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Poly(butylene succinate) (PBS): Materials, processing, and industrial applications



Massimiliano Barletta^{a,*}, Clizia Aversa^a, Muhammad Ayyoob^{b,*}, Annamaria Gisario^c, Kotiba Hamad^{d,*}, Mehrshad Mehrpouya^e, Henri Vahabi^f

^a Department of Industrial, Electronic and Mechanical Engineering, Roma Tre University, Via della Vasca Navale 79, Rome 00146, Italy

^b Department of Polymer Engineering, National Textile University, Sector 30 Korangi Industrial Area, Karachi 74900, Pakistan

^c Department of Mechanical and Aerospace Engineering, Sapienza University of Rome, Via Eudossiana 18, Rome 00184, Italy

^d School of Advanced Materials Science & Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

^e Faculty of Engineering, University of Twente Drienerlolaan 5, Enschede 7522 NB, the Netherlands

^fLMOPS, Université de Lorraine, CentraleSupélec, Metz F-57000, France

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ABSTRACT

The development of biodegradable and compostable materials as alternative to fossil-based plastics is today of paramount importance. Polybutylene succinate (PBS) is a class of biodegradable aliphatic polyester that can be achieved from succinic acid and 1,4 butanediol, which is of broad scientific and industrial interest among other biodegradable polyesters due to its compostability according to ISO EN13432 standard. PBS is considered one of the most interesting compostable polymers because of the good compromise of mechanical endurance, ductility, toughness and impact resistance. It is also characterized by a remarkable thermal resistance with heat deflection temperature (HDT) of over 90 °C. Nevertheless, due to its limited Young's modulus as well as its susceptibility to sudden degradation during melt processing, especially at high temperature, PBS is often blended and reinforced with other polymers, fillers and additives to tackle the issues of better processability, higher stiffness, and improved overall mechanical strength. Most common blends of PBS include poly(lactic acid) (PLA), another widespread compostable (and biobased) polyester, which is often added, in different proportion to PBS, to achieve tailored thermo-mechanical response behavior. Other additives and compatibilizers are also frequently used in PBS blends to achieve a wider processing window with better thermal resistance and better mechanical performance thanks to its customizable composition. Thus, recent advances in polymer blending processes have rendered PBS blends an interesting material platform for applications that require a balance of mechanical strength and flexibility as well as thermal resistance together with compliance to industrial compostability standards. This manuscript reviews briefly the synthesis routes of PBS together with the main thermo-mechanical and physical properties as well as recent progress in developing PBS-based blends for industrial applications. The challenges and future perspectives for the employment of PBS blends in every-day applications are also considered.

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^{*} Corresponding authors.

E-mail addresses: massimiliano.barletta@uniroma3.it (M. Barletta), dr.mayyoob@ntu.edu.pk (M. Ayyoob), hamad82@skku.edu (K. Hamad).

Abbreviations

Abbreviations	
1,2,4-BT	1,2,4-butanetriol
DSM	1,2-decene succinate
BDO	1,4-butanediol
CHDMS	1,4-cyclohexane dimethylene succinate
[BMIM]CI)	1-butyl-3-methylimidazolium chloride
FDCA	2.5-furandicarboxylic acid
ATRS	Acetyl Tributyl Citrate
ACNC	acetulated pape crystalline cellulose
ACINC	acelylateu hano-crystalline cellulose
ARD	agro- industrie kecherches et developpements
APP	ammonium polyphosphate
AHP	APP-CaCO ₃ -aluminum hypophosphite
BTPE	biodegradable thermoplastic elastomers
BOD	biological Oxygen Demand
BUR	bubble expension ratio
BCHDA	butylene 1,4-cyclohexanedicarboxylate
CaHP	calcium hypophosphite (CaHP)
CB	carbon black
PAC	carbonate alkenes
CA	caliponate alkenes
CAD	
CAB	centulose acetate butyrate
CDA	cellulose diacetate
СТА	cellulose triacetate
CF	cotton fiber
CNC	cynuric chloride
DCP	dicalcium phospahte
MAH	maleic anhvdride
DCP	dicumvl peroxide
DSC	differential scanning calorimetry
	dilipoleate
	diversified Natural Decluste Inc
DNP	diversified Natural Products Inc.
DSM	Dutch state mines
EFB	empty fruit bunches
ENR	epoxide natural rubber
EVO	epoxide vegetable oil
EBS	ethylene bis stearamide
FCH	functionalized with lactic acid oligomers
FDM	fused deposition modeling
GMA	glycidyl methacrylate
CU	guanosine
ипт	heat deflection temperature
	high density ashertholens
HDPE	nigh density polyethylene
HA	hydroxyapatie
IDE	isosorbide diester
LDH	layered double hydroxide
LIG	lignin
LOI Test	limiting oxygen index test
LDPE	Low density polyethylene
MDH	magnesium hydroxide
MA-g-PBS	maleic anhydride conjugated on PBS
Mng 100	meganascal
	melioc anhydride
MA-g-PLA	melt four index
MFI	men low maex
MCC	microcrystalline cellulose
MCAPP	microencapsulated ammonium polyphosphate
MMC	mitsubishi chemical corporation
PNZn-lignin	modified lignin with phosphorous, nitrogen and the zinc (II) ions
MMT	montmorillonite
NCC	nanocrystalline cellulose
ND	natural rubbor
	natural rubber
	ivin -uicycionexyicardodiimide
рННК	peak of heat release rate
PA	phytic acid
PAPI	pol(yaryl polymethylene isocyanate)
PBS-co-HS	poly (butylene succinate-co-hexane succinate)

PHBHHx	polv(3-hvdroxybutyrate-co-3-hvdroxyhexanoate)
PBAT	poly(butylene adipate/terephthalate)
PBC	poly(butylene carbonate)
PESA	poly(butylene succinate adipate)
PBS	poly(butylene succinate)
PBSH	poly(butylene succinate-co-3-
	phosphinylpropionate)
PBSF	poly(butylene succinate-co-butylene fumarate)
PBSM	poly(butylene succinate-co-butylene malate)
PBST	poly(butylene succinate-co-butylene terephthalate)
PBS-g-MA	poly(butylene succinate-grafted malic acid
PDLA	poly(D-lactic acid)
PEG	poly(ethylene glycol)
PEBS	poly(ethylene/butylene succinate)
PGS	poly(glycerol sebacate)
POSS	poly(hedral oligomeric silsesquioxane)
PLLA	poly(L-lactic acid)
PMAT	poly(methylene adipate/terephthalate)
PIMO	poly(tetramethylene oxide)
PTES	poly(triethylene succinate)
PBS bb SCA	polybutylene succinate (PBS) with bio-based suc-
DDCI	CINIC ACIO
PBSL	Polybutylene succinate-co-lactate
PCL	polycaprolactone
PDO	polyatoxanone
DE	polyester aupate
DEE	polyethylene Furanoate
PEO_PPO_PEO	polyethylene ovide-block-Polypropylene ovide-
110-110-110	block-Polyethylene oxide
PET	polyethylene Terephthalate
PGA	polyglycolic acid
PHA	polyhydroxyalkanoate
PHB	polyhydroxybutyrate
PHBV	polyhydroxybutyrate -co- valerate
PHBH	polyhydroxybutyrate-co-hexanoate
PHBS	polyhydroxybutyrates
PHH	polyhydroxyhexanoate
РНО	polyhydroxyoctanoate
PHV	polyhydroxyvalerate
PLA	polylactic acid
PMC	polymer matrix composites
PEO	polyoxyethylene
PP	polypropylene
PPC	polypropylene carbonate
PVA	polyvinyle acetate
PVC	DTT slobal shomicals
TUE	PTT global chemicals
	thermograymeteric analysis
TSM	thermonlastic souhean meal
TPS	thermonlastic starch
TTI	time to ignition
TBT	titanium butoxide
TDI	toluene diisocvanate
TMP	trimethylol propane
PEPA	trioxa-1-phosphabicyclo-[2,2,2]octane-4-methanol-
	1-oxide
TPP	triphenil Phosphite
TRP	trivresyl phospahte

1. Introduction

The desire to reduce the environmental impact of manufacturing and promote a sustainable economy has paved the way for new research on green plastics, and one of the biggest challenges to

Table 1

Bioplastic Old Economy	New Economy	
 Styrene-butadiene rubber (SBR) Nitrile Rubber Cellulose acetates (CA) etc. 	 Novel chemistry Polylactic acid (PLA) Polyhydroxyalkanoates (PHA) Poly(ethylene2,5- furandicarboxylate) (PEF) Starch blends etc. 	 Drop-ins Bio-Polyamide (PA) Bio-Polyethylene (PE) Bio-Polyethylene terephthalate (PET) Bio-Polypropylene (PP) etc.

* The concept of a new plastic circular economy is based on biopolymers and biodegradable polymers; Source Biopolymers, facts and statistics 2020, Institute of Bioplastics and Biocomposites, Institute for Bioplastics and Biocomposites (IFBB) Hochschule Hannover, Heisterbergallee 10 A, p-30,453 Hannover, Germany.

increase sustainability in manufacturing is to reduce plastic pollution. To this end, interdisciplinary research must be carried out that addresses the technological and environmental challenges [1], so over the past few decades, researchers have sought to produce sustainable, renewable, and biodegradable polymeric materials suitable for industrial and commercial applications. In this regard, scientists, researchers, environmentalists, and policy makers must coordinate efforts to overcome plastic pollution.

Yet another challenge is to evaluate current efforts in research and technology development to promote environmental sustainability. A true depiction of daily accretion of plastics is very difficult to obtain with some high-income nations producing more waste per capita compared to that of middle- and low-income countries. However, waste management is a limited process to fully control plastic pollution [2,3]. The increased demand for sustainability and environment safety has diverted research interests towards selecting critical materials in industry [4–6]. Biodegradable polymers and bioplastics are at the top of the research list in materials science due to increased demand [7].

Over the past decade, aliphatic biodegradable polyesters have received great interest due to heightened attempts to move toward a circular plastic economy [8–11]. This new concept of a circular economy for polymers and plastics is beginning to gain wide acceptance [12,13], and it stands in contrast with the "Old Economy" of bioplastics that had been developed even before the emergence of petrochemicals, including rubber, cellophane, viscose, celluloid, cellulose acetate, and linoleum. The "New Economy" of bioplastics consist of (1) biopolymers with new chemical structures such as polylactic acid (PLA); and (2) "drop-in" biopolymers that have the same chemical structure as petrochemical-based materials but are obtained from sustainable bio-based feedstock, of which bio-based polyethylene (Bio-PE) and polyethylene terephthalate (Bio-PET) are the most prominent examples (Hannover, 2020). This concept is shown in Table 1.

A wide range of biodegradable polymers can be directly obtained from renewable resources, or can be partly synthesized from renewable natural resources [14]. Most naturally extracted polymers are biodegradable [15,16], and biodegradable polymers can be summarized into three main categories [8]:

\Rightarrow Naturally existing biodegradable polymers

These polymers are derived directly from natural, renewable resources. Nature produces several different types of polymers including but not limited to polysaccharides (such as starch, cellulose, lignin, chitosan, alginate), proteins (such as gelatine, collagen, fibrin, fibropectin, casein, hair, wool, silk), and lipids (in the form of fats and oil). All these polymers can either exist naturally or can be derived synthetically from natural materials.

⇒ Polymers derived from microorganisms or polymers of PHA's family

These polymers are derived from microorganisms such as genetically-modified bacteria and include plastic materials such as polyhydroxyalkanoates (PHAs), polyhydroxybutyrates (PHBs), polyhydroxyvalerate (PHV), and polyhydroxyhexanoate (PHH).

\Rightarrow Chemically produced biodegradable polymers

These polymers are produced via polymerization of raw materials (monomers) obtained from nature, either from sustainable resources or from fossil fuels, and they include poly(lactic acid) (PLA), poly(glycolic acid), polycaprolactone (PCL), poly(butylene succinate) (PBS), poly(butylene adipate/terephthalate) (PBAT), poly(ethylene/butylene succinate) (PEBS), poly(methylene adipate/terephthalate) (PMAT), poly(butylene succinate adipate) (PESA), and other aliphatic–aromatic co-polyesters.

The annual production of plastics is about 368 million tons, and the share of bioplastics is just 1% of the total plastic production [17,18]. However, due to a continued increase in demand for environmentally-friendly materials, plastic production will be decoupled from petrochemicals in the long term, and as a result, alternative feedstock will be used for plastic production including secondary plastics, recycled oil, biomass, and CO₂. The market for bioplastics is continuously growing and diversifying. More sophisticated bioplastics and biopolymers are being developed for emerging applications and products [18–20].

Poly(butylene succinate) (PBS), also sometimes called as poly(tetramethylene succinate), is a biodegradable thermoplastic polymer that belongs to the polyester family [21]. This polymer has received great interest due to its thermo-mechanical and physical properties that are comparable to those of polypropylene [22,23]. Among the aliphatic biodegradable polyesters, PBS is considered to be promising because it offers excellent biodegradability, melt processability, and chemical resistance [24]. PBS is chemically composed of repeating units of butylene succinate ($C_8H_{12}O_4$), and it exhibits excellent characteristics including susceptibility to biodegradation, thermoplastic behavior, thermo-processability with several types of conventional equipment for plastics, and reasonably balanced thermo-mechanical properties [22].

An ethylene glycol and succinic acid polyester was first reported in 1963 by Lorenzo [25]. Wallace Carothers investigated the mechanism of esterification while searching for artificial silk [26,27], but abandoned polyesters later on and focused on polyamides. Flory further studied and improved the synthesis of polyesters with different raw materials [28], and since then, further efforts have been made to industrialize aliphatic polyesters [26,28,29]. Recently, biodegradable polymers have gained extensive attention from leading scientists and chemists. PBS and its co-polyesters had been overlooked, until the biodegradability of these polymers was investigated in the 1990s [16,30,31].

PBS is usually synthesized via co-polymerization of succinic acid and 1,4 butanediol, both of which can be derived from fossil resources as well as renewable resources. PBS is available commer-



Fig. 1. Annual number of publications on PBS over the last decade; search term: poly(butylene succinate); source: web of science.

cially since 1993 under the trade name of BionolleTM and has also been sold since 2017 under the commercial brand BIOPBS by PTT MCC Biochem Company Limited, a 50–50 joint venture between Mitsubishi Chemical Corporation (MMC) and PTT Global Chemical Public Company Limited (PTTGC). In recent times, both fossil-based and bio-based PBS has been sold on the market by new players, most of them located in China and South Korea. The overall availability of PBS in 2020 is not perfectly known, but it should average 100,000 tons worldwide. The current market price depends on the prices for raw material sources, and it averages 4.00 to 4.50 USD/kg for fossil-based PBS and 5.50 to 6.00 USD/kg for bio-sourced PBS.

PBS belongs to the family of aliphatic biodegradable polyesters [32,33] and it exhibits excellent characteristics including good biodegradability, thermoplastic behavior, thermo-processability using conventional equipment for plastics, and reasonably-balanced thermo- mechanical properties [34,35]. The physical properties and the rate of biodegradation can be adjusted by controlling the copolymerization and molecular weight [35]. A variety of PBSbased polymeric materials can be produced using different types and ratios of co-monomers to achieve a wide range of mechanical properties and biodegradation rates [36-38]. A wide thermal processing window makes it suitable as a polymer for injection moulding, cast and blown extrusion and thermoforming [39,40]. However, PBS has limited applicability due to its thermal stability, high flammability and relatively poor mechanical properties [41]. Fig. 1 shows trends obtained from The Web of Science of the increase in publications over the last decade. An increase of more than 120% was seen in the number of publications per year from 2011 to 2020.

A number of methods can be adopted to modify the properties of PBS-based plastics and thus broaden the range of potential applications, including blending, mixing, composite formulation and copolymerization with suitable monomeric units [42–45]. For example, PBS can be modified via copolymerization with other dicarboxylic acids or diols to make it suitable over a wider range of practical applications including packaging, disposable items, agricultural films, nonwoven fabrics, materials for biomedical devices, and others [32,46,47]. After the initial work by Carothers and Arvin [26], extensive efforts have been made to investigate the synthesis routes and resulting properties of PBS and its copolymers [22]. The polymer morphology, crystallinity, structures, physical and mechanical properties and biodegradability of PBS have been reported in previous reviews [1,22,48].

In light of the limited availability of fossil resources and growing concerns related to CO_2 emissions generated by feedstock preparation, scientists and technicians have diverted their attention to the use of sustainable resources in the production of PBS. Recently, renewable and sustainable resources have emerged as candidates to prepare the feedstock necessary for PBS synthesis and its co-polymers [16]. This sustainable approach to obtain feedstock and its suitability for a broader range of applications has multiplied the interest towards this class of polymeric materials. Moreover, demand in the new circular economy also plays an important role in the growing interest in this area.

However, to the best of our knowledge, the synthesis of monomers and PBS from fossil-based or renewable feedstocks as well as the properties of the PBS copolymers have not been sufficiently summarized. Accordingly, this review will provide deep insights into the raw materials, monomers, synthesis processes, processability, thermal and mechanical properties, and biodegradability of PBS and its copolymers. Moreover, the comprehensive review also includes PBS blends and their industrial applications. Finally, future trends will also be discussed regarding the development of PBS-based materials, with a particular focus on additive manufacturing.

2. Synthesis of PBS

The most common route for PBS synthesis is the polycondensation of succinic acid or dimethyl succinate and 1,4-butanediol. Both monomers can be derived from bio- or fossil-based sources. The flow chart for PBS production is shown in Fig. 2.

2.1. Production of succinic acid

In a typical industrial process, succinic acid can be produced via different chemical routes using petroleum-based feedstock. Major industrial routes include paraffin oxidation, catalytic hydrogenations, or electroreduction of maleic anhydrides or maleic acids [49–52]. A manganese- or calcium-based catalyst is used to produce different types of dicarboxylic acids from the paraffin oxidation process at the same time [50]. The yield and purity of succinic acid is poor, even after distillation and purification via crystallization. The hydrogenation of the maleic acid process is well-established and has been in use since the 1930s to produce succinic acid. The hydrogenation reaction can be conducted by carefully using different catalysts. Although a high yield with a high purity can be obtained, this process is expensive, complicated, and has environmental implications [49].

Today, most commercial succinic acid is manufactured via chemical hydrogenation of maleic anhydride to succinic anhydride, followed by hydration to succinic acid. Maleic anhydride, in turn, is derived from the oxidation of butane or benzene. From maleic anhydride, high-purity succinic acid can be produced by electrolysis for food and pharmaceutical products [49,53]. In contrast, the bio-production of succinic acid using bacterial fermentation is more environmentally sustainable [54].

Succinic acid can also be derived from bacterial fermentation of sustainable feedstock, such as glucose, xylose, starch, alpha cellulose derivatives, food waste, crops waste, and wheat milling byproducts [55–58]. There is a long list of different bacterial strains that can be used in a bio-refinery to produce succinic acid. However, it is worth noting that not all strains produce succinic acid as an end-product, and it is sometimes produced as an intermediate product. Among different bacterial strains, actinobacillus succinogenes [59–63], anaerobiospirillum succiniciproducens [64– 68], mannheimia succiniciproducens [69–72] and recombinant Es-



Fig. 2. Flow chart for PBS synthesis of sustainable bio-based and petrochemical feedstock. [22], copyright 2010. Reproduced with permission from John Wiley & Sons Inc.

cherichia coli [73–78] have been widely tested and are wellestablished bacterial strains used for fermentation of feedstock to produce succinic acid. More recently, another genetically modified bacterial strain (Corynebacterium glutamicum) has been tested to have higher efficiency in the production of succinic acid [79–82]. Sometimes, Corynebacterium glutamicum is referred to as an over producer of succinic acid [80]. Several efforts have been made to improve the productivity of the bacterial strains in both batch-wise and continuous processes [83].

In most cases, fermentation is carried out in a batch process, and the highest yield of succinic acid has been reported to be 200 g/L [84]. However, to achieve continuous fermentation, the rate of production of succinic acid has reached a maximum of up to 17.1 g/L/h using mannheimia succiniciproducens MBEL55E [85]. The details of different strains of bacteria, modification of the strains and succinic acid production process have been summarized in different reviews [40,49]. As stated above, most commercial production of succinic acid has been carried out through the hydrogenation of maleic anhydride to succinic anhydride, followed by hydration to succinic acid using petrochemicals as feedstock. However, succinic acid can be produced via two main routes using biotechnology and renewable feedstock. The first route involves electrolysis and the second route is the fermentation of microorganisms with renewable biomass such as the straw and stalk of crops, industrial molasses, wood waste, starch, glucose, and xylose [49.86].

In 2004, bio-based succinic acid was declared by the US Department of Energy to have high potential for use and to be an attractive substitute for petroleum-based feedstock. Recently, biotechnology systems have produced a multitude of related chemical compounds. Some of the leading companies in the manufacture of polymeric raw materials have built pilot plants and demonstrations, or even commercial-scale factories, to produce succinic acid via bio-fermentation [87]. A comparison of sustainable production versus conventional production of succinic acid is shown in Fig. 3.

