds have become a fundamental component of tissue engineering.[143,144] Many polymeric materials have been explored to accelerate their real high-end applications. PUs have been used in various 3D printing approaches, including fused filament fabrication, bioplotting, and stereolithography, to produce complex implants with precise patterns and shapes. PU scaffolds using 3D printing have good cell viability and tissue integration in vivo. Recently, self-healing PU with tunable mechanical properties has been applied in various disease models (e.g., aneurysm, peripheral injury, sternum immobilization) in vivo.[145] This study validated the effectiveness of self-healing PU as a promising therapy for aortic aneurysms, nerve coaptation, and bone immobilization in three animal models, inspiring a variety of new applications with self-healing functions in suturing and accelerating the real high-end applications of PU.

Although PU perfectly matches the performance of PVC, its high cost limits its applications. The safety profile of PU must be tested thoroughly because of its harmful toxicity in humans; especially, data for long-term effects are currently insufficient. The existing toxicity data for PUs are primarily connected to human contact and porous foam production.[146] The possible toxicity impacts of PUs in medical applications are not assessed significantly yet; however, they are worthy of in-depth investigation considering their possible thought applications.

Poly(lactic acid) (PLA). PLA is the most thoroughly tested and commonly used bioplastic in medical applications owing to its intrinsic biocompatibility and easy processability. Typically, PLA is produced from LA through a polycondensation reaction. LA can be obtained either by a chemical process via bacterial fermentation or synthetically via hydrolysis of lactonitrile. Commercial LA is mainly obtained via the bacterial fermentation of carbohydrates by homofermentative organisms belonging to the genus *Lactobacillus*.[147] A crucial step in the overall production of PLA is a fermentation broth containing a complex mixture of impurities such as nutrients and cell debris; thus, the downstream processing of LA is costly.[148] To date, scientists are continuously making efforts to develop more sustainable LA fermentation processes to achieve efficient PLA production. Recently, the employment of acid-tolerant strains for LA production is becoming a comparatively inexpensive, simpler, and easier approach.[149,150] Therefore, there is great interest in the further development of the industrially cost-effective LA process.

The mechanical properties of PLA are dependent on its molecular weight (M_w) and its degree of crystallinity (determined by its tacticity).[151] To further improve the mechanical and barrier properties of PLA, modification via blending with a tough polymer[152] or plasticization block copolymerization[153] has been extensively explored, and the components or processes that contribute to the polymer compatibility and good performance of the combined materials have been identified.

Owing to the progress in PLA modification, PLA has become a promising bioplastic with comparable mechanical properties to those of PS. For example, PLA can be combined with poly(glycolic acid) (PGA) via copolymerization, thereby considerably improving the degradability and mechanical properties of PLA.[154] Owing to the good mechanical properties of PLA, it can be used in catheters, heart pumps, and epidural trays to replace PS. Like PU, PLA can be used as a high-quality and high-resolution 3D scaffold through 3D printing techniques. For example, a patient-specific scaffold design can be obtained by using the patient's anatomical data.[155] Currently, for biodegradable polymers, PLA is commonly used for 3D scaffold printing. PLA is an attractive candidate for in vivo implantation due to its biodegradation time. Lately, different combinations of PLA with other polymers, for instance, PEG, have been used to adjust the physical and mechanical properties of the scaffolds and to optimize the printing process.[156,157]

PLA naturally degrades over time into well-tolerated and safe degradation products that are excreted from the body. PLA is suitable for the design of new biomedical systems. Many studies have concluded that the use of bioplastics could solve environmental problems associated with petroleum-based polymers (e.g., GHG emissions and climate change). However, the production procedure for LA needs to be improved to minimize environmental impacts from PLA; for instance, acidic conditions using improved microbial strains have shown potential.[158] However, challenges continue to exist regarding the assessment of the characteristics of PLA-based materials and their application domains.

■ CONCLUSIONS

Plastics are commonly used across various industries. In particular, the use of medical plastics has increased greatly recently due to the COVID-19 pandemic. The amount of plastics entering the environment is estimated to reach 12,000 Mt by 2050, posing a major global challenge that must be urgently addressed to avoid negative environmental impacts. Simultaneously, this challenge is an opportunity to develop new sustainable medical plastics for the future.

Urgent measures must be considered to properly segregate, sterilize, and recycle medical plastics. Presently, recycling strategies should focus on scaling-up systems, and plastic bioversions, such as bio-PE and bio-PP, can be integrated into current recycling systems. This can immediately reduce the accumulated waste to a certain extent. The design of closed-loop recycling processes for plastic waste could play a significant role in moving toward a CE. When a successful CE system is created, better recovery of high-quality plastics can be realized.

From a long-term perspective, bioplastics are considered promising, especially for reducing GHG emissions. Studies must investigate alternative bioplastics, including those of natural origin. Current advances in bioplastics have afforded safer approaches to overcome the concerns regarding petroleum-based plastics. One of the current challenges of bioplastics is their production cost; however, the exploitation of waste and renewable resources could reduce the environmental drawbacks. Another challenge is the lack of scientific data concerning the toxicity of bioplastics and their long-term health effects on the human body. Proposed bioplastics should undertake a series of careful toxicological studies, typically including long-term and accurate chemical−physical characterization, in view of achieving suitable medical applications. This indicates the need for interdisciplinary approaches among clinicians, biologists, chemists, and environmentalists to define the best-fit alternatives to petroleum-based plastics based on safety and long-term effectiveness.

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■ ACKNOWLEDGMENTS

This work is supported by the Ministry of Science and Technology, Taiwan (MOST 109-2221-E-027-114-MY3 and MOST 110-2634-F-027-001), the National Taipei University of Technology International Joint Research Project (NTUT-IJRP-109-05), the JSPS Grant-in-Aid for Scientific Research (B) (19H02769), the MEXT Grant-in-Aid for Scientific Research on Innovative Areas (Hybrid Catalysis for Enabling Molecular Synthesis on Demand; 18H04639 and 20H04798), JST CREST (JPMJCR19T4), the Frontier Chemistry Center (Hokkaido University), the Photoexcitonic Project (Hokkaido University), and the Creative Research Institute (CRIS, Hokkaido University).

■ ABBREVIATIONS

CAGR, compound annual growth rate; CE, circular economy; PVC, poly(vinyl chloride); PE, polyethylene; PP, polypropylene; PS, polystyrene; H_2O, water; CO_2, carbon dioxide; CH_4, methane; UV, ultraviolet; GHG, greenhouse gas; T_g, glass transition temperature; DEHP, di-(2-ethylhexyl)phthalate; LCA, life cycle analysis; HCl, hydrochloric acid; CO, carbon monoxide; HTC, hydrothermal carbonization; LDPE, low-density polyethylene; HDPE, high-density polyethylene; MAPP, maleated polypropylene; PLA, poly(lactic acid); T_m, melting point; HIPS, high impact polystyrene; ABS, acrylonitrile–butadiene–styrene; PHA, polyhydroxyalkanoate; Fe, iron; PCL, polycaprolactone; PBS, polybutylene succinate; PBA, polybutylene adipate; PU, polyurethane; PBT, polybutylene terephthalate; EVA, poly(ethylene vinyl-*co*-acetate); PVOH, poly(vinyl alcohol); TPS, thermoplastic starch; LA, lactic acid; PEG tubes, percutaneous endoscopy gastronomy tubes; M_w, molecular weight; PGA, poly(glycolic acid)

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https://doi.org/10.1021/acssuschemeng.2c00160