Bioamber, a joint venture between the US-based DNP (Diversified Natural Products Inc.) Green Technology and France-based ARD (Agro- industrie Recherches et Développements), announced in 2008 the successful commissioning and the starting of the world's first production plant for bio-based succinic acid. The plant was integrated into an already existing biorefinery located in Pomacle (France) and it had an initial annual production capacity of 2000 t of succinic acid. The plant started to produce bio-based succinic acid in December 2009 using an E. coli bacterial strain specifically modified to produce succinic acid from wheat-based glucose. Bioamber also collaborated with Japanese-based Mitsui for to produce bio-based succinic acid. Similarly, Royal DSM invested in the development of bio-based succinic acid through a partnership with Roquette, a French starch-based derivatives producer. The new company, Reverdia, started commercial production of succinic acid on a pilot plant yielding 300 tons annually. Succinic acid is being produced from starch using a modern enzyme-based technology. These companies planned to scale production to up to 20,000 tons per year in late 2011.

In October 2009, BASF, a large player in commodity chemicals and plastics, signed a development and production partnership with Purac to develop industrial-scale fermentation for biobased succinic acid. For said purpose, BASF developed a bacterial strain (Basfi succiniproducens) to ferment glycerin or glucose. Production of succinic acid started at a commercial scale in 2010 at a Purac production facility in Spain. US-based Myriant Technologies secured a grant of \$50 million from the US Department of Energy to establish a commercial production plant for bio-based succinic acid in Louisiana. The facility currently produces succinic acid via fermentation of unrefined sugar using E. coli bacterial strains in a 20,000-liter bioreactor.

Currently, bio-based succinic acid production is increasing dayby-day due to high demand for single-use and commodity plastics. However, the development of suitable bacterial strains or enzymes is another issue that needs to be addressed to achieve largescale commercial production. The yield and yield concentration from feedstock need to be improved to make it more cost effective, and there are other challenges related to the fully bio-based PBS, such as higher consumption of biomass/ton of biopolymer to reduce its competition with food production. However, the consumption of biomass feedstock can be reduced by half (as shown in Fig. 4) by carefully selecting the chemical constituents for PBS production. If bio-based succinic acid is produced only from sustainable feedstock for PBS, the overall consumption would be half of the total consumption for fully bio-based PBS, and this will reduce the risk of competition with food production as well as the carbon footprint. A comparison of worldwide succinic acid produc-



Fig. 3. Synthesis of succinic acid through sustainable feedstock versus conventional synthesis from petrochemical-derive maleic anhydride. [88], copyright 2015. Reproduced with permission from Elsevier Science Ltd.



Fig. 4. A comparison of worldwide succinic acid production using petrochemical and fermentative methods. [88], copyright 2015. Reproduced with permission from Elsevier Science Ltd.

tion using petrochemical and fermentative methods is presented in Fig. 4 [88].

2.2. Production of 1,4-butanediol (BDO)

The second component of PBS (1,4-Butanediol (BDO)) is also an organic compound, and it is commonly used as a solvent in industrial cleaners. The second most important use of BDO is in the synthesis of over 2.5 million tons of valuable polymers [78]. Commonly 1,4-butanediol is synthesized on commercial scale from petrochemical-based feedstock via several routes [53,89,90]. It is a very important chemical building block in the preparation of important polymers such as spandex, polybutylene terephthalate, and polyurethanes. The commercial synthesis of BDO uses petrochemical feedstock in various industrial processes, including the Reppe process, Davy process technology, and the Lyondell Basell propylene oxide route [86]. It was first prepared commercially in 1930 using Reppe Chemistry, which consists of a chemical reaction of formaldehyde with acetylene and subsequent stages of hydrogenation [91]. Different routes of industrial production of BDO have been developed for preparation at a commercial scale.

- \checkmark Among these, the most important is the use of the Reppe reaction process of acetylene with formaldehyde to produce an intermediate, and then the hydrogenation of intermediate compounds is used to produce BDO. This method was initially developed by Walter Reppe in the 1930s [91]. The production of BDO via the Reppe reaction is a major route that is mainly used by BASF and BASF/ Idemitsu. Initially, hydrated calcium carbide was used as a source of acetylene, but the partial oxidation of natural gas is mainly used. Nowadays, BDO can be produced in the petrochemical industry from maleic anhydride, propylene oxide and butadiene using different routes. However, the Reppe reaction process still holds a large share of about 42% of global production [92].
- √ The second most important route is the synthesis via three step Mitsubishi 1,3-butadiene acetoxylation process, acetoxylation, hydrogenation and hydrolysis [28,29,30]. This process technology was developed by Mitsubishi in the late 1970s [53,93,94]. The Mitsubishi acetoxylation process is flexible enough to produce both BDO and/or tetrahydrofuran (THF).
- ✓ Relatively later, Lyondell Basell developed technology to use the propylene oxide route. In this process, BDO is manufactured using propylene oxide in three major steps: isomerization of propylene oxide to allyl alcohol, hydroformylation of allyl alcohol to 4-hydrobutyraldehyde, and hydrogenation of the 4- hydrobutyraldehyde to BDO [95].
- √ Using relatively new technology, the Davy Process produces BDO via maleic anhydride or maleic anhydride feedstock. Maleic anhydride can be made through the oxidation of butanes or benzenes as feedstock [96,97]. The process was originally developed by Davy in collaboration with CONSER and SISAS. In the Davy technology, maleic anhydride is produced via butane oxidation. Maleic anhydride and an intermediate maleic acid is produced to obtain BDO after hydrogenation, and THF and γ butyrolactone can also be produced along with BDO in a single reaction strain.
- √ As an alternative to the above-mentioned processes, bio-based routes have also been developed to achieve sustainable production of BDO [92,98–101]. In this process, renewable feedstock is fermented to produce succinic acid that is then purified and reduced catalytically to DBO. In addition, several other processes



Fig. 5. Synthesis of poly(butylene succinate): (a) Esterification reaction of succinic acid with 1,4-butanediol, (b) Transesterification of 1,4-butanediol with dimethyl succinate, (c) Oligomers are then polycondensed to produce high molecular weight PBS resin.

have been developed to produce DBO from renewable feedstock including the direct fermentation of sugar using microorganisms [102].

2.3. Synthesis of PBS

Poly (butylene succinate) (PBS) is an aliphatic polyester with succinic acid and 1,4-butanediol as monomers. These monomers are obtained from renewable or fossil-based resources, and the details are further discussed in the sections above. PBS is mainly synthesized via condensation of succinic acid (or dimethyl succinate) and 1,4-butanediol (BDO), both of which are mainly derived from maleic anhydride.

In a general preparation procedure for PBS, synthesis can be subdivided into two steps: (1) esterification of succinic acid and BDO or transesterification of dimethyl succinate and BDO, producing PBS oligomers and (2) polycondensation of the oligomers and removal of BDO, as shown in Fig. 5a–c.

In a typical synthesis process, the reactor is immersed in a well-controlled oil bath or a heating system, and it is equipped with a magnetic/mechanical stirrer, a condenser/distillation column and a nitrogen gas inlet/outlet. Precisely-calculated stoichiometric amounts of succinic acid and BDO are added. Sometimes, an excess of BDO, but not above 15%, is fed into the reactor. The temperature is raised to 160–190 °C and is maintained until the succinic acid has completely melted under a N₂ gas atmosphere. Water and/or methanol are distilled out, and the temperature is then raised to 220 – 240 °C under a vacuum also applied and reaction continued for a well-established time range [35,103].

Researchers have explored the efficiency of various catalysts to find the most suitable for PBS synthesis. Several research groups have reported their findings of the catalytic activities, efficiencies, and mechanisms. A wide range of catalysts have been studied for the polycondensation of PBS, including organo-metal based catalysts, $Sc(NTf_2)_3$, $Sc(CF_3 SO)_3$, titanium(IV) isopropoxide phosphate acid, titanium tetrabutoxide, and composites of titanium and tin [40]. Jacquel et al. investigated six different organometallic catalysts including, Ti(OBu)₄, $Zr(OBu)_4$, $Sn(Oct)_2$, $Sb(OBu)_3$, Hf(OBu)₄, and Bi(ODec)₃ for efficiency and found that Ti(OBu)₄ is top-ranked, followed by Zr, Sn, Sb, Hf, and Bi, respectively, [35]. It is generally believed that antimony, tin and titanium compounds are considerably more effective than others. $SnCl_2$ is a very common catalyst known for aliphatic polyester preparation, and it is used to prepare high molecular weight polyesters. Sometimes, it is used in combination with p-toluenesulfonic acid to help control the discoloration of the polymer [34,104,105]. Previously, few catalysts were used either to obtain higher molecular weight PBS, such as lanthanide triflates [106], distannoxane [107–109], tetraisopropyl titanate [110-112], and tetrabutyl titanate [113-116]. Many efforts have been made to investigate esterification of succinic acid and 1,4-butanediol. The kinetics of the esterification reaction of ethylene glycol and succinic acid were first reported by Dostal and Raf, and short after by Flory in the late 930 s. Flory concluded from the earlier data reported by Dostal and Raf and the results of his own experiments that "succinic acid-co-ethylene polycondensation is predominantly a tri-molecular reaction process. The rate of the esterification reaction is proportional to the first power of the hydroxyl groups' concentration and to the square of the concentration of the carboxyl group." Therefore, polyesterification and esterification follow similar course, and accordingly, the rate of the reaction is not affected by either an increase in the molecular weight or increase in the viscosity [117-120]. The esterification kinetics of succinic acid and 1,4-butanediol were reported by Park et al. with and without a catalyst in the temperature range of 170 to 190 °C. The rate of the reaction is temperaturedependent. It increases with an increase in the reaction temperature, and in the absence of a catalyst, succinic acid acted as the acid catalyst [121]. Later on, the detailed mechanism of the kinetics of polyesterification was studied by Fradet and Maréchal [122]. More recently, Mathieu Garin et al. reported on the kinetics of PBS synthesis of and stated that the high molar mass synthesis of PBS merely follows classical Flory theory. Moreover, a very high molecular weight PBS polymer exhibited a higher crystallization temperature and faster rate of crystallization [123]. Different synthesis methods have been adopted to obtain PBS with a reasonably high molecular weight. Han et al. presented a simple technique using PBS oligomers as starting materials in the presence of succinic acid and 1,4-butanediol to synthesize a very high molecular weight PBS [124]. Labruyere et al. introduced a polymerization technique for PBS oligomers and then a depolymerisation of PBS oligomers to butylene succinate lactones. Then, PBS was produced with a higher molecular weight using ring-opening polymerization [125]. Ring-opening polymerization of macrocyclic lactones in the presence of poly(ethylene glycol) as macro initiator can produce a block copolymer with a very high molecular weight that is not possible using conventional melt polycondensation of succinic acid and 1,4-butanediol [126]. The 1:1 stoichiometric balance of succinic acid and 1,4-butanediol is another important factor that allows the

PBS chains to attain a maximum chain length [127]. However, side reactions or volatilization at higher reaction temperatures can lead to a stoichiometric imbalance of the reaction mixture. As a result, the required molecular weight was not achieved. In addition, removing the by-products of esterification from the reaction mixture can shift the equilibrium to the forward side, and a polyester is produced with a higher molecular weight.

Solution polymerization under azeotropic conditions is another solution to remove the by-products. Continuous azeotropic dehydration of the reaction mixture results in a polymer with high molecular weight [128–130]. Another method is the direct melt polycondensation under a high vacuum after esterification at a low temperature and low vacuum [131]. Researchers are continuously trying to achieve a synthesis method that is more convenient and environmentally friendly. In such an attempt, Sivan Velmathi et al. synthesized PBS with a high molecular weight after 20 min of residence time under microwave irradiation. Chain extension methodology is also used to obtain a very high molecular weight of the polymers, which is not possible via conventional methods [132-137]. Researchers similarly used chain extension techniques in another attempt to obtain PBS and its copolymers with a very high molecular weight [37,138,139]. Through chain extension, PBS was produced with a high molecular weight using different types of chain extenders including hexamethylene diisocyanate [32,124,140–143], bisoxazoline [138], maleic acid [37], epoxy based chain extenders [144,145], terephthaloyl biscaprolactamate and adipoyl biscaprolactamate [146]. These chain extenders couple a pair of two PBS or PBS and another polymer chain to improve the molecular weight of the resultant polymer. In addition, the molecular weight of the PBS can be enhanced during polymer processing by adding suitable reactive compounds. Different types of blends and composites are being formed using reactive processing techniques [147-150], and there are several key factors that have determined the resultant molecular weight of the aliphatic polyesters produced via condensation polymerization, especially PBS. During polymerization, water condensation must be continuously removed from the reaction mixture during esterification. 80 to 90% of the total water produced during esterification should be removed. Otherwise, the reaction will take longer, and the PBS cannot reach a high molecular weight. To obtain PBS with higher molecular weight using polycondensation, by-products must be removed up to maximum level during esterification. As esterification is initiated, the by-products start to be produced within the reaction mixture. Therefore, the esterification temperature is a very important factor that can affect the rate of esterification, and this rate can be improved with an increasing temperature, leading to a larger amount of by-products. The major by-product is tetrahydrofuran, along with the water of esterification that forms due to the dehydration of butanediol in the reaction mixture. Sometimes, reaction inhibitors and other techniques are used to suppress the production of tetrahydrofuran. As a result, the residual tetrahydrofuran ratio in the final PBS product is less than 0.1%. The application of an inert environment during esterification and a vacuum during condensation are also very important to obtain a high molecular weight. An adequate vacuum is required to remove the water from the reaction mixture during condensation at an elevated temperature. A cold trap (~ -120 °C) provides a stable vacuum by condensing any small volume of water or other by-product (e.g., tetrahydrofuran), and thus, PBS can be produced with a high molecular weight. Similarly, the selection of catalysts is critical to obtain an improved molecular weight within a short reaction time. The catalysts characterized by a high reactivity and resistance to hydrolysis are crucial. Reaction inhibitors, thermal stabilizers, end capping stoichiometric balance and end capping agents are other parameters that control the rate of the reaction, chain length, and thermal degradation during polymerization. Hence, those parame-

Table 2

The various types of catalysts employed in the synthesis of PBS polymers.

Family	Catalyst	Refs.
Metals and metallic	Tin	[40]
composites	Titanium + tin	[40]
Salts	SnCl ₂	[36,107-109]
	Lanthanide triflates	[35]
Organo-metallic	Ti(OBu) ₄	[35]
	Zr(OBu) ₄	[35]
	Sn(Oct) ₂	[35]
	Sb(OBu) ₃	[35]
	Hf(OBu) ₄	[35]
	Bi(ODec) ₃	[35]
	Titanium (IV) isopropoxide	[40]
	phosphate acid	
	Distannoxane	[111-113]
	Tetrabutyl titanate	[117-120]

ters should be optimized to improve the yield and the molecular weight of the PBS polymer (Table 2).

3. PBS based copolymers

PBS copolymers have recently gained a significant amount of attention. The macromolecular microstructures are designed considering PBS as a major component in the polymeric backbone, and a summary of recent PBS copolymers is listed in Table 3. A melting temperature (T_m) above 100 °C is crucial to process thermoplastic polymers for use in commodity plastics. Only a few aliphatic polyesters such as poly(ethylene succinate), poly(butylene succinate), and poly(ethylene oxalate) exhibit melting temperatures above 100 °C in the family of aliphatic poly(alkylene dicarboxylate) polyesters [61]. The other important factor that makes a polymer suitable for production at a commercial scale is its thermal stability. For example poly(ethylene oxalate) is a polymer with a very stable melting temperature at 177 °C, but it has attracted less attention due to its poor thermal stability. On the other hand, PBS melts in the range of 115 °C, with heat distortion at 97 °C, and it exhibits mechanical properties comparable to those of polypropylene (Table 3).

The physical and mechanical properties of PBS can be tailored through several approaches that have been extensively explored, including random and block copolymerization, chain coupling and chain extension, and addition of functional groups in the main chain. Usually, random copolymerization of PBS with other monomers results in a decrease in the melting point, heat distortion, degree of crystallinity and tensile strength. In contrast, an increase is observed in the impact strength and elongation at break due to copolymerization. Contrary to the above statement, a random PBS copolymer with butylene fumarate demonstrated a melting point constant at up to 20% mol [78]. Therefore, the comonomers content is kept at 15% maximum when the melting temperature of PBS copolymers needs to be greater than 100 °C. A 5 to 15% change in the chemical composition of the PBS polymer backbone is sufficient to tailor the mechanical properties of the PBS-based copolymers without any significant loss to the thermal properties.

4. Properties of PBS

4.1. Mechanical properties

PBS-based polymers show very interesting properties and excellent processability. They can be processed into melt blow, for monofilament, multifilament, spilt and flat yarns. PBS can also be processed as commodity plastics through injection-moulding for

PBS copolymers and related improved performance due to the copolymerization process.

PBS copolymer	Improved properties	Refs.
Poly(butylene succinate)-poly(ethylene glycol) (PBS-PEG) multiblock copolymers	Shape memory effect	[114,151]
Poly(butylene succinate) –b-poly(ethylene succinate)	1 5	
poly(butylene succinate-co-terephthalate)	Thermal stability	[152]
Poly(butylene succinate-co-3-phosphinylpropionate) (PBSH)	Flame retardancy and mechanical properties	[153]
poly(butylene succinate/diglycolate)	Biological interaction for tissue regeneration	[154]
Poly(butylene succinate- co-carbonate)	Toughness and tear resistance	[155]
Poly(butylene succinate-co-butylene fumarate)	Elastic modulus and thermal stability	[156–159]
Poly(butylene succinate-co-fumarate)		
Poly(butylene fumarate) and Poly(butylene succinate) Multiblock Copolymers		
Poly(butylene succinate) (PBS)-co- poly(triethylene succinate) (PTES)	Biomedical properties and elongation	[160]
Poly(butylene succinate-co-L-lactate)	Fracture resistance and strength	[161]
Poly(butylene succinate- co - ε -caprolactone)	Thermal stability and crystallinity	[162-165]
Poly(butylene succinate) and Poly(ε -caprolactone)		
Poly(butylene succinate-ran- ε -caprolactone)		
Poly(butylene succinate-ran-caprolactone)		
Poly(ethylene succinate-co-ethylene adipate)	Thermal properties	[166-168]
Poly (butylene succinate-co-butylene adipate)		
Poly(butylene succinate-ran-butylene adipate)		
Poly(butylene succinate-co-butylene furandicarboxylate)	Biodegradability	[169]
Poly(butylene furandicarboxylate-co-succinate)s	Biodegradability	[170]
Poly(butylene succinate-co-ethylene succinate) copolyesters	Crystallinity	[171,172]
Poly(butylene succinate-co-dilinoleic succinate)	Electrospinning-ability	[173]
Poly(butylene succinate-co-furandicarboxylate)	Elastic modulus, strength, and ductility	[174]
Poly(butylene succinate-co-butylene malate) (PBSM),	Molecular weight	[152,175]
Poly(butylene succinate-co-butylene fumarate) (PBSF),		
Poly(butylene succinate-co-butylene terephthalate)		
Poly (butylene succinate-co-terephthalate)		
Poly(butylene succinate-co-butylene furandicarboxylate)	Thermomechanical properties	[176]
Poly(butylene succinate-ran-butylene adipate)	Thermal stability	[45,177]
Poly(butylene succinate-ran-butylene adipate) random copolymers		
poly(2,5-furandimethylene succinate)-b-poly(butylene succinate)	Toughness and elongation at break	[178]
Poly(butylene succinate-co-butylene azelate)	Crystallinity	[179–181]
poly(butylene succinate-co-decamethylene succinate)	Toughness	[182]
poly(butylene succinate-co-hexamethylene succinate)	Thermal, crystallinity and mechanical properties	[183]
Poly(butylene succinate-co-diethylene glycol succinate)	Crystallinity	[184–186]
Poly(butylene succinate)-b-poly(diethylene glycol succinate)		
Poly(butylene succinate) and Poly((R) -3-hydroxybutyrate)	Thermal stability	[187]
Poly(butylene succinate) copolymers with tartaric acid-based monomers	Biodegradability	[36]
Poly(butylene succinate-co-butylene oxabicyclate)	Toughness and elongation at break	[188]
PLLA-block-poly (butylene succinate)-block-PLLA	Toughness and elongation at break	[189,190]
Poly(lactic acid) (PLA) and poly(butylene succinate) (PBS) copolymer		-

(continued on next page)

Table 3 (continued)

PBS copolymer	Improved properties	Refs.
Poly(butylene succinate-co-butylene dimerized fatty acid)	Thermal stability, toughness, and elongation at break	[191]
Poly(butylene-co-isosorbide succinate)	Strength	[192]
Poly(propylene succinate-co-butylene succinate)s	Thermal stability	[193]
Poly(butylene succinate)-b-poly(butylene sebacate)	Biodegradability	[194,195]
Poly(butylene succinate-block-1,3-propylene sebacate)		
Poly(ethylene terephthalate)-b-poly(1,4-butylene succinate)	Biodegradability	[196]
Branched poly(butylene succinate)-co-1,2-octanediol	Thermal stability	[197]
poly(butylene succinate) (PBS) with different amino acids including L-aspartic acid	Elongation at break	[198]
Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(butylene succinate)-b-poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacryloyloxyethyl phosphorylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacrylcholine)-b-Poly(2-methacr	Improved responses for medical applications and cancer therapy	[199]
Phosphorylcholine)		
Poly[p-dioxanone-(butylene succinate	Biodegradability	[200,201]
Poly(p-dioxanone)-b-poly(butylene succinate) multiblock copolymers		
Poly(butylene succinate) (PBS) and its copolymers with 1,4-cyclohexane dimethylene succinate (CHDMS) or	Biodegradability	[202]
butylene 1,4-cyclohexanedicarboxylate (BCHDA)		
Poly(butylene/diethylene succinate) block copolymers	Elongation at break	[203]
Poly(butylene succinate) (PBS)-based random copolymers containing thioether linkages	Biocompatibility	[204,205]
Poly(butylene succinate-co-butylene itaconate) Copolymers	Elongation at break	[206]
Poly (butylene succinate-co-hexane succinate) (PBS-co-HS),	Biodegradability	[167]
Poly(butylene succinate-co-salicylic acid) copolymers	Biodegradability	[207]
Poly[2-(dimethylamino)ethyl methacrylate]-poly(butylene succinate)-Poly[2-(dimethylamino)ethyl methacrylate]	Improved responses for drug delivery applications	[208]
poly(butylene succinate) (PBS) and poly(tetramethylene oxide) (PTMO) block copolymers	Strength	[209]

Material	Composition	Modulus (MPa)	Strength (MPa)**	Elongation at break(%)	Refs.
PBS	-	-	19.3	375	[33]
PBSA20	20 mol% Adipate	-	17.3	430	
PBSA40	20 mol% Adipate	-	13.4	450	
PBSA50	20 mol% Adipate	-	9.5	330	
PBSA60	20 mol% Adipate	-	8.1	310	
PBSA80	20 mol% Adipate	-	11.7	375	
PBS-0.03M*	0.03mol% Malic acid-branched PBS	160	23	100	[214]
PBS-0.08M*	0.08mol% Malic acid-branched PBS	210	29	50	
PBS-0.12M*	0.12mol% Malic acid-branched PBS	190	28	40	
PBS-0.3M*	0.3mol% Malic acid-branched PBS	220	39	50	
PBS-0.2TMP*	0.2 mol% Trimethylolpropane-branched PBS	200	37	130	
PBS-0.5TMP*	0.5 mol% Trimethylolpropane-branched PBS	270	37	135	
PBS-0.21TA*	0.21mol% Trimesic acid-branched PBS	210	33	360	
PBS-0.21GP*	0.21mol% Glycerol propoxylat- branched PBS	210	41	310	
PBST50-0	0.0 mol% Pentaerythritol	117	21.3	294	[217]
PBST50-0.1	0.1 mol% Pentaerythritol	110	24.5	334	
PBST50-0.2	0.2 mol% Pentaerythritol	114	22.2	318	
PBST50-0.4	0.4 mol% Pentaerythritol	132	17.7	162	
PBST50-0.6	0.6 mol% Pentaerythritol	127	17.3	98.3	
PBST50-0.8	0.8 mol% Pentaerythritol	132	20.6	58.8	
PBST50-1***	1.0 mol% Pentaerythritol	133	181.1	29.3	
PBS/RC-10***	10% Recycled cellulose	320	21.7	11.5	[223]
PBS/RC-20***	20% Recycled cellulose	435	19.1	10.6	
PBS/RC-30***	30% Recycled cellulose	623	16.5	7.5	
PBS/RC-40***	40% Recycled cellulose	668	13.1	3.5	
PBS/RC-50***	50% Recycled cellulose	865	14.5	2.6	

* The tensile properties of these materials were measured along the extrusion direction of the fabricated tensile samples.

** The strength is determined from stress at break.

*** Both the PBS and cellulose were dried before the fabrication of the composites.

various applications. The bio-based origin and mechanical properties, including the tensile strength, Young's modulus, elongation at break and tear strength have made this polymer of great interest for various applications. The mechanical properties of PBS are similar and/or better than those of PE, PP and better than those of low-density polyethylene (LDPE), except for the flexural modulus [210]. The addition of co-monomers with side branches can lead to improved tensile properties. To tailor the properties of PBS, 1,2,4butanetriol (1,2,4-BT) was copolymerized as a long-chain branching moiety. This results in a slight increase in the glass transition temperature (T_g) and crystallization temperature (T_c) . However, the degree of crystallinity decreased gradually. The complex viscosities, loss modulus and storage modulus were significantly enhanced with long-chain branching. Moreover, a higher tensile strength was observed without a significant compromise on elongation at break [197,211]. In addition, ethyl and n-octyl branches can be introduced on the PBS polymer chain to tailor its properties significantly [212]. An increase in the degree of chain branching resulted in a decrease in various parameters including Tg, crystallinity, spherulite growth rate, and melt viscosity decreased. On the other hand, an increase in branching improved the mechanical properties, such as the elongation at break and tear strength, without any loss to the modulus and tensile strength. In another study, Tserki et al. investigated the effect of the chemical composition on the properties of homo- and co-polyesters made from dimethyl esters of succinic and adipic acid esterification with 1,4-butanediol. PBS homopolymers are highly crystalline and exhibit a heat of fusion (ΔH_f) of 68.4 J/g and melting point (T_m) of 114.1 °C (Table 4). However, its counterpart poly(ethylene adipate) exhibits a T_m of 60.5 °C and ΔH_f of 52.8 J/g, respectively. The set of different chemical composition co-polyesters showed different properties. Tg decreased in the range from -31.3 °C to -60.7 °C, with an increasing content of adipate units. Similarly, the mechanical strength was significantly affected with increasing adipate content. The 50/50 mol% co-polyester showed the lowest mechanical strength while 100% PBS exhibited the maximum mechanical strength. Contrary to the tensile strength, the elongation at break increased gradually from 20 to 40 mol% through the addition of adipate content. The higher molecular weight of PBS can exhibit a higher tensile strength, as is observed through chain extension, leading to an increase in the tensile strength [33]. However, the glass transition temperature increased in contrast to the decrease in crystallinity and melting temperature. Papageorgiou et al. investigated the crystallization, rate of crystallization, and melting temperatures of succinate based co-polyesters obtained with various aliphatic diols. The addition of 2–4 methylene groups resulted in melting temperatures at 133.5 °C, 114 °C, and 58 °C for PBS, poly(ethylene succinate), and poly(propylene succinate), respectively. The corresponding values for melt enthalpy were 210, 180, and 140 J/g. Similarly, poly(propylene succinate) showed the lowest degree of crystallization; 213].

The processability of the PBS can improve significantly for melt blown applications by incorporating branches on the polymer backbone. This can also improve the Young's modulus and elongation at break [214]. The mechanical properties can be tuned for better elongation at break with the addition of 1,2-decene succinate (DS) as a branching agent. When copolymerized with PBS, 1,2-decene succinate (DS) had no effect on the crystallization behavior and the crystal structure of the copolymer. However, the elongation at break improved while Young's modulus and the tensile properties deteriorated [215]. In addition, the branching of poly(butylene succinate-co-butylene terephthalate) (PBSTs) can result in a decrease in the crystallinity and melting temperatures, leading to a significant decrease in the elongation at break, but the thermomechanical and rheological properties of the PB-STs mainly improved [216]. The melt strength and processability for melt blowing can improve through the addition of long chain branching to PBS [217].

Bionolle resins belong to the family of synthetic aliphatic polyesters produced by Showa High Polymer Co., LTD. of Japan. This company introduced commercial-grade PBS, with the trade name of "Bionolle", from the synthetic aliphatic family of biodegradable polyesters. Bionolle are low molecular weight polyesters produced by polycondensation of dicarboxylic acids and glycols and are obtained as high molecular polyesters using isocyanate as chain extender. Bionolle is presented in different grades as copolymerized with different monomeric units. For example, PBS is graded as Bionolle 1000, Bionolle 3000 is a poly(butylene succinate-co-adipate), Bionolle 6000 is a poly(ethylene succinate), and Bionolle 7000 is poly(ethylene succinate-coadipate) [140,218]. The loss of the mechanical properties and the degradation profiles of PBS and its copolymers was investigated in a contrast of LDPE [140]. PBS can boast higher mechanical properties than I-LDPE, and it can be processed in applications such as commodity plastics. However, Showa High Polymer Co., LTD. of Japan has discontinued Bionolle production since 2016. Bio-based PBS is being produced by different players in the market, such as PTT-MCC. PTT-MCC is a strategic joint venture between PTT Global Chemical Public Company Limited (PTTGC) and Mitsubishi Chemical Corporation (MCC) and Anqing Hexing Chemical Co. Ltd. from China.

A polymer matrix composite (PMC) is another approach that has been widely being employed to tailor the properties of polymeric materials. PMCs are used worldwide in almost every industry, from agriculture to aerospace. Bio-based composite materials are also prepared from biopolymers such as PLA, PBS, PBAT, and PHA for use in industrial applications. PBS composites are produced with different reinforcing materials depending upon end products. Bio-based sustainable fibers are used as reinforcing agents for sustainable and biodegradable PBS based composites. Plant fibers are very important candidates to prepare biocomposites. Poly(butylene succinate) composites reinforced with a short sisal fiber were prepared via melt mixing and subsequent injection moudling. A study used short sisal fibers as a reinforcing agent for PBS with the addition of fibers with a length of up to 5 mm. A considerable increase in the tensile and flexural moduli was noted with an increased fiber content of up to 10 wt.%. Similarly, the storage modulus also increased with an increased fiber content [219]. The rheological parameters are of utmost importance to process fiber based bio-composites. However, traditional capillary rheometers are not suitable for this purpose, and a torque rheometer is a suitable apparatus to satisfy the required purpose. In a similar study by Feng et al., PBS/sisal fiber (SF) composites were investigated for their rheological parameters. The results indicated that an increase in the SF content resulted in more pronounced shear thinning, and this was associated with breakage, disentanglement, and a change in orientation [220]. The main source of sustainable natural fibers is agricultural waste, and waste from different crops can be used as reinforcing components in polymers, especially for biopolymers for fully biodegradable biocomposites. One such study in Taiwan mixed PBS with chemically-modified fibers and powder obtained from agricultural waste. The modified fibers considerably improved the mechanical and thermal properties of the composites [221]. Similarly, cotton has long been a rich source of fibers. The cotton fiber (CF) can also be used as a filler to reinforce many polymeric composites. Calabia et al. reported the mixing of untreated and silane-treated CFs in PBS. The results revealed that the tensile strength of the PBS/CF composites increased to up to 78% with the addition of 40% untreated CF. It increased further to up to 118% with the addition of silane treated CFs. However, the thermal stability decreased with an increase in the fiber content compared to pure PBS [222]. Like agricultural waste, recycled industrial waste can also be used to prepare low-cost composites. In a similar attempt, cellulose obtained from recycled Tetra pack (a landfill waste otherwise) was used as filler to prepare a PBS/cellulose composite. Considerable increases were attained in Young's, storage, and loss moduli by adding the recycled cellulose. Rice husk, wheat straw, and sugarcane bagasse are other rich sources of natural fibers, and Table 5

Glass transition temperature (Tg) and melting point $\left(T_{m}\right)$ values for two commercially available PBS.

PBS grade	Company	Tg	T _m
Bionolle 1020 MD	Showa Highpolymer (Tokyo, Japan)	-32	115
PBS	Anqing Hexing chemical Co.Ltd	-44.3	109
PBS	Anqing Hexing chemical Co.Ltd	-38.3	100

these can be obtained from agricultural waste [223,224]. Aside from fibers, other organic and inorganic materials can also be used as PBS reinforcements and fillers, including glass microspheres, graphene, thermoplastic starch, bio-flour, bio based lignin, organoclay, melamine phosphate, carbon fibers, basalt fibers and many other materials [225–231]. Carbon black was also incorporated to enhance the mechanical properties of PBS and PBS-based nanocomposites [232–234]. In a similar attempt, balanced mechanical properties were achieved by forming PBS/CB nanocomposites.

As revealed in Fig. 6a, the stiffness and toughness increased considerably with the addition of carbon black nanoparticles. This increase in the stiffness and toughness was attributed to the inherent strength of carbon black and the compatibilization of PBS/CB composites through the addition of compatibilizer i.e. PBS-g-MA, which led to well dispersed nanofillers and a strong interfacial interaction between the polymer matrix/nanoparticle. Fig. 6b clearly shows that Young's modulus, yield strength and elongation at break also increased with an increase in nano-sized carbon black filler content [234]. Composites are the most common, cheap, and easiest way to formulate products with the desired properties. Recycling other materials and the use of sustainable materials as reinforcing agents is crucial to obtain a modern concept of the circular plastic economy [235].

4.2. Thermal properties

The thermal properties of PBS are directly dependent on the molecular weight and thermal history. Generally, the glass transition temperature (T_g) of PBS varies between -40 °C and -10 °C [24], and its melting point (T_m) ranges between 90 °C to 120 °C. Table 5 displays the T_m and T_g values for two commercially-available PBS samples. Also, Fig. 7a shows differential scanning calorimetry (DSC) curves of the PBS at the first and second heating rate. The performance of PBS changes not only by its molecular weight, but also with the crystallization temperature and crystallization rate [236].

The crystallization temperature varies between 70.1 °C and 82.1 °C as a function of the cooling rate. The enthalpy of the crystallization for PBS is between 51.5 J/g and 53.7 J/g, and the percentage of crystallinity is estimated to be between 24.5 and 25.6. Two kinds of crystal modifications, namely α and β -forms, are observed in PBS [236–238]. The form is more thermodynamically stable, and the β form appears under strain. The XRD analysis reveals main characteristic diffraction peaks for PBS situated at 2θ values of 19.7°, 21.9°, and 22.88°, and these are, respectively, assigned to the (020), (021), and (110) planes of the α forms [239]. The melting peak of a commercially-available PBS at different heating rates in DSC is presented in Fig. 7b, and two melting peaks can be observed. The melting of crystals formed during non-isothermal melt crystallization leads to the apparition of the first small peak, and the second peak is related to the melting of crystals formed during DSC heating, melting and recrystallization. The first small peak moved to lower temperatures by increasing the heating rate, while the second peak stays at the same temperature [236].



Fig. 6. Enhanced mechanical properties of PBS via nanosized corban black. (a) Stress/strain curves of PBS 100% and PBS nanocomposites; (b) Other mechanical properties including Young's modulus, yield strength and elongation at break versus% addition of nanosized carbon. [234], Copyright 2014. Reproduced with permission from John Wiley & Sons Inc.



Fig. 7. (a) Differential scanning calorimetry (DSC) curve of PBS synthesized [240], copyright 2005. Adapted with permission from Elsevier Science Ltd. (b) A zoom on DSC curves for PBS (M_w =190,000, from Anqing Hexing Chemicals) and melting peak at different heating rates. [239], copyright 2014. Adapted with permission from John Wiley & Sons Inc.

4.3. Thermal degradation

The thermal degradation of PBS takes place in one step, and it begins around 300 °C and ended at around 430 °C under a nitrogen atmosphere [240] (Fig. 8a). There is no remaining residue at the end of the TGA test. The peak of the derivative thermogravimetric (DTG) of PBS, which corresponds to the maximum degradation, is around 400 °C. These values can change if the condition of the analysis changes (i.e., heating rate or atmosphere). In the case of PBS, the thermal degradation temperatures of PBS are reported to be quite similar in nitrogen and air [40,241]. Fig. 8b also displays the TGA curves of PBS and its copolymers under nitrogen at 5 °C/min, and it shows similar behavior. The TGA curve of PBS under air also shows one step of degradation between 300 °C and 450 °C [242].

The thermal degradation mechanism of PBS is presented in Fig. 9 [243–245]. First, a β -hydrogen bond scission takes place, and the β -hydrogen goes to an adjacent carbonyl group. This ac-

tion leads to cleavage of the -O-CH₂- bonds. Consequently, two chains form with alkenyl or carboxylic acid end-groups, and several degradation pathways occur. From pathway 1, an alkenyl- terminated chain and a succinic acid form after the scission of a β -hydrogen bond. The succinic acid is transformed to succinic an-hydride by the release of H₂O, as seen in Fig. 9. Pathway 2 consists of the formation of carboxylic acid terminated chains and 1,4-butadiene. Then, two main pathways are possible: the decomposition of the carboxylic acid end of the chains to form succinic anhydride (1 and 2 in Fig. 9); and the elimination of CO₂ from acetate leading to the formation of an acid, pathway 4. The intramolecular transesterification reaction has also been reported to form some cyclic molecules, pathway 5.

4.4. Flame retardancy

Nowadays, the performance of biopolymers is adequate to replace fossil-derived polymers for some primary applications, such



Fig. 8. (a) Thermogravimetric analysis (TGA) curves for PBS under nitrogen at 10 °C. [240], Copyright 2005. Adapted with permission from Elsevier Science Ltd. (b) TGA and derivative thermogravimetric curves for poly(butylene succinate) (PBSu) and two PBSu-rich poly(butylene succinate-co-propylene succinate)s under nitrogen at 5 °C. [243], Copyright 2010. Adapted with permission from John Wiley & Sons Inc.



Fig. 9. Mechanism of the thermal degradation of PBS [243-245].

as films and packaging. However, their performance is still inadequate, especially regarding flammability, for other applications such as architecture, construction, and transportation [246]. PBS, like almost all biopolymers, suffers from an inherently high flammability. It is necessary to consider the flammability of PBS and its contribution to fire hazards in developing new materials based on PBS. There are two different ways to improve the flame retardancy of the polymers: additive and reactive ways [247]. The additive way consists of incorporating flame retardants as 'additives', generally in powder form, into the polymer via conventional melting. The reactive method is defined as the chemical reaction of flame retardants onto the polymer chains. The chemical bond between the flame retardant and the polymers can be created during polymerization or by chemical modification of the side chains [248]. Once the flame retardant is incorporated into the polymer, it can act during combustion of the polymer with several possible scenarios. The scenario of the flame-retardant action depends on its chemical structure and on the type of polymer. This can happen in a gas and/or condensed phase (Fig. 10). Several actions are possible in the condensed phase, including a barrier action, cool-



Fig. 10. Schematic representation of the general mechanism of the action of flame retardants in gas and condensed phases. [255], copyright 2021. Adapted with permission from Elsevier Science Ltd.

ing, and melt dripping. The barrier action consists of the formation of char or residue during combustion due to the reaction between the polymer and flame retardant and its protective action on the surface of the polymer. The char or residue that forms plays two principal roles: heat shielding that limits the transfer of heat to the material and a diffusion barrier action that decreases the release of gases produced during the decomposition of the polymer into the gas phase and diffusion of the oxygen to the surface layer of the polymer. The creation of char is a result of the interaction between the flame retardant and the polymer, and it resulted in the transformation of a part of the carbon to a high flame-resistant carbonaceous char. The cooling action consists of an endothermic reaction during the decomposition of some flame retardants. Also in some cases, the release of the condensed water along with the endothermic decomposition dilutes the gas phase.

Some flame retardants also act on the rheology of the polymer, facilitate dripping, and separate the polymer from the flame area. In general, the action of the flame retardant in the gas phase can be divided into two types including the dilution of the gas phase by a lease of inert gases or the inhibition of fire propagation by trapping high energy radicals, such as H° and OH° [248]. Currently, several families of commercial flame retardants are available, including mineral, halogenated, phosphorus, organosilicon, and nitrogen flame retardants [247]. Halogenated flame retardants are well known as the most effective additives to achieve flame retardancy of polymers. However, some halogenated flame retardants present environmental and health risks [249]. Therefore, non-halogenated flame retardants have been extensively investigated over the past decade. Moreover, the development of bio-derived flame retardants is highly encouraged [250].

Once the flame retardant is incorporated into the polymer, it is necessary to evaluate its performance in terms of flame retardancy. Specific tests include cone calorimetry, limiting oxygen index (LOI), and UL94. Herein, a brief description of these tests is given. Cone calorimetry is the main test used at the laboratory scale to assess the fire behavior of the polymers. It is based on the ISO 5660 standard and was developed by Babraukas at the US National Bureau of Standards in the early 1980s [251]. This test measures the rate of heat released during the combustion of a material by applying Huggett's principle (1 kg of consumed oxygen corresponds to 13.1 MJ of released energy) [252]. Some important parameters are obtained including the peak of the heat release rate (pHRR), total heat release (THR) and time to ignition (TTI). The pHRR value is representative of the intensity of the flash over phenomena during a fire. LOI is a standardized test (ISO 4589) to determine the minimum concentration of oxygen (in an N_2/O_2 mixture) required to maintain inflammation for 3 min or a distance 50 mm. A material with an LOI less than 21 is considered to be combustible. The UL94 test was developed by the "Underwriter's Laboratories 94" (US Insurance Laboratories). NF EN 60,695-11-10 Standard describes the flammability tests with a burner at 50 W. The most widely used test is the UL94 test that measures the flammability and flame propagation of the materials. The sample is exposed to a Bunsen burner, and cotton wool cellulose is placed under the test tube. The flame is applied twice for 10 s, and the ignition time and the possible inflammation of the cotton wool due to the drop of glowing polymer are noted. Depending on these parameters, the material is rated as V0 (the best), V1, or V2 [248].

A survey of the literature revealed a limited number of papers addressing the flame retardancy of PBS compared to that of other polymers. Table 6 displays a summary of the results collected from the recent literature on flame-retardant PBS. First, the flame behavior of different pure PBS grades is listed. Then, the flame retardant used in PBS blends is characterised including its loading percentage and flame retardancy properties. Although Table 6 does not include an exhaustive list of papers on the flame retardancy of PBS, the highly flammable character of different grades of PBS can be recognized since the pHRR and THR are, respectively, ranged

Summary of results obtained on flame retardancy properties of PBS containing flame retardants. Data were extracted from the literature: name of flame retardant, percentage of its incorporation in PBS, cone calorimetry parameters (parameters obtained from cone calorimetry test: time to ignition (TTI), peak of heat release rate (pHRR), and total heat release (THR)), limiting oxygen index (LOI), and UL94 values. The first part of the table is dedicated to the flame properties of pure PBS and the second part of table is devoted to the flame retardant solutions. For each case, the percentage of flame retardant loading in PBS (wt.%) is given.

	wt.%	Irradiance*(kW. m^{-2})	TTI(s)	pHRR(kW. m^{-2})	$THR(MJ/m^2)$	LOI	UL94	Refs.
GS PLA, Mitsubishi Chemical Corp. (Japan)	-	50	48	765	170	21	Fail	[234,262,263]
Anging Hexing ChemicalCo., Ltd. (Anhui, China)	-	35	96	592	120	-	-	[264]
Showa, Bionolle [™] 1001, henzhen Huixin Plastic Chemical Co., Ltd.	-	50	43	1413	132	18.3	no rating	[254]
PBS film grade 1903 F, from Xinfu Pharm	-	35	72	562	22.1 (kJ/g)	-	-	[256]
Flame retardant/additive								
Carbon black (CB)	10	50	39	294	129	28.5	NC	
Magnesium hydroxide (MDH)	40	50	58	117	79	32	V0	[262]
Expanded graphite (EG)- magnesium hydroxide (MDH)	25	50	55	173	101	29.4	V0	[263]
Graphene (Gr)- magnesium hydroxide (MDH)	25	50	52	287	114	28.2	V1	[263]
Eucommia residue	30	35	42	336	92	-	-	[264]
Lignin	30	50	40	1183	97	19.6	No rating	[254]
Lignin modified with phosphorus (CP-lignin)	30	50	31	1028	91	23.1	V2	[254]
Chemically modified lignin withphosphorous, nitrogen and the zinc (II) ions (PNZn-lignin)	10	35	68	244	6.1 (kJ/g)	-	-	[255]
Lignin modified with a phosphorus polymer	20	35	40	270	20.4 (kJ/g)	-	-	[256]
Flax fiber	30	35	53	245	14.6(kJ/g)	-	-	[260]
Flax fiber- Ammonium polyphosphate (APP)	35	35	55	208	16.8(kJ/g)	-	-	[260]
APP-CaCO ₃ -aluminum hypophosphite (AHP), calcium hypophosphite (CaHP)	20	35	44	251	118	-	-	[265]
APP-poly(isosorbide carbonate)	30	35	105	216	47	-	-	[266]
APP-Sepiolite-Lignin	20	35	32	267	104	-	-	[267]
APP- Melamine- Montmorillonite (MMT)	23	35	35	170	47.2	40	V0	[268]
Multi-walled carbon nanotube modified with APP- Pentaerythrite (PER)	20	35	-	73.6	79.6	-	V0	[269]
Layered Double Hydroxide (LDH)-APP- Melamine	20	35	151	250	84	33	V0	[270]
Halloysite (HNT)-APP-Melamine-PER	30	30	40	113	34.98	58	V0	[271]
Ethyl cellulose microencapsulated APP-Charring agent	20	35	73	419.3	71.26	34.5	V0	[272]
Bamboo fiber- microencapsulated APP	70	-	-	236.2	36.1	34	V0	[261]
Phytic acid (PA) and guanosine (GU)	30	50	10	357	67	26	V2	[257]
Melamine phosphate, graphene or polyhedral oligomeric silsesquioxanes (POSS)	20	50	30	425	49.5	34	V0	[273]
Melamine phosphate- melamine phosphite- melamine hypophosphite	30	35	81	279	60.9	29	V0	[231]
APP-carbon nanotubes	20	35	40	252	43.8	28.5	V1	[274]

* Irradiance: the heat flux applied on sample in cone calorimeter test.



Fig. 11. (a) Synthesis of modified-lignin (CP-lignin). (b) Heat release rate (HRR) curves as a function of time obtained from the cone calorimeter test for PBS and PBS containing lignin and CP-lignin. [254], Copyright 2010. Adapted with permission from John Wiley & Sons Inc.

between 562 kW/m² and 1413 kW/m², and 120 MJ/m² 170 MJ/m². Also, the LOI value is low between 18 and 21, nor is the rating reported in the UL94 test. For now, all flame-retardant solutions for PBS suggested in the literature are based on incorporating flame retardants via melt blending, and the reactive way which consists of a chemical modification of PBS has not yet been explored. A wide variety of flame retardant systems and additives have been investigated to improve the flame retardancy of PBS, including conventional flame retardants (such as magnesium hydroxide (MDH), expanded graphite, ammonium polyphosphate, melamine, etc.), nanoclays (e.g., montmorillonite (MMT), layered double hydroxide (LDH)), and biomaterials used to improve the flame retardancy (e.g., lignin, bamboo, phytic acid, cellulose), Table 6. It seems that the strategy to improve the flame retardancy of PBS was principally based on the use of conventional non-bio-derived flame retardants. However, it is necessary to promote the development of bioadditives for biopolymers in order to maintain a final material that is fully bio-derived. Herein, some relevant works are discussed to present the flame retardancy of PBS using bio-derived and mineral flame retardant additives.

Among bio-derived additives, lignin is on the most studied materials to improve the flame retardancy of polymers [253]. At high temperatures, it produces a high quantity of char residue and acts in the condensed phase. Chen et al. [254] investigated the incorporation of lignin and modified-lignin in PBS as a flame retardant. First, the reaction between cyanuric chloride (CC) and trioxa-1phosphabicyclo-[2,2,2]octane-4-methanol-1-oxide (PEPA) was performed, as shown by Fig. 11a. The molecule resulted from this step (CNC-PEPA) was then reacted with lignin to obtain a nitrogenphosphorus modified lignin, namely CP-lignin (Fig. 11a). The TGA curves revealed that the remaining residue at 700 °C was 61% for CP-lignin against 21% for untreated lignin. The modified lignin at 10 wt.%, 20 wt.%, and 30 wt.% was incorporated into PBS via melt blending. The fire performance was evaluated using a cone calorimeter test. Fig. 11b displays the HRR curves obtained in the cone calorimeter test for PBS and PBS containing lignin and CP-lignin, and the TTI, pHRR and THR values are listed in Table 6. Although the pHRR decreased in the presence of 30 wt.% of CP-lignin, the fire performance is still poor since the pHRR is 1028 kW/m², which is characteristic of a highly flammable material. Also, the TTI decreased in the presence of the lignin of CP-lignin. Moreover, the high loading percentage of the additive is harmful for other properties of PBS, especially the mechanical ones.

In another work [255], the effects of incorporating lignin that is chemically-modified with phosphorous, nitrogen and zinc (II) ions (PNZn-lignin) on the flame retardancy of PBS were studied (Fig. 12a). They found that incorporating 10 wt.% PNZn-lignin into PBS significantly affects its flame behavior, as demonstrated by a decrease in pHRR at 50% and in THR at 67%, with respect to those of pure PBS (Fig. 12b). The characterization of char residue remaining at the end of the cone calorimeter test helped elucidate the mechanism of action of the PNZn-lignin in PBS. They concluded that the presence of phosphorus led to the formation of phosphoric acid species during combustion, which promoted the dehydration of lignin and PBS, and therefore the formation of a high quantity of char residue. They also showed that Zn (II) ions exhibited excellent smoke suppression. The formation of a compact, intact, and thick char layer acted as a heat and diffusion barrier on top of the material, and it was presented as the main mechanism of action. Another group [256] investigated the effect of two different types of lignin on the flame retardancy of PBS. They reported that alkali lignin is more efficient than organosolv lignin in a decrease of pHRR due to the release of sulfur dioxide during decomposition. Alkali lignin at 20 wt.% enabled a reduction in the pHRR to 290 kW/m².

It seems that different strategies have been applied to use lignin as a flame retardant in PBS including the use of different types of lignin (e.g., alkali, organosolv), chemical modifications of lignin with phosphorus and nitrogen moieties, and a combination of lignin with conventional flame retardants, Table 6. However, the conventional flame retardants or chemicals used were not bioderived materials, and therefore the final flame retardant systems were not totally bio-derived.

Although most phosphorus elements in conventional flame retardants come from non-bio-derived sources, some bio-derived phosphorus molecules exist. One of them is phytic acid that contains six phosphate groups. Chen et al. [257] prepared a flame retardant containing phosphorus and nitrogen by a reaction between phytic acid and guanosine, both extracted from natural plants, as shown by Fig. 13. The incorporation of 30 wt% of PA-GU significantly led to a decrease in pHRR to 357 kW/m² against 413 kW/m² for pure PBS. THR also decreased from 132 MJ/m² for pure PBS to 67 MJ/m² for PBS containing 30 wt% PA-GU. The authors presented a mechanism of action for PA-GU based on different analyses performed on the condensed phase which consisted of the decomposition of phytic acid into polyphosphoric acid during combustion and its esterification with the guanosine contained therein. In the



Fig. 12. (a) Chemical structure of modified lignin (PNZn-lignin), (b) heat release rate (HRR) curves as a function of time obtained from cone calorimeter test for PBS and PBS containing O-lignin (alkali lignin) and PNZn-lignin. Reproduced and adapted from. [255], copyright 2010. Adapted with permission from American Chemical Society.



Fig. 13. Chemical reaction between phytic acid (PA) and guanosine (GU) to prepare a new bio-derived flame retardant (PA-GU). [257], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

presence of the carbon rings of guanosine, the aforementioned reaction led to the formation of a cross-linked char layer. The expansion of this char layer due to the action of the released gases creates an expanded char layer. The char layer was thermally stable and prevented the transfer of flammable gases to the flame zone, and it thus improves the flame retardancy of PBS.

In recent years, considerable interest has been given to the development of biocomposites containing natural fibers [258,259]. The flame retardancy of PBS containing several natural fibers, including flax and bamboo fibers, has been reported [260,261]. Dorez at al. [260] performed preliminary work on the effect of incorporating several fibers at 30 wt.% (cellulose, hemp, flax, bamboo, sugar cane) on the flame retardancy of PBS. Based on the results of cone calorimetry tests, they reported that the best results in terms of flame retardancy were obtained in the case of flax fibers. Then, they found that the incorporation of 30 wt.% flax fibers in PBS generally decreased the onset temperature in TGA. Also, the TTI decreased in the cone calorimeter test. However, the char residue yield increased, and consequently, the pHRR decreased significantly to 270 kW/m against 485 kW/m² for pure PBS. They also showed that it is necessary to combine flax fibers with ammonium polyphosphate (APP) to reach a pHRR of 208 kW/m². However, the TTI decreased significantly to 55 s, instead of 150 s for pure PBS. It is worth mentioning that APP is not a bio-derived flame retardant, and the final flame retardant system in this study was finally non-bio-derived. Bamboo fibers have also been combined with microencapsulated ammonium polyphosphate (MCAPP) in PBS to improve the flame retardancy [261]. Another study [261] showed that the combination of the bamboo fiber at 50 wt.% and MCAPP at 20 wt.% was necessary to achieve V0 in the UL94 test. Also, the pHRR and THR values decreased significantly to 236.2 kW/m^2 and 36.1 $MJ/m^2,$ respectively.

Other types of eco-friendly additives with low environmental and health impacts have been used to improve the flame retardancy of PBS, including MDH and expanded graphite (EG). MDH is currently one of the most used and cost-effective mineral flame retardants in the world. Its decomposition takes place via an endothermic reaction (Eq. (1)), allowing to cool the pyrolysis zone (leading to a decrease in the degradation rate of the polymer), and it releases water diluting the gas phase. Its decomposition reaction is:

$$2Mg(OH)_2 => 2MgO + 2H_2O(\Delta H = 1300kJ/kg)$$
(1)

Also, the magnesium oxide produced from the decomposition of MDH forms a protective insulating layer that slows down the degradation of the polymer. However, a high loading quantity of MDH is usually needed to achieve a high flame retardant performance, which is detrimental to the other properties of the polymer, especially its mechanical properties. To reduce the loading quantity of MDH, Chen et al. [262] investigated the effect of the MDH particle size on the flame retardancy of PBS. They selected three particle sizes for MDH (average particle diameter of 20 μ m, 5 μ m, and 500 nm) and melt blended with PBS at different loading ratios from 10 to 60 wt.%. At least 40 wt.% MDH was needed to achieve V0 in the UL94 test (Fig. 14a), whatever the particle size. The best results in the LOI test were obtained in the case of PBS containing a 500 nm particle size. However, the results obtained with 5 µm were close to those obtained with a 500 nm particle size. In the cone calorimeter test, the best results were obtained with 5 µm particle, as demonstrated by the decrease in pHRR to



Fig. 14. (a) Limiting oxygen index (LOI) and UL-94 results as a function of different MDH loading percentages and particle sizes in PBS, and (b) heat release rate (HRR) curves obtained in cone calorimetry for PBS containing 40 wt.% MDH with various sizes. [262], Copyright 2016. Adapted with permission from John Wiley & Sons Inc.



Fig. 15. (a) HRR curves obtained in cone calorimetry test for BPS containing MDH and its combination with EG and Gr, (b) stress-strain curves for the same samples obtained in the tensile test. [263], copyright 2019. Reproduced with permission from Elsevier Science Ltd.

117 kW/m² against 765 kW/m² for pure PBS (Fig. 14b). These authors concluded that MDH with a medium particle size (5 μ m) offers the best flame retardancy. The mechanism of action for all MDH is mainly an endothermic reaction. However, they suggested that a medium particle size can bring a better barrier protection in the condensed phase.

Another strategy to decrease the loading percentage of MDH consists of its combination with other flame retardants [263]. For example, Chen et al. [263] studied the combination of MDH at 20 wt.% with expanded graphite (EG) and graphene (Gr) at different loading percentages (2.5 to 10 wt.%) on the flame retardancy of PBS. They showed that it is possible to achieve similar fire properties close to those of PBS/MDH40 wt.% through a combination of MDH at 20 wt.% and EG or Gr at 5 wt.% (Fig. 15a). Thus, it is possible to reduce the loading percentage of the filler from 40 to 25 wt.% and obtain similar flame retardancy. They explained that the thermal expansion of EG occurs simultaneously with the decomposition of MDH. This action leads to the formation of a gradient-structured char layer that forms a "labyrinth effect"

and decelerates the diffusion of gases into the flame. Moreover, the mechanical tests demonstrated the beneficial effect of a combination of MDH and EG on the elongation at break (Fig. 15b). The incorporation of MDH at 40 wt.% or its combination at 20 wt.% with 5 wt.% Gr into PBS significantly decreased the elongation at break, while a combination of MDH and EG showed better results with respect to that of pure PBS.

In conclusion, it can be observed that all types of flame retardants, except for the halogenated one, have already been tested in PBS to improve the flame retardancy behavior. Nevertheless, the number of studies on bio-derived flame retardant solutions in PBS are still limited compared to those of other bio-derived polymers, e.g., PLA, and, in some cases, bio-derived flame retardants have been combined with non-conventional flame retardants to achieve a high flame retardancy. This issue should be considered by researchers for future study since it is a key point to develop fully bio-derived polymers. Some solutions presented in the literature seem not to be applicable to industrial scalability. Developing bio-derived flame retardant and flame retardant biopolymers



Fig. 16. Maximum Tensile Strength (MPa) and Maximum Tensile Elongation (%) of bioplastics compared to petroleum-derived plastics. [275, 276], copyright 2020. Adapted with permission from American Chemical Society.

should also consider all aspects of sustainability, including fire performance, economic, health and environmental issues.

5. PBS blends

PBS is a material of broad interest for many applications. Fig. 16 summarizes the maximum tensile strength, elongation at break and heat deflection temperature (HDT) of several bioplastics as well as conventional and compostable (fossil based) plastic materials.

As mentioned earlier, PBS boasts a good compromise of stiffness and toughness, without neglecting the fairly high HDT (\sim 93 °C) that makes it an excellent choice as food packaging material. If compared to other attractive polymers that could be used to design compostable plastics, PBS can be more or less stiff (i.e., compare it to PBAT or PLA, for example) or, otherwise, PBS can be more or less ductile than those. This is the reason why blending PBS is so strategic in the design of blends of compostable plastics. PBS can also be bio-sourced, thus allowing it to be involved in the design of fully biodegradable, bioderived and compostable plastics. In this respect, PBS can therefore be used as a main or secondary polymeric phase. Also, it can assume a different role in the blends, that is, as a strengthening polymeric phase or as a plasticizing polymeric phase. Based on previous considerations, the following paragraphs report in broader detail on the blends of PBS with many other polymers (both bio-derived or fossil-derived). The final aim is to demonstrate the suitability of PBS to interact with many other polymeric phases, changing its role according to the final need of the designers and thus allowing for additional, crucial, degrees of freedom in material design.

As one issue, which can highly influence the performance of the resultant blend, compatibility between the blend components should be always considered to prevent the occurrence of any phase separation, and thus, to enhance the properties of the blend. In this regard, it will be more useful to start such discussion on the compatibilization and intermolecular interactions between components in PBS-based blends before presenting the most common PBS blends. Hereafter, concepts of compatibility and miscibility, alongside with various strategies employed to enhance the compatibility in PBS-based blends are to be introduced in the following section.

In polymer blends, the intermolecular interactions between the blend components and the related phase separation are very critical to determine the properties of this blend. Here, polymer blends can be classified into miscible and immiscible systems. In the first, the two components, case of binary blends, are fully dissolved in each other, leading to a morphology which is homogeneous at the nanoscale. Such ultrafine morphologies generally show improved properties due to the absence of phase separations. On the other hand, a less solubility of the two components results in a partial miscibility, where a coarser morphology is obtained as compared to that of the miscible systems. For this type of systems, the solubility is limited to the small amounts of one component in the other one, and in term of properties, these systems show acceptable degree of improvements. On the other hand, due to the phase separation in immiscible system, the performance is usually destroyed as compared to the pure components. Up to here, one can notice that the concept of miscibility is mainly related to the interaction, and solubility of the components and final morphology of the blend. On the other hand, compatibility is technically more related to the performance of the blend, where compatibilized blends are those with improved properties as compared to the pure components, and accordingly, both the miscible and partial miscible systems can be considered as compatibilized ones. Importantly, to improve their performance, the immiscible polymer blends can be compatibilized through inducing chemical or physical interactions between the polymeric chains. For example, enhanced mechanical properties of a blend can be achieved by inducing the interactions that can form bridges, through which, stress is transferred from one component to another. Considering the target in this review, it will be worth handling the compatibilization strategies of PBS-based blends and possible intermolecular interactions of these blends. Starting from immiscible PBS-based blend, in which PBS and the other component (the case of binary blend) are insoluble in each other, the miscibility can be improved through the addition of a copolymer that consists of PBS and other component. Here, this copolymer can act as a bridge between the two phases, where each side of the copolymer can dissolve in the counterpart phase. Such strategy might work when blending PBS with those have no functional groups, such as PE, PP, and PS. Due to the absence of functional groups in these polymers, there will be no chemical interactions with the functional groups of PBS (-OH and -COOH) in the blends. For example, PBS-co-PE can be used as a compatibilizer for PBS/PE blends. This method can be also used to improve the compatibility between PBS and other polymer that have limited number of functional groups, such as PLA and

PCL, where the functional groups are usually presented at the end of the polymeric chains. For example, Liu et al. studied PBS/PCL blends containing 20 wt.% PCL, and for enhancing the performance of the fabricated blend, PBS-co-PCL was used as a compatibilizer, where the functional end groups in both the polymers were found to be insufficient for achieving enough level of miscibility between the two phases [206]. Due to the addition of 5 wt.% of this compatibilizer, a significant improvement in the interaction between the two phases (PBS and PCL) was achieved, and this reduced the interfacial tension between the phases and enhanced the mechanical properties, including modulus and elongation at break, of the compatibilized blend as compared to those of non-compatibilized one. Another technique that can be employed for such target is to functionalize the non-functional polymers before mixing with PBS. For example, in the case of PBS/PE blends, some function groups are grafted into the PE chains, and this can be conducted through reactive extrusion of the PE together with an initiator, like DCP (dicumyl peroxide), and low molecular weight compounds that provide the active groups, like MAH (maleic anhydride).

In addition, the compatibility can be achieved through the addition of low-molecular-weight reactive chemicals to the blend during the mixing process. Several additives are usually used as compatibilization agents, such as MAH, lysine triisocyanate (LTI), triphenyl phosphite (TPP), and epoxy. The mechanism by which additives enhance the compatibility in the blend is mainly associated with the type of blended polymers and the additives themselves. Therefore, blended polymers that contain functional groups, such as, -OH, -COOH, and -NH₂, can be compatibilized using bifunctional chemicals, and as a result, block copolymers are formed at the interface between the two immiscible polymers. This decreases the interfacial tension and enhances the miscibility of the blend. The addition of initiators, like DCP, is another example on this technique, where this addition leads to form free radicals on the polymeric chain, which themselves act as active site to induce chemical reactions between the chains of the two polymers in the blend. Ma et al. fabricated PBS blends with polyhydroxybutyrateco-valerate (PHBV) and polyhydroxybutyrate (PHB, homopolymer), and DPC was used to enhance the final properties of these blends [277]. The results showed that the addition of the DCP led to a fine distribution of PBS within the PHBV phase, and this, accordingly, improved the interfacial adhesion and enhance the mechanical performance of the blend as compared to that of the DCP-free blend. Table 7 summarises the PBS polymer blends, the employed compatibilizer, and the related properties.

5.1. Binary blends

5.1.1. Blends of PBS with cellulose acetate (CA)

Cellulose and its derivatives are commonly used to modify PBSbased plastic materials since these are cheap and largely bioavailable. The compatibility of cellulose with PBS is limited. Therefore, it is always functionalized before being used. Cellular acetate is an amorphous polymer that is obtained starting from cellulose by acetylation of hydroxyl to the acetyl groups. In cellulose triacetate (CTA) manufacturing, cellulose is completely acetylated. On the other hand, in acetate (CA) and cellulose diacetate (CDA), the hydroxyl groups are only partially acetylated. The increase of acetyl side groups reduces the hydrophily and biodegradability of the cellulose acetates, increasing their ductility. Zhou et al. studied blends between PBS and CDA obtained by solution blending [278]. PBS and CDA are miscible between them, featuring hydrogen bonds for CDA concentrations of 60% and increased hydrophily compared to PBS alone. Furthermore, the incorporation of CDA into the blend resulted in a significant inhibition of the crystallization capacity of the PBS, presumably due to a steric encumbrance of the acetyl groups. Consequently, the blend exhibited a significant increase in elongation at break. Číhal et al. have studied blends between PBS and CTA [279]. PBS and CTA generate homogeneous blends and are perfectly miscible up to a PBS content of 30 wt.%. For PBS content below 30 wt.%, the crystallization of the PBS is prevented by the presence of the CTA. For PBS contents equal to 50%, a slight decompatibilization of the blend is noted, with the formation of a crystalline phase in PBS. The addition of PBS results in a significant improvement in the gas impermeability of the CTA, acting as a molecular filler for structures formed by the CTA. Conversely, an increase in the PBS content in CTA significantly reduces the elastic modulus of the resulting blend. Tachibana et al. studied blends obtained from PBS and cellulose acetate butyrate (CAB) [280]. CAB is obtained via acetylation of cellulose esterified with acetyl and butyric groups. The miscibility between CAB and PBS is excellent up to 40 wt.% in CAB. The resulting blend is completely amorphous. For CAB concentrations below 40 wt.%, a decompatibilization of PBS is observed, which tends to crystallize. CAB concentrations at 10 wt.% result in a 42-fold increase in elongation at break with a slight increase (of about 10%) in tensile strength. This result is ascribed to the ability of CAB to partially inhibit, even at low concentrations, the crystallinity of PBS, improving its ductility. Furthermore, small CAB contents can still promote the formation of hydrogen bonds with the PBS, altering the original crystalline state of the PBS. Wang et al. further investigated PBS/CAB blends [281]. The results showed that the PBS/CAB blends have a promising rheological profile and a greater thermal stability and, therefore, an alleged increase in processability. Furthermore, by correctly modulating the CAB content in PBS, it is possible to modulate the properties of the resulting blends, obtaining materials characterized by good ductility and toughness. The blends between PBSA and acetylated nano-crystalline cellulose (ACNC) are reported in [282]. Studies have shown that small amounts of ACNC can disperse uniformly within PBSA matrices, significantly increasing the mechanical properties of PBSA, improving the elastic modulus, melt viscosity and thermal stability of the resulting composite material. Maeda et al., instead, prepared a blend consisting of CA nano-fibres dispersed in PBS [283]. The fibers, introduced with a content of 20 wt.%, can increase the elastic modulus of the PBS up to 250% if aligned within the polymer matrix. If arranged randomly within the PBS matrix, they can still determine a 200% increase in the elastic modulus.

5.1.2. Blends of PBS with polybutylene adipate-co-terephthalate (PBAT)

In the field of biodegradable polymers, PBAT represents a more successful case by virtue of the good compromise between the relatively low selling price and the high flexibility in applications. PBAT is an aliphatic/aromatic co-polyester that reconciles the excellent biodegradability of aliphatic polyesters with the good properties of aromatic polyesters. It is obtained through the polycondensation of butanediol, adipic acid and terephthalic acid [284]. PBAT is a very ductile polymer, characterized by an elongation at break in the range of 600-700%, a low elastic modulus (about 125 MPa), a melting temperature between 115 and 125 °C and a Heat Distortion Temperature (HDT) of about 55 °C (ASTM D648; 1.82 MPa, 6.4 mm). The high ductility and low elastic modulus are common features with PBS, which makes studies on blends between PBS and PBAT rather rare. However, PBS has an HDT higher than 90 °C, which could lead to an application interest in the use of PBS/PBAT blends with greater thermal resistance than PBAT as is. Muthuraj et al. studied blends between PBS and PBAT obtained by reactive extrusion with a co- rotating twin-screw extruder [285]. The blend showed good compatibility ascribed to transesterification, although two distinct phases were observed during scanning electron microscopy. In addition,

Composition, compatibilization, and properties of PBS polymer blends.

Blending element	Compositional Range,%	Compactization strategy	Crystallization	Mechanical properties	Thermal properties	Refs.
Cellulose diacetate (CDA)	Whole range	-	CDA slows or inhibits PBS crystallization	Stiffness decreases consistently with CDA content Elongation increases consistently with CDA content	Decrease in melting temperature by increasing CDA content	[278]
Cellulose Acetate (CA) Cellulose triacetate (CTA)	0–15% CTA	-	CA acts as nucleant, CTA slows PBS crystallization	Stiffness highly improved by increased CA or CTA content Elongation and strength decrease with CA/CTA content	Slight decrease in melting temperature by increasing CTA content	[388]
Cellulose triacetate (CTA)	50-100% CTA	-	CTA slows or inhibits PBS crystallization	Stiffness highly improved by increased CTA content	Decrease in melting temperature by increasing CTA content	[279]
Cellulose triacetate (CTA)	0–30% CTA	-	CTA slows PBS crystallization	Stiffness increases with CTA content Elongation and strength reduced with CTA content	Slight decrease in melting temperature by increasing CTA content	[389]
Cellulose acetate butyrate (CAB)	Whole range	_	CAB slows or inhibits PBS crystallization	Stiffness increases with CAB content (up to 60%)	Decrease in melting temperature by increasing CAB content	[390]
Cellulose acetate butyrate (CAB)	Whole range	-	CAB slows or inhibits PBS crystallization	Toughness highly improved for 10 wt.% of CAB	Decrease in melting temperature by increasing CAB content	[290]
Cellulose acetate butyrate (CAB)	Whole range	-	Slower than PBS, amorphous material for CAB > 60%	Stiffness and strength increase with CAB Elongation is optimized for 40 to 60 CAB%	Decrease in melting temperature by increasing CAB content	[281]
Polybutylene adipate- co-terephthalate (PBAT)	Whole range	-	PBAT acted as a nucleating site to promote the formation of crystalline nuclei of PBS.	The blend PBS/PBAT (60/40) showed simultaneously improved strength and ductility	Less T _g as compared to neat polymers. The blend showed a higher thermal stability as compared to neat PBS.	[286]
Polybutylene adipate- co-terephthalate (PBAT)	Whole range	-	-	The elongation at break of the blend with 50% PBS was higher than that of the neat PBS.	-	[286]
Polybutylene adipate- co-terephthalate (PBAT)	Whole range	-	In the blends with higher content of PBAT, PBS crystallization was inhibited	Increasing the PBS content led to increase the stiffness and to decrease the elongation at break of the blends	-	[289]
Polybutylene adipate- co-terephthalate (PBAT)	0 –15% PBAT	Small-molecular weight additive (peroxide(2,5-bis(tert- butylperoxy)-2,5- dimethylhexane	Compared to that of the non-compatibilized, the crystallization temperature has been increased in the compatibilized counterparts	The impact resistance of the compatibilized blends was four times higher than that of the non- compatibilized counterpart. This was also found in the case stiffness	-	[318]
Polycaprolactone (PCL)	0-40% PCL	Block copolymer (Polyethylene oxide- block-Polypropylene oxide-block-Polyethylene oxide (PEO-PPO-PEO))	The crystallinity of polymers decreased for all blends.	The addition of PEO-PPO-PEO resulted in a reduction in the stiffness of the blend and an increase in its toughness and ductility.	-	[292]
Polycaprolactone (PCL)	0–20% PCL	Copolymer (PBS-co-PCL)	The crystallization rate of the PCL in the blend is accelerated by the addition of compatibilizer, whereas the rate of the PBS decreased.	The stiffness and ducting elongation of the blend were higher than those of the neat polymers.	-	[206]
Polyoxyethylene (PEO)	0–10% PCL	-	The low content of PEO promotes the growth of spherulites while higher contents of PEO prevent the growth of PBS spherulites.	-	-	[299]

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 Table 7 (continued)

Blending element	Compositional Range,%	Compactization strategy	Crystallization	Mechanical properties	Thermal properties	Refs.
Polyhydroxybutyrate -co- valerate (PHBV)	0–30% PBS	Small-molecular weight additive (dicumyl peroxide (DCP))	By the addition of 5% DPC, the crystallinity of PHBV did not change much, while the crystallinity of PBS reduced to 25%	Elongation at break, tensile strength, and toughness of the blend was improved significantly by the addition of DPC	Melting temperature of PHBV and PBS in the blend are suppressed by the presence of DCP	[309]
Polyhydroxybutyrate -co- valerate (PHBV)	Whole range	Small-molecular weight additive (maleic anhydride (MA))	PHBV crystallization might be hindered by the presence of PBS	Synergistic effect can be achieved on stiffness by blending PHBV and PBS	Glass transition is slightly lower when compatibilizers are added	[310] [311]
Polyhydroxybutyrate -co- valerate (PHBV)	Whole range	Small-molecular weight additive (maleic anhydride (MA) and dicumyl peroxide (DCP))	PHBV crystallization is slowed by PBS content and vice versa	-	PHBV crystallization temperature decreases by increasing PBS content	[312]
Poly(Hydroxybutyrate- co-Hydroxyhexanoate) (PHBH)	0–50% PHBH	Small-molecular weight additive (maleic anhydride (MA))	-	Strength and elongation at break is improved by adding 10 wt.% of PBS. Stiffness decreases consistently with PBS content	-	[313]
Polyhydroxybutyrate (PHB)	0–50% PHBH	Small-molecular weight additive (dicumyl peroxide (DCP))	PBS slightly suppresses PHB crystallization, especially when DCP is added. PHB favours PBS nucleation	Strength and elongation of PHB can be improved by the addition of PBS. Stiffness is decreased by the addition of PBS	Melting temperature of PHB is increased by PBS	[277,308]
Polyhydroxybutyrate (PHB)	Whole range	-	PBS (up to 50 wt.%) favours the crystallization of PHB	Stiffness decreases by increasing PBS content	Melting and crystallization temperatures of PHB is increased by PBS content	[309]
Poly(lactic acid) (PLA)	80–100% PLA	Small-molecular weight additive (dicumyl peroxide (DCP))	The crystallization of the PBS component in the blends occurred when the content of DCP was less than 0.3 phr.	The elongation at break of the blend was sharply increased by the addition of DCP and this was conjugated with an improving in the tensile strength.	The T_g of the compatibilized blends was similar to that of the neat PLA.	[326]
Poly(lactic acid) (PLA)	Whole range	-	The degree of crystallinity achievable in two phases increased by increasing the amount of PBS in the blend.	The PBS content between 10 and 40 wt.% resulted in a dramatically increase of the elongation at break of the blend (>300%)	The presence of a small amount of PBS resulted in a slight reduction ($\sim 2 \ ^{\circ}C$) of the T _g of the PBS	[317]
Poly(lactic acid) (PLA)	Whole range	-	-	Toughness and elongation at break increased by increasing the PBS amount, whereas, strength and stiffness decreased.	-	[318]
Poly(lactic acid) (PLA)	70% PLA	Toluene diisocyanate (TDI). Polylactide functionalized with maleic anhydride (MA-g-PLA)	-	Toughness and elongation at break increased by the addition of TDI, due to the formation of urethane or amide bonds between the two phases. TDI is more suitable to improve the compatibility between the phases as compared to MA-g-PLA.	-	[322]
Poly(lactic acid) (PLA)	Whole range	Triphenil phosphite (TPP)	The crystallinity of PLA increased by the addition of the PBS and TPP	The mechanical properties were not influenced largely by the addition of TPP as a compatibilizer.	The $T_{\rm g}$ of PLA decreased by the addition of the PBS and TPP	[323]
Poly(propylene carbonate) (PPC)	Whole range	-	The crystallization temperature of the PBS increased by the addition of PPC.	Tensile strength of the blend is less than that of neat PBS.	The T_g of PBS increased by blending it with PPC. Thermal stability of the blend is less than that of neat PBS but it was better than neat PPC.	[347]

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Blending element	Compositional Range,%	Compactization strategy	Crystallization	Mechanical properties	Thermal properties	Refs.
Poly(propylene carbonate) (PPC)	50% PPC	Small-molecular weight additive (maleic anhydride (MA) and dicumyl peroxide (DCP)) + Titanium butoxide (TBT) as a catalyst	-	The elongation at break of the blend was largely improved by the addition of the compatibilizer	-	[354]
Poly(propylene carbonate) (PPC)	Whole range	Small-molecular weight additive (propylene oxide (PO))	-	The tensile and impact strengths of the compatibilized PBS/PPC (10/90) and (30/70) blends were higher as compared to that of the non-compatibilized counterpart.	Thermal stability of the blend is less than that of neat PBS but it was better than neat PPC. The thermal stability of the compatibilized PBS/PPC (30/70) blend improved as compared to the non-compatibilized counterpart.	[357]
Polyvinyl acetate (PVA)	0-30% PVA	-	The maximum degree of the crystallinity of the PBS phase is reduced by the addition of PVA.	Mechanical properties of PBS, including stiffness, tensile strength, and elongation at break, were improved by the addition of PVA	-	[358]
Thermoplastic starch (TPS)	70% TPS	Small-molecular weight additive (tartaric acid (TA))	-	The tensile strength, elongation at break, and impact strength of the compatibilized PBS/TPS (10/90) blend were higher as compared to those of the non-compatibilized counternart	-	[362]
Thermoplastic starch (TPS)	Whole range	_	_	The blends containing TPS with no amylose showed higher mechanical properties as compared to those containing TPS with 26% 0% amylose. Tensile strength and elongation at break of the blend increased by the increasing the amount of the PBS, whereas the stiffness decreased.	Thermal stability of the blends is less than that of the neat PBS.	[364]
Thermoplastic starch (TPS)	50-70% TPS	-	-	-	The addition of TPS resulted in an increase in the crystallinity of the material against a lower crystallization rate.	[367]
Thermoplastic starch (TPS)	0-40% TPS	Maleic anhydride grafted on PBS (MA-g-PBS)	-	The strength and elongation at break of TPS/PBS blends were greatly increased with the addition of MA-g-PBS.	-	[370]
Thermoplastic starch (TPS)	20-80% TPS	Copolymer (PBS-co-TPS) + NN'- dicyclohexylcarbodiimide (DCC).		The strength and stiffness of the compatibilized blend were higher as compared to those of the non-compatibilized counterpart.	Melting temperature and T_g were slightly changed in the blends as compared to the neat PBS.	[371]

the resistance to the tensile test of the blend is greater than the tensile strength of the individual components (increase up to 30%) without compromising the excellent elongation at break of PBAT, showing a synergistic effect between the two polymers. Finally, the PBS/PBAT blends show an HDT that is approximately equal to the weighted average of the two constituents within the mixture. Boonprasertpoh et al. studied PBS/PBAT blends over the en-

tire compositional range [286] and showed that the two polymers blended by extrusion with a co-rotating twin-screw system show a phase separation with the formation of so-called drop structures for low levels of each individual constituent in the other one (up to concentrations of 30 wt.% of PBS in PBAT and vice versa). On the other hand, for PBS and PBAT content higher than 30% in the blend, the formation of a co-continuous structure between the two poly-



Fig. 17. Schematic diagram and morphology observation of the structural evolution of the PBS95/PBAT5/peroxide blends with various peroxide concentrations (C_p). [287], copyright 2019. Adapted with permission from Royal Society of Chemistry.

mers is observed. Contrary to what was observed in [285], Boonprasertpoh et al. verified a reduction in the tensile strength of the blend with respect to the values of the individual constituents for low and medium levels of PBAT in PBS (between 10 and 50 wt.%).

Nobile et al. studied film forming starting from PBS/PBAT blends obtained by cast extrusion on a chill roll [288]. They noted that a high PBAT content inhibits the crystallization of PBS. Furthermore, as the PBS content in the blend increased, they observed a reduction in the elongation at break and a corresponding increase in the stiffness and tensile strength. Finally, an increase in the PBAT content in the blend was associated with an increase in the viscosity.

More recently, Wu et al. studied the transformation of partially compatible PBS/PBAT blends into PBS/PBAT blends made fully compatible by nano-structuring in the presence of small amounts of peroxides (0.02 phr, dicumyl peroxide) as a compatibilizing agent [287]. At low concentrations of PBAT (5 wt.%), there is the formation of drop-shaped dispersed PBAT nanophases with a diameter of about 20 nm. For PBAT concentrations of 15 wt.% such dispersed phases take on the appearance of a nano-foil to finally assume the appearance of nano-drops for even higher PBAT levels of 20 wt.%. The formation of nano-structured PBAT phases within PBS matrices is ascribed to the generation of copolymers between PBS and PBAT due to the compatibilization promoted by peroxides (Fig. 17). Basically, these copolymers lower the surface tension between the PBS and PBAT, allowing for better compatibilization through the formation of PBAT nano-structures that are well dispersed and distributed within the PBS matrix. In the absence of peroxides, such nano-structuring does not occur, generating a classic structure of dispersed phases of a micro-metric size of PBAT in PBS (at low concentrations of the former).

Wu et al. also observed that nano-structured PBS/PBAT blends have an impact resistance of up to four times higher than that of micro-structured blends and greater stiffness. However, nanostructured blends are characterized by a decidedly more modest elongation at the break value (in some cases, less than half the value reached by micro-structured blends). Furthermore, control of the reaction between PBS and PBAT with the formation of a co-polymer in the presence of peroxides is extremely difficult to manage. For peroxide levels that are too high (0.2 phr) or too low (0.007), the reaction between PBS and PBAT is either too active (with the formation of an excessively viscous and difficult to process melt) or not sufficiently active (with a poor formation of the co-polymer between PBS and PBAT). In both cases, formation is promoted of a dispersed phase micro-structure of PBAT drops within the PBS matrix.

Wu et al. further extended this concept, applying it to the manufacture of composite materials (Fig. 18) in which the matrix is composed of nano-structured blends between PBS and PBAT and the reinforcement is instead composed of a natural fiber coming from agricultural waste, such as from miscanthus fiber or oat husks [289]. These composites are characterized by an increase in the tensile modulus of 650% for an addition of 40 wt.% of the reinforcement phase. The addition of a miscanthus fiber proved to be more promising with an increase in modulus of up to 3.0 GPa, an HDT of 110 $^{\circ}$ C, and less hydrophilicity of the composite. However, oat chaff allows composites to be obtained with good impact resistance (i.e., 83 J/m).

5.1.3. Blends of PBS with polycaprolactone (PCL)

PCL is another biodegradable aliphatic polyester. It is a polymer characterized by a high elongation at break, and it has good machinability from the melt. However, it is characterized by a modest mechanical resistance and a low melting point ($\sim 60 \, ^{\circ}$ C), which limits its industrial use. There are very few studies in which PBS and PCL are employed in blends, probably because both materials possess a high ductility. However, PBS possesses a greater thermal stability (HDT > 90 °C) and a melting temperature that is over 50 °C higher than the melting temperature of PCL. Most studies on PBS/PCL blends are related to the development of ternary blends with the aim of producing a biodegradable plastic material alternative to fossil-based plastics. Reddy et al. investigated the development of a ternary PBS/PCL blend reinforced with a thermoplastic soybean meal (TSM) [290]. The TSM was unstructured and plasticized by mixing with glycerol and urea, and it was subsequently blended at 30 wt.% with different proportions of PBS and PCL by extrusion. The addition of PCL appears to promote the compatibilization between TSM and PBS, with TSM transiting from a drop-dispersed structure within the PBS matrix to a fibrillar struc-



Fig. 18. Schematic illustration of the fabrication of double network green composites in a one-step reactive extrusion. [289], Copyright 2020. Reproduced with permission from Elsevier Science Ltd.

ture within the PBS/PCL blend. The increase in the PCL content in the blend promotes an increase in the elongation at break and the impact resistance. Can et al. studied PBS/PCL blends (up to 40 wt.% of PCL) compatibilized by adding 1 wt.% of a block copolymer between Polyethylene oxide-block-Polypropylene oxide-block-Polyethylene oxide (PEO-PPO-PEO) in a co-rotating twin-screw extrusion [291]. PBS and PCL show a distinct phase separation with PCL forming spherical domains within the matrix in PBS. The use of the compatibilizer involves a better interaction between the two phases, which results in a decrease in the PCL domains. In the presence of a compatibilizer, there is also a reduction in the stiffness of the blend and an increase in its toughness and ductility. Liu et al. studied PBS/PCL blends (setting the PCL content at 20 wt.%) compatibilized by adding a copolymer between PBS and PCL or PBS-co-CL [292]. The addition of 5 wt.% of compatibilizer resulted in a significant improvement in the interaction between the two phases, noting a significant reduction in the interfacial tension. Furthermore, an increase was observed in the elastic modulus of the blend with respect to constituent polymers (which in some cases more than doubled), as well as an increase in its deformation at break. Finally, the crystallization rate of the PCL in the blend is accelerated by the addition of compatibilizer. when the crystallization rate of the PBS slowed down. The melting temperature of the PCL in the blend is 4 °C lower than the corresponding melting temperature of the PCL as it is, which suggests that the presence of the compatibilizer influences the crystalline structure of the PCL, favouring the formation of imperfect crystals. Chen et al. developed PBS/PCL blends to act as a carrier for an organic anti-vegetative (4,5-dichloro-2-octyl-isothiazolone) [293]. The researchers have shown that by modulating the presence of PBS (up to 30 wt.%) in the blend, it is possible to control the rate of degradation of the same in a marine environment, progressively releasing the active species. More recently, He et al. studied the preparation of the blended PBS/PCL reinforced with carbon nanotubes [294]. In this work, the poor miscibility of PBS and PCL was noted. Despite the poor interaction between the two phases, it is known that PBS and PCL are able to mutually influence their own crystalline structure when present inside a blend. Increasing the interaction between the two constituents would therefore make it possible to obtain blends with properties that have not yet been explored. The experimental results showed that the carbon nanotubes preferentially disperse in the PBS phase (more rigid), favouring the stiffness of the blend without altering its ductility/toughness. More recently, Nicolino et al. studied PBSA and PCL-based blends in different proportions [295]. PBSA and PCL

were immiscible within the blend. However, the blends with PBSA levels between 30 and 50 wt.% have a stiffness comparable or superior to that of PCL, denoting the presence of an interaction between the phases. Furthermore, for the same PBSA content in the blend, an acceleration was noted in the biodegradation rate. This result indicates that it is possible, through suitable compatibilization, to improve the properties of the blends between PBSA and PCL, without compromising their biodegradability. In a subsequent study, Nicolino et al. studied the use of a titanium-based catalyst (up to 0.5 wt.%) to increase the compatibility of PBSA and PCL (40 wt.% in PCL) through transesterification [296]. As the catalyst concentration increased, a mutation of the structure of the blend was observed which passed from co-continuous to a dispersed phase structure. Furthermore, the presence of the catalyst has determined a greater interaction between the phases with a consequent increase in the yield stress and elongation at yield with the same elastic modulus. Instead, Sadeghi et al. studied the use of PBS/PCL blends to manufacture biodegradable membranes to treat waste water [297]. Adding PBS to PCL increases membrane hydrophilicity as well as the biodegradability. The addition of 30 wt.% of PBS to PCL allows the manufacture of membranes that are much more efficient in the treatment of wastewater with an increase in the flow of pure water, the recovery ratio of the flow, and the permeate flow.

5.1.4. Blends of PBS with polydioxanone (PDO)

PDO is a polymer consisting of repeating ether-ester units. It is a material that has a glass transition temperature between -10 and 0 °C and a good tendency for crystallization. It is generally extruded into fibers and is used to produce yarns, mainly for biomedical use. It is a very interesting material by virtue of its high flexibility (given by an ethereal functionality), excellent tolerability and high biodegradability. Ebrahimpour et al. studied the miscibility of PDO with PBS to evaluate potential synergies between the two materials in preparing blends between PDO and PBS [298]. Using dilute solution viscosimetry, the researchers showed that PBS blends with PDO levels at 20 wt.% were completely immiscible. PBS/PBO blends at 50 wt.%, it is possible to obtain perfect miscibility between the two constituents. Finally, the temperature does not significantly influence the miscibility of the constituents.

5.1.5. Blends of PBS with polyoxyethylene (PEO)

PEO is a polyether obtained by the polymerization of ethylene oxide, which is conventionally characterized by a molecular



Fig. 19. Hydrolytic and enzymatic degradation process of PBS. [1], copyright 2016. Reproduced with permission from Elsevier Science Ltd.

weight higher than 20,000 g/mol. The physical state of the PEO varies from liquid to solid as a function of the molecular weight. PEO is therefore solid with a high molecular weight, and in this case it has melting temperatures of about 68 °C. It is a highly soluble polymer in water, which makes it particularly suitable for use within bioplastics engineered to accelerate biodegradability [299]. Furthermore, it is perfectly miscible, in all proportions, with most aliphatic polyesters, and, therefore, with PBS [300]. The biodegradability of aliphatic polyesters proceeds through a wellknown two-step process, accelerated in the presence of enzymes (Fig. 19). The degradation is influenced by different factors, including the chemical structure of the polymer, the level of hydrophobicity/hydrophilicity, the molecular weight and the index of poly-dispersion, the degree of crystallinity, and the morphology of the structure [301]. During the first phase of the degradation, the hydrolysis reactions promote the formation of molecules with a low molecular weight. However, in this phase, there is no real reduction in the mass of the polymer, but only a rearrangement of its structure with an increase in the degree of crystallinity linked to the greater mobility of the molecule fragments formed by hydrolysis [302]. During the second phase of degradation (which is normally activated for molecular months slightly higher than 1×10^4 Da), the mass loss is obtained [303]. Enzymes, in particular lipase, can catalyse degradation, significantly increasing the kinetics [304].

The high hydrophobia of PBS slows down the degradation processes, which are, on the other hand, normally accelerated when PBS is mixed with highly hydrophilic polymers (for example, with PEOs) or when PBS co-polymers with high hydrophilic segments are engineered [1]. Huang et al. studied how the addition of small quantities of PEO to the PBS could accelerate the hydrolytic degradation and modify its micro-structure [299]. The researchers have also shown that the presence of PEO alters the crystallinity of PBS, strongly increasing its hydrophilicity and thus accelerating its degradation through surface erosion. In particular, PEO accelerates the hydro-solubility of the blend with PBS, particularly when it is added at higher levels (at least 5%). Furthermore, the PEO is placed in the blend with the PBS preferentially between the spherulites of PBS, favouring the penetration of water into the material and the consequent dissolution. Fabbri et al. instead studied the potential of random PBS copolymers with the addition of PEG-like sequences (polyethylene glycol) [305]. The results showed that the copolymer has an extremely reduced degree of crystallinity compared to the PBS homopolymer, with a reduction in the melting temperature and a morphological alteration of the crystalline structure (formation of crystals with reduced precision). Furthermore, the copolymer biodegradation rate is decidedly accelerated. Basically, the introduction of chains containing different oxygen levels through ether bonds allows to customize the balance of the hydrophilic/hydrophobic behavior of the PBS, conditioning, among other properties, its crystallinity and speed of dissolution.

5.1.6. Blends of PBS with polyhydroxyalkanoates (PHA)

PHAs are a broad class of linear polyesters produced by fermentation of sugars or lipids from various bacterial strains [306]. These biodegradable polymers are suitable to produce bioplastics. However, they are also expensive materials, difficult to process, and, in some cases, extremely fragile [307]. The toughness and processability of the PHAs can be modified by developing copolymers in which the number of CH₂ groups present in the main chain as well as the size of the side chain are customized. The preparation of blends between linear polyesters and PHA is certainly an economical way to customize the properties of the resulting material, although the PHAs are substantially immiscible with other aliphatic polyesters. Ma et al. studied PBS blends with polyhydroxybutyrateco-valerate (PHBV) and polyhydroxybutyrate (PHB, homopolymer) compatibilized with peroxide dicumyl to obtain properties that can reconcile the advantages of the individual base materials [277]. The compatibilizer made it possible to obtain dispersed phases of PBS within the PHBV of reduced dimensions, improving the interfacial adhesion. The elongation at break of the resulting blend improved significantly, and the result was ascribed to the ability of the PBS dispersed in the PHBV matrix to increase the toughness of the blend due to expansion, deformation, and fibrillation of the PBS particles. Furthermore, the addition of the compatibilizer modifies the spherulite structure of the PBS, generating a socalled cloud-like morphology due to a reduction in the size of the spherulites and intra-spherulite spaces [308]. Similarly, they also demonstrated an improved tensile strength, resilience, and elongation at break of injection-moulded PHB/PBS blends, again through the same compatibilization mechanism. Furthermore, the addition of PBS to the PHB determines a significant acceleration of the crystallization rate of the latter due to a multi-nucleation mechanism that can be ascribed as homogeneous, heterogeneous and self-induced nucleation [309]. Chikh et al. studied the compatibilization of PHBV/PBS blends by introducing maleic anhydride and, subsequently, sepiolite [310]. The results showed that the presence of maleic anhydride favours the interaction between the two phases of the blend, which, however, remain immiscible in all proportions. Basically, maleic anhydride, activated in the presence of very low levels of dicumyl peroxide, binds to PHBV forming MA-g-PHBV, which has a significant emulsifying effect on PHBV and PBS due to a reduction in the surface tension existing between the two phases of the blend. 50:50 blends between the two phases lead to the formation of co-continuous blends. Conversely, a reduction in the content of one of the two phases below 25 wt.% involves the formation of a dispersed phase of the polyester present in a lower concentration within the matrix of the main polymeric phase. The addition of sepiolite in addition to maleic anhydride improves the compatibilizing effect, improving the miscibility between the two phases and leading to the formation of dispersed structures of smaller dimensions, indicating an increase in the affinity between the two phases. However, the simultaneous use of the two compatibilizers produces a significant increase in the complex viscosity of the blend, this being a prelude to a reduction in its processability. Chick et al., however, showed that the presence of maleic anhydride - grafted - polyhydroxybutyrate-co-hexanoate (MA-g-PHBH) and sepiolite also increase the stability of the blend, which preserves the mechanical properties even after subsequent extrusion cycles, suggesting an improvement in the recyclability of the material thus designed [311]. Kennouche et al. studied the compatibilization of PHBV/PBS blends by adding maleic anhydride and halloysite nanotubes [312]. The researchers confirmed the compatibilizing effect of maleic anhydride, which, by binding to PHBH and forming MA-g-PHBH in the presence of dicumyl peroxide, induces a better dispersion of the PBS inside the PHBV, when the same is added in tenors of 20 wt.%. The halloysite nanotubes are in turn dispersed mainly inside the PBS phase, presenting better wettability in the latter. The simultaneous addition of maleic anhydride and halloysite seem, on the other hand, to determine a reduction in the compatibilizing effect of the maleic anhydride, probably due to some form of interaction between the two agents, which inhibits the emulsifying effect. Compatibility with maleic anhydride was also investigated by Thirmizir et al. in the case of the blend (PBS/PHBH, polyhydroxybutyrate-co-hexanoate) using the same mechanism that involves an initiator based on peroxide dicumyl and the formation of MA-g-PHBH [313]. Blends with variable PBS content between 10 and 50 wt.% have been studied. The experimental results showed the effectiveness of the methodology, also in the case of PHBH, in a manner analogous to what has been shown in previous studies relating to PHB and PHBV. The presence of PBS blended with poly-3-hydroxybutyrate-co-4-hydroxybutyrate (PHB-co-HB) and its effect on the degradation mechanisms was recently studied in [314]. The research showed an increase in the processability of PHB-co-HB in the presence of PBS levels. The enzymatic degradation of the blend has shown that, in the presence of lipase, PBS favours the dissolution of the plastic material. Conversely, soil degradation studies have shown that the presence of PBS can disadvantage the degradation of PHB-co-HB by virtue of its presence in the soil of highly selective and effective enzymes on polyhydroxyalkanoate. Finally, the hydrolytic degradation of PBS/PHB-co-HB blends is strongly linked to the characteristics of the phases and to the dispersion that occurs between them. Ultimately, Sun et al. showed that PBS/PHB-co-HB blends have a relatively high thermal stability, but that, at the same time, they can be dissolved due to multiple degradation mechanisms via enzymes or in the presence of water.

5.1.7. Blends of PBS with poly(lactic acid) (PLA)

Poly(lactic acid) (PLA) polymers are, by far, the most explored biodegradable aliphatic polyesters in the scientific literature due to their good functional and technological properties, as well as their relatively low cost and market availability. The stiffness and low ductility and toughness of PLA is also very well known, and this imposes the need to engineer the material, often through the preparation of blends with more ductile/tough biodegradable polyesters such as PBS, for which there is vast prior research [315]. Ji et al. studied the compatibilization of PLA/PBS blends using dicumyl peroxide [316]. The presence of the peroxide determined the formation of PLA-co-BS copolymers between PLA and PBS in the melted phase, which greatly improved the compatibility between the two polyesters, reducing the interfacial tension. The presence of branched/crosslinked structures between PLA and PBS in the presence of the compatibilizer has also shown a nucleating effect for each individual constituent of the blend. However, these structures have a lower mobility, especially in the presence of high peroxide levels, which can lead to a reduction in the degree of achievable crystallinity and in the crystallization rate due to chain entanglement. This is especially true in the case of PBS, which tends to more easily generate branched/reticulated structures by presenting a molecular structure with many secondary hydrogen atoms that facilitate the action of peroxide in the extraction. The study made it possible to identify that 0.2-0.3 wt.% of peroxide produced the best results in terms of mechanical properties, with a tensile strength of about 73-80 MPa and elongations at break of about 200% for blends at 20 wt.% in PBS. Deng et al. investigated PLA/PBS blends by reversing the role of two polymers within the material or by varying the PBS content between 0 and 100 wt.% [317]. The increase in the PBS content inside the blend was associated with an increase in the degree of crystallinity achievable in two phases with as-is PLA that is instead completely amorphous. The presence of even a small content of PBS implies a slight reduction (of about 2 °C) of the glass transition temperature of the PBS. The strong incompatibility between the two materials, which are immiscible in all proportions, determines a depression of the properties of the blend with respect to the expectations or by applying the model in series and in parallel and considering the properties of each individual constituent of the blend. However, the PBS content between 10 and 40 wt.% allows to dramatically increase the ductility of the blend (over 300%). This is due to the formation of a co-continuous phase between the two polymers, even for a low concentrations of PBS. This is due to the profound difference between the viscosity of the two polymers at typical process temperatures (about 175 °C), where PBS has a shear viscosity value more than ten times lower than PLA (about 162 Pa \times s compared to 1759 Pa \times s of the PLA).

A further increase in the concentration of PBS inside the PLA (from 50 to 80 wt.%), instead, causes a deterioration in the ductility of the blend, which then assumes values very close to those achievable by PLA as it is. This result has been ascribed to the phase inversion (Fig. 20) that materializes for a concentration of PBS equal to 50 wt.% or higher. Under these circumstances, the PLA becomes a secondary phase and fails to generate the formation of a co-continuous structure with the PBS. Conversely, PLA forms a dispersed drop phase in the PLA matrix, which drastically worsens the ductility of the resulting blend.

The increase in crystallinity of the PLA in the presence of PBS was confirmed by Qiu et al., who studied the PLA/PBS blends by varying the PBS content between 0 and 100 wt.% [318]. The results showed a progressive increase in the toughness of the blend for PBS tenors of at least 50 wt.% compared to a reduction in the stiffness and tensile strength. PBS levels below 50% show a depression of the elongation level at the break in the corresponding PLA/PBS blends, similarly to what has been previously demonstrated [317]. Finally, the researchers developed a predictive model of the deformation behavior of the blend, confirming its viscoplastic nature, which can be well described by the Chaboche viscoplastic model. More recently, Ostrowska et al. iterated the study of PLA/PBS blends varying the content of the latter from 0 to 100 wt.% [319]. The results indicated that the blends show mechanical properties representative of the weighted average of the properties of the individual phases. In some cases, the values for the blend were surprisingly higher than those expected for both constituents. More recently, studies on PLA/PBS blends have focused on the synergistic effects of adding compatibilizers/plasticizers. Fortunati et al. studied the plasticization of PLA/PBS blends with PBS present at 20 wt.% by adding ATBC (Acetyl Tributyl Citrate) and IDE (isosorbide diester) [320]. ATBC was found to be efficient in the plasticization of PLA (very similar solubility parameters calculated according to the small cohesive energy equation), but incompatible with PBS to the point of making it unprocessable for ATBC levels equal to 30 wt.%. IDE is also more effective on PLA although they have different solubility parameters, as evidenced by the reduction of the glass transition temperature (about 30 °C), cold crystallization temperature (about 35-45 °C), the temperature for melting (up to 10 °C) of the PLA phase. Both plasticizers are inefficient on PBS. The FDI content equal to 15 wt.% produce a strong plasticizing effect of the PLA/PBS blend, whether the plasticizer is premixed with PLA or directly introduced into the blend. The glass transition temperature of the PLA in the blend is reduced by about 20 °C. The elongation at break also increased by about 24 times compared to the corresponding non-plasticized blend, against a reduction in the elastic modulus from 2.4 GPa to about 500-750 MPa and the strength at break from about 33 MPa to about 20 MPa. Finally, it is of fundamental importance to note the effect of the



Fig. 20. Schematic representation of the evolution of the morphology of the PLA/PBS blends by increasing the amount of PBS. [292], copyright 2015. Reproduced with permission from Elsevier Science Ltd.

IDE on the crystallization of PLA, which results in a reduction of about 25 °C in the cold crystallization temperature of PLA in the PLA/PBS blend (20 wt.%) added with 15 wt.% of FDI. The PLA crystallization becomes easier in the presence of the IDE, which improves the smoothness of the PLA molecules, also by virtue of its low molecular weight (174 g/mol). In contrast, Hao et al. studied the role of polyaryl polymethylene isocyanate (PAPI) for compatibilization of PLA/PBS blends [321]. As the PAPI content increased, an improvement in the interfacial adhesion between the PLA and PBS in the blend was found due to the formation of PLA-co-BS copolymers. In addition to improving the compatibility between the two phases of the blend, these site favour nucleation. A similar path for the compatibilization of the PLA/PBS blend was followed by Phetwarotai et al. [322]. The researchers studied the additivation of the blend using two types of compatibilizers (Toluene Dilsocyanate (TDI) and MA-g-PLA, polylactide functionalized with maleic anhydride) and two plasticizers (triethyl citrate (TEC) and tricresyl phosphate (TRP)). The results of the experiment showed the greatest compatibilizing effect of TDI, presumably due to the formation of urethane or amide bonds between the two phases in PLA and PBS. The compatibilization for MA-g-PLA is more complex to control since there is a risk to promote a chain cleavage reaction of the polyesters to activate the formation of PLA functionalized with maleic anhydride in the presence of peroxides. The introduction of the compatibilizer with one of the plasticizing agents (TEC or TRP) improves the toughness and ductility of the blend by a few percentage points, also favouring the reduction of the cold crystallization temperature of the PLA phase (about 16 °C for 15 wt.% plasticizer in the blend). Ratsameetammajak et al. studied the use of fatty acids (lauric acid (LA), palmitic acid (PA), stearic acid (SA)) for plasticization of PLA/PBS blends (10 wt.%), using up to 4 wt.% plasticizer [323]. The use of very low levels of plasticizer has presumably not allowed a full evaluation of its efficiency, although LA seems to be the most effective at depressing the glass transition temperature and the cold crystallization temperature of the PLA in the blend. Somsunan et al. studied the use of PEA (polyester adipate) to plasticize PLA/PBS blends with increasing levels of the latter (up to 30 wt.%) [324]. The plasticizing effect of PEA is confirmed by reducing the glass transition temperature of PLA in the blend (by more than 10 °C). PEA works by reducing the intramolecular interactions between the chains of PLA and PBS, increasing their mobility. PEA does not show a plasticizing effect on PBS, worsening all its mechanical characteristics, as this result is attributable to a poor miscibility of the plasticizers in the PBS, which has a high solubility value. The PEA also determines a reduction in the tensile strength and stiffness (respectively 76 and 38% with 15 wt.% of PEA in the blend), compared to an increase in the elongation at break (up to 266%). Finally, PEA also promotes the crystallization of PLA as it is, minimally influencing its transparency. Ma et al. studied the use of TPP (Triphenil Phosphite) for compatibilization of PLA/PBS blends (20 wt.%) through a reactive extrusion process [325]. The addition of compatibilizer effectively compatibilized the two phases of the blend as demonstrated by an increase in the viscosity of the melt during reactive extrusion.

The addition of very modest TPP content (0.5 wt.%) made it possible to significantly increase the mechanical properties of the blend (especially toughness) with precision due to the decrease in size of the dispersed phase (PBS in PLA). A reduction in the glass transition temperature of PLA in the blend was also obtained with an increase in the TPP content. More recently, a chain extender with epoxy functionality (up to 6 wt.%) has been used for compatibilization of PLA/PBSL (30 wt.%) blends (Polybutylene succinateco-lactate) [326]. The presence of the chain extender (introduced at 2 wt.%) allowed an increase in the compatibility between the two phases, significantly reducing the average size of the dispersed phase (PBSL in PLA). The compatibilization is determined by the ability of the chain extender additive to react with both the PBSL and PLA phase, forming structures in which the PLLA, PLLA and PBSL or PBSL are grafted onto the chain extender skeleton (Fig. 21). In this way, a strong compatibilization is obtained within single phases of the blend and at the interface between them. By increasing the chain extender content to 4 wt.% a further compatibilization effect is obtained between the two phases, and a reduction in the mobility of the PBSL phase due to the formation of branched chains of PBSL on the backbone of the chain extender within the phase dispersed in PBSL. In these circumstances, the maximum effectiveness of the chain extender is found, and this causes an increase in the elongation at break of the blend (doubles compared to the value of the blend without additives) and in the mechanical strength (up to about 70 MPa, or slightly less than twice the value of the blend without additives). A further increase in the content of the chain extender (up to 6 wt.%) is counterproductive, with a reduction in the tenacity of the blend, both due to excessive interactions between the two phases and to a reduction in the motility of the PBSL phase.

Numerous studies have shown improvements in the properties of the blends between PLA and PBS due to the introduction of an organic or inorganic reinforcement. In this work, we will review the most recent studies concerning the use of the bioavailable reinforcements, being the use of inorganic reinforcements already reviewed in works entirely focused on PLA and related blends [327,328,329,330,331,332,333,334]. Zhang and Zhang studied PLA/PBS blends (30 wt.%) reinforced with cellulose nanocrystals crimped on PBS (PBS-g-CNC) in the presence of a dicumyl



Fig. 21. Compatibilizing effect on poly-L-lactic acid (PLLA) and polybutylene succinate-co-lactate (PBSL) of the chain extenders with the epoxy functionality. [346], copyright 2021. Reproduced with permission from Elsevier Science Ltd.

peroxide (DCP) [335]. The role of the DCP is confirmed by a reduction in the domains of the PBS-dispersed phase in the PLA matrix, which is already obtained for very low additive levels (0.2 phr of DCP and 2.0 phr of PBS-g-CNC). Even in the absence of PCP, PBS-g-CNC efficiently disperses in both PBS and PLA, causing an increase in the mechanical properties of the blend and an improvement in crystallization (from 12 to 30%). In particular, the impact resistance of the blend increases from 72 to 105 J/m in the presence of both additives. Conversely, the addition of PCP affects the mobility of the polymer chains and depresses the crystallinity of both PBS and PLA. In the absence of compatibilization, the addition of CNC to PLA/PBS blends is, on the other hand, counterproductive [336], with the mobility of PLA chains reduced by the presence of CNC, which ends up inhibiting the crystallization of the blend. Cao et al. studied PLA/PBS/MCC blends (micro-crystalline cellulose) at a weight ratio of 60:30:10 in the presence of a chain extender with epoxy functionality (added up to 1.0 wt.%) [337]. The presence of the chain extender improves the elongation at break of the blend at up to 0.5 wt.% and an impact resistance (up to 60%), increasing the affinity (the forces of interfacial cohesion) between the dispersed phase in PBS and the matrix in PLA. Further increases in the additive are counterproductive, as they block the dispersed PBS phase by promoting the chain extension reaction of the PBS itself. In this way, the mobility of the PBS is compromised, and a corresponding reduction in the elongation at breakage of the blend is observed due to a lower flexibility of the dispersed phase. Similarly, an excessive increase in the chain extender penalizes the crystallinity of the blend since it reduces the mobility of the polymer chains of PLA and PBS. This is also confirmed by a significant increase in the melt viscosity with the addition of the chain extender. Chuayjuljit et al. studied PLA/PBS blends (30 wt.%) reinforced with wood flour with content between 5 and 30 phr [338]. Although the addition of wood flour produces an improvement in the crystallinity of the blend and an acceleration in the dissolution due to greater hydrophilicity of the material, the flour causes a worsening of the mechanical properties, and this is more evident with a greater concentration of wood flour. This result is presumably ascribed to a poor interfacial cohesion between the wood flour (highly hydrophilic) and polymeric portion (tendentially hydrophobic). The use of chitosan functionalized with lactic acid oligomers (FCH) inside PLA/PBS blends (20 wt.%) was studied in the presence of DCP [339]. Small levels of FCH (1 wt.%) in the presence of DCP enhances the compatibility of the blend and increases its processability and thermal stability. Akindoyo et al. studied the use of rice husk and coconut shell fiber to improve the performance of PLA/PBSL blends (30 wt.%), exploring reinforcement levels between 0 and 10 wt.% [340]. The coir shell fiber is most effective to improve the tensile performance of the PLA/PBS blend, with a tensile strength that can increase up to approximately 200%. The fiber of the coconut shell also favours an increase in the crystallinity of the blend. In contrast, the rice husk favours an increase in the thermal stability of the blend as well as its dissolution favouring an additional incorporation of water. More recently, Rasheed et al. studied PLA / PBS blends (20 wt.%) reinforced with modest nanocrystalline cellulose (NCC) content (up to 1.5 wt.%) obtained from bamboo fiber [341,342]. The NCC particles are dispersed uniformly in both polymeric phases (immiscible) assuming a rod-like format. Furthermore, the fracture surface shows that the interfacial cohesion force between the NCC fibers and the polymeric phases is high, which is a sign of a good interaction. The fracture surface shows that the NCC fiber is not easy to delaminate and that its breakage can occur by a brittle fracture rather than by simple delamination from the polymer matrix (Fig. 22a-c).

The addition of NCC up to 1 wt.% determines an increase in the mechanical properties of the blend, specifically the tensile strength (a little less than 20%) and the elastic modulus (about 250%), as well as the thermal stability. However, the CNC determines a worsening of the elongation at break of the polymeric material (by about 30%).

5.1.8. Blends of PBSA with PLA

Preparing blends between PBSA and PLA is of considerable interest given that PBSA can contribute to achieving biodegradable polymeric materials entirely from renewable sources, with an excellent complement of stiffness, tensile strength, toughness, and ductility. Lascano et al. studied PLA/PBSA blends (10-30 wt.%) compatibilized using a chain extender (a styrene-acrylic oligomer with epoxy functionality added in extremely modest quantities, 0.5 phr) [343]. Compatibilization is achieved by the same mechanism that intervenes in the chain extension compatibilization between PLA and PBSL discussed in epoxy (Nishida et al., 2021). The effect of the compatibilization translates into a strong increase in the elongation at break of the compatibilized blend when compared with the same blend in the absence of a chain extender. An increase in ductility by an order of magnitude and a significant increase in impact resistance (about 30%) were measured. Similarly, Palai et al. demonstrated the efficacy of PLA/PBSA blends (5-20 wt.%) compatibilized with the same styrene-acrylic oligomer with epoxy functionality (added up to 3 wt.%) to manufacture flexible films [344]. More recently, Aiotta et al. presented a study of a PLA/PBSA blend (15-40 wt.%) that is always compatibilized through the use of oligomeric styrene-acrylic with epoxy functionality (added up to 2 wt.%) [345]. The deformation was studied by a dilatometric analysis that revealed a transition from cavitational to deviatoric response as the PBSA content in blend increased from 20 to 40 wt.%. This result was ascribed to the different morphology of the blends, which for a 40 wt.% content in PBSA produces a co-continuous



Fig. 22. Dispersion of nanocellulose (NCC) in the PLA/PBS matrix (a) NCC = 0 wt%, (b) NCC = 0.5 wt%, (c) NCC = 0.75 wt%, (d) NCC = 1 wt%, and (e) NCC = 1.5 wt%. [341], copyright 2021. Reproduced with permission from MDPI AG.

structure and for 20 wt. PBSA% is dispersed into a phase structure of PBSA drops in the PLA matrix. The co-continuous structure also has the greatest impact resistance. Conversely, the structure with the PBSA in a dispersed phase inside the PLA matrix is strongly influenced by the chain extender, which presumably increases the interfacial cohesion forces between the two phases, altering the deformation behavior of the blend.

5.1.9. Blends of PBS with poly(carbonate alkenes) (PAC)

Polypropylene carbonate (PPC) is a poly(alkene carbonate) or a copolymer obtained by catalytically polymerizing carbon dioxide and propylene oxide. It possesses excellent properties, such as a high elongation at break, flexibility and biocompatibility, although it possesses limited stability that compromises its industrial applicability [346]. When mixed with aliphatic and biodegradable linear polyesters, it in turn gives rise to biodegradable blends [347,348]. In contrast with the case with PLA where a partial miscibility is found between PPC and PLA [348], Pang et al. have, instead, verified that PBS and PPC are substantially immiscible in all proportions, with their biphasic behavior evidenced by the presence of two distinct glass transition temperatures between them [347]. The increase in the share of PBS blended with PPC determines a corresponding increase in the yield strength and breaking strength, which has an approximately linear trend with the PBS content. Wang et al. studied the blends of PBS and poly (butylene carbonate) (PBC), varying the mutual proportions over the entire compositional range [349]. The results of the experiment showed that PBS and PBC are also completely immiscible. However, the presence of PBC in the blend accelerates the crystallization rate of the PBS and increases the impact resistance by approximately 9 times when introduced at 40 wt.%. More recently, the study of PBS/PPC blends [350] was resumed using a compatibilizer and a so-called

vane extruder, which is not equipped with screws [351]. The researchers tried to improve the compatibility between the two constituents by introducing a compatibilizer based on dicumyl peroxide within the formulation. The results of the experiment showed that the peroxide promotes entanglement between the PPC and PBS chains, showing, as an effect, a slight increase in the glass transition temperature of the PPC and in the melting temperature of the PBS phase inside the blend. Yun et al. studied PBS / PPC blends compatibilized by adding l-aspartic acid [352]. L-aspartic acid was extremely efficient to improve the processability of the material, as well as in making the two phases compatible by reducing the interfacial tension between them. The addition of small quantities of l-aspartic acid (2 wt.%) allows a significant increase in both the yield strength of the blend and Young's modulus. Henke et al. studied the addition of 20 wt.% of PPC within the PBS/PPC blends, showing a good increase in the impact resistance of the blend [353]. Calderon et al. studied the use of maleic anhydride and dicumyl peroxide as activator for compatibilization of PBS/PPC blends [354]. The researchers have noted the ability to promote radical branching reactions in both PBS and PPC. Moreover, this effect determines a compatibilization between the two phases with a corresponding reduction in the interfacial tension. In a further study, Calderon et al. investigated the role of TBT (titanium butoxide) as a catalyst for the compatibilization of PBS/PPC blends, always in the presence of maleic anhydride activated with dicumyl peroxide [355]. The use of the catalyst made it possible to improve the dispersion between the two phases, reducing the interfacial tension between them. Furthermore, the compatibilizing effect led to a significant increase in the deformation at break (+ 177%). The compatibilizing efficacy of polypropylene carbonate-grafted- maleic anhydride (PPC-g-MA) in the PBS/PPC blends was also discussed [356]. Sun et al., instead, focused their attention on the compatibilization of PBS/PPC blends by using a chain extender with epoxy functionality [357]. The addition of the chain extender with very modest contents (<0.4 wt.%) determines the increase in the tensile strength and the impact resistance of the PBS/PPC blends, although the effect is particularly evident on blends with greater PPC content, which, however, are of minor practical importance.

5.1.10. Blends of PBS with polyvinyl acetate (PVA)

Polyvinyl acetate (PVA) is a transparent, amorphous polymer that is widely used as an adhesive and for other applications in the paper industry. It is widely used in blends with numerous bio-derived polyesters [358], and it exhibits good miscibility promoted by strong hydrogen bonds that can form between the α hydrogens of PVA and the carboxy groups present on aliphatic linear polyesters. Contrary to abundant scientific literature that distinguishes blends between PVA and other biodegradable aliphatic linear polyesters, little has been reported on PBS/PVA blends. Recently, Li et al. carried out a pioneering study, in which PBS/PVA blends were studied with regard to the characteristics of miscibility, highlighting the main thermo-mechanical properties for PVA contents varying between 0 and 30 wt.% [358]. The results of the experiment confirmed a partial miscibility also for PBS/PVA blends precisely because of the strong interactions present between the two phases. The PVA phase disperses uniformly forming dropshaped structures within the PBS matrix. These structures become progressively larger as the PVA content increases within the blend. The PVA also determines an increase in the crystallization speed of the PBS, due to the effect of the heterogeneous nucleation, although the maximum degree of the crystallinity achievable on the PBS phase is reduced due to the inhibiting presence of PVA which, evidently, limits its maximum capacity to reorganize itself into crystalline structures. Finally, the addition of PVA produces a surprising and significant increase in elongation at the break (up to about 45%) in the elastic modulus (up to about 10%) and in the strength at break of the blend (up to about 20%).

5.1.11. Blends of PBS with thermoplastic starch (TPS)

Thermoplastic starch is by far one of the materials, along with PLA, that has been the subject of numerous studies in conjunction with PBS. Thermoplastic starch (TPS) is obtained starting from starch by adding a plasticizer of various kinds, such as, for example, glycerol, sorbitol, urea or, more simply, water. The plasticizer deconstructs the starch, loosening the intramolecular bonds and allowing its processing, in particular in blends with other plastic materials [359]. TPS is widely used as a constituent element of blends with biodegradable polyesters by virtue of its excellent biodegradability in all conditions and its extremely low cost (as of this writing, about 1.35 Euro/kg or about a quarter of the price of a bio-derived PBS).

Zhen et al. studied the use of TPS (50 wt.%) as a constituent element of a blend with PLA (from 50 to 0 wt.%) and PBS (from 0 to 50 wt.%) in the presence of a compatibilizer [361]. The experimental results showed the fundamental role of PBS in increasing the ductility of the blend (elongation at break of 45% for PBS contents of 50 wt.%) as well as the thermal resistance of the material (Vicat Softening Point of about 105 °C for PBS content higher than 10 wt.%). The tensile strength, on the other hand, decays as the PBS content increases (it halves for PBS content of 50 wt.%, settling at about 15 MPa). More recently, Meng et al. studied the compatibilization of PLA/PBSA/TPS blends with a PLA:PBSA=4:1 ratio and TPS levels from 0 to 55 wt.% in the presence of stearic acid [360]. The blends were obtained through both a single step and a double step extrusion process. PLA/PBSA/TPS were also compared to PLA as is. The single-step twin-screw extrusion process followed by single-screw extrusion filming proved to be more efficient, limiting the thermo-mechanical degradation of the material, allowing for an improvement in the tensile properties of 15–20% and in resistance to impact of 30%, even in the face of a reduction in energy consumption of about 35%. The blends showed a decrease in the properties of the tensile strength and stiffness compared to PLA as is, which was more significant with a higher TPS content inside the material. PLA and PBSA form a co-continuous phase in the blend, which is interrupted by the presence of starch that is strongly incompatible with polyesters due to the strong hydrophilicity that contrasts with a strong hydrophobia of PLA and PBSA. The elongation at break of the blend was maximized for a presence of TPS equal to 30 wt.% in correspondence with a value of about 20% being detected (in any case very modest).

Fig. 23a and b show the fracture surfaces of the blend object of study, with a sharp discontinuity between the interfacial microgranules of starch and the polyester resin. Contrary to what was expected, the absence of stearic acid in the formulation favours an improvement in the mechanical performance of the blend, although it should favour a compatibilization effect between the individual constituents of the polymeric material. Zhang et al. instead, used tartaric acid (1-3 wt.%) to compatibilize PBS/TPS blends (30 wt.%) in the presence of glycerol as plasticizer [362]. The presence of tartaric acid allows to obtain an effective compatibilization of the PBS/TPS blend, favouring dispersion between the two constituents and the interfacial affinity between them. In particular, the presence of tartaric acid determines an increase in the tensile strength (from about 15 to 17 MPa), impact resistance (from 2.8 kJ/m² to 6.3 kJ/m²) and elongation at break (17.8 to 36.7%) of the PBS/TPS blend. The compatibilization mechanism due to the effect of tartaric acid is shown in Fig. 24, where the best dispersion of the TPS phase is highlighted, assuming a corrugated and elliptical morphology due to a higher viscosity of the melt. Ni et al. have also shown it is possible to obtain PBS/TPS blends by plasticizing the TPS in situ by adding a mixture of water and glycerol [363]. The presence of water did not induce significant thermo-hydrolytic degradation and the molecular weight of the PBS in the blend was substantially unaltered. Li et al. have shown that by blending PBS with TPS derived from starch entirely consisting of amylopectin (waxy starch), a greater processability of the material was obtained [364]. The tensile strength can increase up to 30% and the elastic modulus, especially in the presence of low PBS content (less than 40 wt.%) can also increase up to 40%. The elongation at break also generally improves in the presence of starch consisting entirely of amylopectin, with a particularly evident effect for high PBS levels (starting from 60 wt.%). These results were also confirmed for PBS/TPS blends in the presence of dibenzoyl peroxide [365] and for PBSA/TPS blends [366]. Wang et al. studied PBS/TPS blends with PBS content ranging from 30 to 50 wt.%. The TPS was plasticized by adding glycerol (30 or 40 phr on the starch as it is) [367]. The addition of starch and glycerol resulted in an increase in the crystallinity of the material against a lower crystallization rate. The blend with a greater glycerol content (40 phr on starch as such) has better compatibility between PBS and TPS. Khalil et al. studied PBSA/TPS blends [368]. The proportions between PBSA and TPS varied over the entire compositional range (from 100 to 0 wt.% of PBSA). The TPS was obtained instead by adding 30 wt% of glycerol to starch on a dry basis. The researchers, exploiting the immiscibility between the two constituents, evaluated the continuity of the phases in PBSA and TPS as the composition of the blend varies, finding a continuity higher than 90% already for the 50/50 wt% composition. This is extremely promising for the controlled release of highly polar migrants. Yun et al. studied PBS (from 100 to 60 wt.%)/TPS blends (plasticized with glycerol or ethylene glycol up to 40 wt.%, even in the presence of and dicumyl peroxide) [369]. A greater number of functional groups of glycerol resulted in a better plasticizer efficacy of the latter compared to ethylene glycol. This is reflected in a worse dispersion (greater aggregation) of the



Fig. 23. SEM images of the cryogenic fracture surface: (a) tensile test samples; (b) hybrid films based on PLA/PBSA/TPS (the index S50 indicate the content of TPS in the blend set at 50 wt%). [360], copyright 2019. Reproduced with permission from Elsevier Science Ltd.

starch in the presence of ethylene glycol. On the other hand, the use of MA-g-PBS (maleic anhydride conjugated on PBS) was studied as a strategy for the compatibilization of PBS/TPS blends (with PBS contents varying between 40 and 60 wt.%) and the addition of the same inside the blend as a compatibilizer [370]. Suchao-in et al. studied the compatibilization between PBS and TPS in the blend by the formation of PBS-g-TPS compounds (chemical grafting between PBS and TPS) [371], using NN'-dicyclohexylcarbodiimide (DCC) as a conjugating agent to generate an ester bond between the two constituents. The conjugating agent promotes the formation of bonds between the hydroxyl groups of the starch and the carboxylic end groups of the PBS, with a considerable increase in the miscibility between the two phases and a consequent improvement in the mechanical properties (doubled elastic modulus of the blend). A similar approach was studied by Fahrngruber et al. to compatibilize blends with starch as is and with plasticized starch (thermoplastic starch (TPS)) [372], finding a slight increase in the elongation at break, the tensile strength and the tear strength of the material. Suttiruengwong et al. studied the compatibilization of PBS/TPS blends (plasticized with low levels of glycerol <10 wt.%) through the use of maleic anhydride/dicumyl peroxide and methylene diisocyanate [373]. The compatibilizers produced a better dispersion between PBS and TPS as well as a slight improvement in its mechanical properties, an effect probably attributable to the formation of primary bonds between PBS and TPS, with the formation of PBS-g-TPS. Different TPS plasticization strategies have also been studied [374]. Liu et al. introduced an ionic liquid (1-butyl-3-methylimidazolium chloride, [BMIM]Cl) as a plasticizer for TPS (20 wt.%) in a blend with PBS, comparing it with glycerol. The ionic liquid, added at 30 phr with respect to the starch allowed for better dispersion between the two phases (Fig. 25), obtaining an elongation at break of the PBS/TPS blend equal to about 90% of the elongation at break of the PBS as it is. The presence of the ionic liquid is also allowed to favour a greater crystallization of the blend (up to 60%). Finally, the plasticization with ionic liquid allows to obtain tensile strength values of 30 MPa, 10 MPa lower than the tensile strength of PBS as it is, but 6 MPa higher than the PBS/TPS blend plasticized with glycerol. Unfortunately, the cost



Fig. 24. Compatibilization of PBS and TPS by tartaric acid. [362], copyright 2019. Reproduced with permission from Elsevier Science Ltd.



Fig. 25. Compatibilization mechanism of the ionic liquid inside PBS/TPS blends. [375], Copyright 2020. Reproduced with permission from Royal Society of Chemistry.

of ionic liquids is very high (up to 3200 Euro/kg), and it does not currently allow for industrial use except in niche applications. The use of ionic liquids was subsequently revived [375,376]. This study confirms the strong interaction generated between PBS (60 wt.%) and TPS in the presence of ionic liquids (10 phr) and an inorganic salt (0 - 4 phr) due to ionic compatibilization. The anionic part of the salts forms an electronic interaction with the oxygen atoms of the hydroxyl groups on the starch molecules and of the ester groups of the polyester. Conversely, the cationic part can interact with the hydrogen atoms of the hydroxyl groups of starch and PBS, with an improvement of up to 30% in tensile strength, elongation at break and modulus. Similar results were more recently obtained where ionic liquids (2-8 wt.%) were used to plasticize PBS/TPS blends (30 wt.%) from rice starch [377]. Xu et al. studied the compatibilization of PBS/TPS blends (40 wt.%) with 1 -buyl-3-methylimidazoliumhalide as an ionic liquid (25 phr on starch) [378]. The addition of the ionic liquid reduces the crystallinity of the mixtures of PBS/TPS and also the size of the starch particles in the PBS matrix. The ionic liquid compatibilizes the two phases, favouring the transition to a homogeneous morphology. The results of the tensile test showed that the presence of the ionic liquid in the blend determines the increase in elongation at break from 22% to 93%.

Lai et al. have studied the preparation of bio-composites by adding bio-derived fibers (loofah fiber and kenaf at 10 phr) to blend SAWS and TPS (up to 30 wt.%) [379]. The researchers have found a significant increase in the stiffness of the material due to the addition of fibers (increase in the elastic modulus from 200 to almost 500 MPa) in the face. However, there was a drastic reduction in the elongation at break (from about 120% to a few percentage points), even when compared to the elongation at break of unreinforced PBSL/TPS blends. The impact resistance of the vegetable fiber reinforced blend is also halved compared to the PBS value as it is, going from about 23 J/m to about 12 J/m. However, in this case, no significant differences were found between the results of the PBSL/TPS blends in the presence and absence of the vegetable fiber. Finally, the composite shows an increased capacity to absorb water, which suggests an increase in the biodegradability of the material in the presence of vegetable fiber. Ayu et al. studied a bio-composite obtained by dispersing empty fruit bunches (EFB) inside PBS/TPS blends plasticized with glycerol [380]. The affinity between the vegetable reinforcement and the blend was very poor as expected. However, the presence of the reinforcement phase allowed to obtain a slight improvement in the mechanical performance of the blend with the tensile and flexural strength increasing by 6 and 12.2%, respectively, in the presence of EBS content of 20 wt.%. Furthermore, the presence of bio-derivation reinforcement determines a greater water absorption [379], which suggests an increase in the degradability of the material. Nazrin et al. studied PLA/PBS/TPS blends reinforced with nano-cellulose [381]. The researchers showed that the presence of the nano-cellulose leads to an improvement in the thermo-mechanical properties (increase in flexural strength of up to about 20%) as well as in impermeability to gases, against a significant reduction in the cost of the material. Moreover, the addition of compatibilizers promotes a fine dispersion of nano-cellulose to within the polymer, improving the dispersion of the individual constituent phases within the material itself.

5.1.12. Biodegradable thermoplastic elastomers based on PBS

Recently, the interest in biodegradable thermoplastic elastomers (BTPE) has grown significantly in response to market demand for solutions to reduce pollution and environmental impact. One possible way to prepare BTPE is to armour biodegradable polyesters with natural rubbers (NR). NRs offer numerous properties among which we can mention flexibility, elasticity, resilience, damping capacity and adhesiveness. Furthermore, NRs are unsaturated polymers that degrade in the presence of high temperatures or in the presence of oxygen, ozone or UV radiation. This characteristic makes them inadequate for use in certain applications and also enhances their biodegradability and environmental compatibility. On the other hand, the epoxidized NR (ENR) are more stable and are largely insoluble to hydrocarbons and impermeable to gaseous molecules. Therefore, these are of considerable interest for practical use. NREs obviously have a lower biodegradability, so it is of interest to blend them with biodegradable polyesters such as PBS to obtain BTPE [382]. Faibunchan et al. studied ENR and PBS blends (50 wt.%) obtained by melt blending to characterise their morphology and optimize the production of BTPE.

Scientists have identified the best process conditions to obtain BTPEs, which are associated with excellent stiffness, tensile strength, and elongation at break properties. These properties are associated with the formation of co-continuous structures between ENR and PBS characterized by a finer dispersion of one phase in the other phase. The use of epoxidized NR with 50% epoxide (ENR-50) compared to 25% (ENR-25) improves the compatibilization between NR and PBS (40 wt.%) by virtue of the higher polarity of ENR-50 or by virtue of the chemical interactions that are more effective to achieve a greater presence of the epoxy functionalities of ENR-50 and the apolar groups of PBS (Fig. 26) [383]. These greater interactions between the two constituents of the blend determine the formation of a co-continuous structure. Therefore, this blend has better thermo-mechanical properties with a significant increase in crystallinity. They also hypothesized that the crystallinity and morphology could be altered during heating and cooling cycles of the material, as described in Fig. 27. In practice, the behavior in the crystallization of the resulting polymeric material is closely related to its temperature. In the molten state, or at the melting temperature, the crystal structures are completely converted to an amorphous state (Fig. 27a). At the crystallization temperature, the molecular segments of the polymeric material align, generating the formation of PBS crystallites from a small growing nuclei (Fig. 27b). The process may eventually expand until crystallization is complete. In the solid state at room temperature, the separated phase morphology of the material consists of regular PBS crystallites that are perfectly dispersed within an amorphous phase in ENR (Fig. 27). generating a complete phase reversal. Faibunchan et al. also studied blends between ENR/PBS with PBS content between 50 and 30 wt.%, produced by melt blending in the absence and in the presence of dynamic vulcanization. In the latter case, the researchers used dicumyl peroxide as a vulcanizing agent [384].

Dynamic vulcanization changes the morphological structure of the blend, passing from a co-continuous phase to a dispersion of cross-linked ENR particles with micrometre size inside the PBS matrix (Fig. 28a and b). These particles have an increasingly finer size as the concentration of PBS inside the blende increases. In addition to improving the mechanical properties of the blend (particularly the elastic modulus, tensile strength, and hardness), vulcanization surprisingly improved the biodegradability of the material, probably due to the lower crystallinity exhibited by the blend and, finally, its greater tendency to absorb moisture.

Meanwhile, Ghosh et al. investigated the possibility of developing BTPEs using branched thermoplastic polyurethanes containing silicones designed to be biodegradable [385]. Fig. 29 shows a scheme to synthesize BTPE through such means. The material has a glass transition temperature of about - 40 °C, exhibiting excellent ductility, toughness, impact and tensile strength. The material also has demonstrated high processability and multiple areas of applicability due to its self-cleaning, self-healing behavior and, above all, a remarkable shape memory effect.

More recently, Liang et al. studied the behavior of bio-derived vulcanized thermoplastic elastomers based on a matrix in PBS (with varying levels between 50 and 20 wt.%) and silicone rubber reinforced with silica (35 wt.%). Compatibility was achieved by using dicumyl peroxide [386]. The vulcanized elastomer showed excellent mechanical properties, good elasticity and high processability. At the end of the melt blending process, a dispersion of drop-shaped particles of PBS was observed within a uniformly distributed silica-reinforced silicone matrix. After dynamic vulcanization, a phase inversion was obtained, with the PBS acting as a matrix and the silica-reinforced silicone dispersed therein in the form of distributed particles (Fig. 30). Prasoetsopha et al. studied blends between PBS (60-100 wt.%) and NR, highlighting that the maximum recommended percentage for NR is 20 wt.%, where the formation of a co-continuous structure between the two constituent phases is observed. For higher percentages, the dispersion of NR in the PBS matrix worsens, resulting in larger agglomerates and a substantial worsening of all mechanical properties [387].

5.2. Ternary blends with PBS

The ternary blends are studied to obtain, through a correct balancing of the single constituents, the final properties that would not be achievable using the individual constituents [391,392]. In this regard, Zhang et al. studied ternary blends composed of PLA, PHBV and PBS [401], particularly with a primary phase constituted by PLA or PHBV present at 60 wt.%. PLA-based blends were added with PHBV and PBS, alternating concentrations of 10 and 30 wt.% for the two additional constituents. Similarly, the blends based on PHBV as main phase were added with PLA and PBS, also in this case alternating the concentrations of 10 and 30 wt.% for the two additional constituents. The results showed limited miscibility only between PHBV and PLA.

Blends based on PLA as the main polymer phase are more ductile and tough after incorporating PHBV and PBS (the elongation at break is almost fivefold and the impact resistance increases by about 40% for blends with PBS at 30 wt.%), which also improves its thermal stability (the HDT increased by about 3-4 °C). The loss of stiffness with respect to as-is PLA is limited (max 0.5 GPa). PHBV-based blends are more flexible (with an elongation at break higher than 80% and an impact resistance of about 30 J/m) and have greater thermal stability (HDT of 72 and 87 °C for blends with 30 wt.% of PLA and PBS, respectively). However, PHBV-based blends have a lower stiffness compared to PLA-based blends, an effect that is partially remedied through the addition of PLA at 30 wt.%. Ravati et al. studied ternary blends consisting of PLA, PBS and PCL



Fig. 26. Descriptive model of the formation of different morphological structure between NR and ENR-25 rubbers and ENR-50 rubber with PBS. [383], copyright 2019. Reproduced with permission from John Wiley & Sons Inc.



Fig. 27. Scheme of the micro-structure of ENR/PBS blends in different status: (a) heating, (b) crystallization at 90 °C and (c) low-temperature solid. [383], copyright 2019. Reproduced with permission from John Wiley & Sons Inc.

(a)

Interaction between ENR and PBS



Fig. 28. Chemical interaction between ENR and PBS in blends achieved by: (a) melt blending; (b) dynamic vulcanization. [384], copyright 2020. Reproduced with permission from Springer Nature.

[402]. It is very interesting to note that the variation in the relative composition of the three constituents results in completely different morphological structures, with the phase present in a smaller quantity that precipitates, forming completely dispersed droplet structures, at the interface between the other two phases which are substantially immiscible (Fig. 31a–h). Furthermore, the morphological structure changes as the relative percentage changes between the two phases, as shown in Fig. 32.

In contrast, ternary blends between PBS, PCL and PBAT exhibit very different behaviors. Basically, PBAT and PBS tend, while remaining substantially immiscible, to form a phase that is completely separate from the PCL (Fig. 33).

Ravati et al. attributed this behavior to the value of the socalled spreading coefficients for various ternary blends (Table 8), as defined by the Harkins equation:

$$\lambda_{ij} = \gamma_{jk} - \gamma_{ik} - \gamma_{ij} \tag{1}$$

where γ represents the interfacial tension for the different polymer pairs [402] and λ is the spreading coefficient that provides an estimate of the component *i* to diffuse in the component *j* and locate between the components *j* e *k*.

The positive values of λ_{ij} determine that phase *i* is able to split phases *j* e *k* (contact is achieved between two phases at a time, i.e., complete wetting morphology). A negative value for all values of λ in a ternary blend indicates that contact can also be made between three phases simultaneously (i.e., partial wetting), as listed in Table 9 and shown by Figs. 34a–h.



Fig. 29. Synthesis scheme of BTPE based on thermoplastic polyurethane with silicone. [385], copyright 2018. Reproduced with permission from American Chemical Society.



Fig. 30. Preparation of blends between PBS and silicone rubber reinforced with silica. [386], copyright 2021. Reproduced with permission from American Chemical Society.

Spreading coefficients (mN/m) for different ternary blends.

PBS/PLA/PCL		PBS/PLA/PBAT	PBS/PLA/PBAT		PBS/PBAT/PCL	
λpbs/pcl	-0.63 ± 0.35	λ _{pbat/pbs}	0.31 ± 0.24	λρβατ/pcl	0.16±0.15	
λpcl/pla	-0.02 ± 0.35	λ _{pbs/pla}	-0.36 \pm 0.24	λpcl/pbs	-0.27±0.15	
λpla/pbs	-0.04 ± 0.35	λ _{pla/pbat}	-0.31 \pm 0.24	λpbs/pbat	-0.38±0.15	



Fig. 31. Schematics and corresponding micrographs of partial wetting behavior at different concentrations of phases after annealing: (a-c) ternary 45.5%PES/45.5%PLA/50%PCL blend; (d-f) ternary 45.5%PES/45.5%PLA/50%PCL blend; (g,h) ternary PBS45%/PLA45%/PCL10% blend. PCL was extracted by acetic acid in (c), (e), (f), and (h). [402], copyright 2013. Reproduced with permission from Elsevier Science Ltd.

Surface and interfacial tensions ($\gamma^{d} e \gamma^{p}$ dispersive and polar contribution).

Polymer	γ	γ ^p	γ^{d}	Interfacial tension			
PBS	$43.6{\pm}0.4$	10.5±0.1	33.1±0.3	Pairs	γij	Pairs	γij
PCL	39.7±0.2	8.2±0.1	31.5±0.1	PBS/PCL	$0.32{\pm}0.1$	PCL/PBAT	$0.06 {\pm} 0.03$
PLA	38.8±0.2	8.5	30.3±0.2	PBS/PLA	0.33±0.12	PBS/PBAT	0.11 ± 0.02
PBAT	41.4±0.3	$9.1 {\pm} 0.1$	32.3±0.2	PLA/PCL	$0.03 {\pm} 0.13^{a}$	PLA/PBAT	$0.08{\pm}0.1^{a}$

^a It should be noted that the minimum value for interfacial tension is zero.

Fenni et al. studied the crystallization of ternary blends between PLA, PBS and PCL alternating for all the constituent percentages of 45, 45 and 10 wt.% [393,394,395]. Fig. 35 shows the presence of the minor phase of the blend (i.e., that present at the 10 wt.%) which has an interface between the phases of the two macro-constituents (i.e., the two phases of blend present at 45 wt.%) that form among themselves perfectly immiscible cocontinuous structures. Kassos et al. studied the effect of incorporating small amounts of PBS into PLA/PCL blends [396]. The morphological analysis evidenced the immiscibility between the various constituents, in particular at more elevated concentrations of PCL and PBS. The results indicate that incorporating a small concentration of PBS has a synergistic effect on the properties of the mixture PLA/PCL (Table 10). Miscibility improved and a general increase in mechanical properties is observed for a ternary blend containing 5 wt.% of both PBS and PCL with respect to blends containing 10% of each polymer. In addition, Garcia-Campo et al. studied blends composed of PLA (60 wt.%) with PHB (10 wt.%) and PBS or PBSA (30 wt.%) obtained via reactive extrusion with a co-rotating twin-screw system in the presence of epoxidized vegetable oils (added to 5 wt.%). The aim of the study was to increase the ductility of PLA [397].

Blending PLA with the other constituents resulted in a reduction in the elastic modulus from about 3.5 GPa to 1.7–1.9 GPa (with multiple values being obtained normally in the presence of epoxidized vegetable oils). The tensile strength was also reduced from about 57.6 MPa to values between 35.1 and 53.4 (with PBSA and vegetable oils causing the most drastic drops). Finally, the elonga-



Fig. 32. Schemes (a) and (b) Morphology changes of the ternary blends A/B/C due to the percentage variations of the three phases and of their ratio in the blend. [402], copyright 2013. Reproduced with permission from Elsevier Science Ltd.

Miscibility, thermal behavior, and mechanical properties of PBS ternary blends.

Blending elements	Compositional Range,%	Miscibility	Crystallization	Mechanical properties	Thermal properties	Refs.
Poly (Lactic Acid) PLA Polyhydroxybutyrate -co- valerate (PHBV)	10 to 30% PBS	PLA and PHBV shows partial miscibility PBS is completely immiscible	PHBV incorporation promotes crystallization in both PBS and PLA PHBV crystallization is suppressed by PLA/PBS	Ternary blends of PHBV (main phase) with PBS and PLA (secondary phases) exhibits optimal balance stiffness/toughness	PHBV and PBS increases the thermal resistance of PLA	[401]
Poly (Lactic Acid) PLA Polyhydroxybutyrate (PHB)	30% PBS 30% PBSA	Immiscible, with miscibility improved in presence of epoxidized vegetable oil (EVO)	PLA cold crystallization restricted by the presence of PHB	Improvement of impact resistance by addition of PBS and PBSA as third components of the ternary blends Reduction in stiffness/strength by the addition of PBS or PBSA	HDT and VICAT of the ternary blends are lower than As-is PLA	[397]
Poly (Lactic Acid) PLA Poly(butylene adipate-co-terephthalate) PBAT	Several	Complete wetting tri-continuous	Not investigated	Not investigated	Not investigated	[402]
Poly (Lactic Acid) PLA Polycaprolactone PCL	PBS 0 – 15% in ternary blends	Completely immiscible, especially for higher PCL and PBS loadings	Minimally influenced	PBS and PCL improve toughness and ductility of ternary blends of PLA when their concentration is low (5%) Stiffness and strength of PLA decreases with PBS and PCL	Glass transition of PLA is decreased in ternary blends with 5 wt.% of PCL and PBS	[396]
Poly (Lactic Acid) PLA Polycaprolactone PCL	10 or 45% PBS in ternary blends	partial wetting, but substantially immiscible	dependent on morphology of the ternary blends	Not investigated	Negligible influence of blend morphology and polymer content.	[393] [394]
Poly (Lactic Acid) PLA Poly (Vinyl Phenol) PVPh	PLA: PVPh = 1:1 PVPh up to 50%	PVPh improves miscibility of the ternary blends	PVPh suppresses crystallization of PBSA PVPH accelerates slightly crystallization rate of PLA	Not investigated	A unique glass transition can be achieved by using PVPh at 50 wt.%	[398]
Polyhydroxybutyrate -co- valerate (PHBV) Poly (Ethylene Glycol) PEG	0 to 70% PBS	PHBV and PBS are totally immiscible PEG only partially improved their miscibility	PEG suppresses the crystallization of the blends	PBS:PHBV: PEG=50:20:30 ensures balance of toughness/stiffness	Melting temperature of PHBV decrease by PEG	[399]



Fig. 33. PBS/PBAT/PCL: (a) low content of PBAT in PBS; (b) low content of PBS in PBAT. [402], Copyright 2013. Reproduced with permission from Elsevier Science Ltd.



Fig. 34. (a–f) partial wetting; (b–h) complete wetting; (c–g) both phenomena, achieved starting from scenario (d–e). [402], Copyright 2013. Reproduced with permission from Elsevier Science Ltd.

tion at break goes from values of about 7.6% of as-is PLA to values that reach 170% in the presence of PBA and PBSA added with epoxidized soybean oil. The presence of PBS, PBSA and epoxidized vegetable oils also determine a significant increase in the impact resistance of PLA, which goes from 1.59 to over 10 kJ/m². Surprisingly, the addition of PBS does not allow an increase in the HDT of the PLA, despite as-is PBS having an HDT higher than that of PLA by at least 30 °C. The HDT of the blends does not appear to be affected significantly by the presence of the epoxidized vegetable oils.

Processing of PBS-based materials

The main methods to obtain final products from conventional polymeric materials are based on melt processing, in which the material is heated to a temperature above its melting point, and then, it is solidified to take the required shape using a suitable procedure. Usually this is conducted for the common polymeric materials, like PE and PLA, through various processing techniques, including, but not limited to, extrusion, injection moulding, stretch blow moulding, extrusion blown film, cast film and sheet, thermoforming, and electrospinning (Fig. 36). Even though, the fundament



Fig. 35. Morphology of the ternary blends PLA, PBS e PCL with variable compositions of the three constituents set at 45, 45 e 10 wt.%. [393], Copyright 2019. Reproduced with permission from Elsevier Science Ltd.

tals of these techniques are well-known due to their long history and their importance in the industrial fields, a basic understanding is needed on the relationship between the properties of the polymeric materials and the employed processing conditions (temperature, time, pressure, etc.). Accordingly, when discussing these techniques for new a polymeric material, the properties of this material should be fully understood. For example, to optimize processing conditions, and to improve the quality of the final plastic part, rheological, thermal, and crystallization properties of the polymeric material should be investigated and determined prior to the processing. Up to this end, it will be worth saying that such discussion should be given a full attention when it is made for a specific polymeric material, like PBS in this work, and here, to reach critical conclusions on the processability of this material, the propertyprocessing conditions relationship should be closely considered. In this regard, to reach critical points related to the processing techniques of PBS, more space should be offered here, but considering the main target of the present work, which is to review various concepts related to PBS, like material chemistry and applications, it was selected to just focus on the additive manufacturing (AM) process, as an emerging technology.

AM technology, also known as 3D printing, is applicable to fabricate various types of materials, e.g., polymers, metals, and concretes, through layer-by-layer deposition [401,402]. It is a highly flexible method for rapid prototyping and manufacturing of products with complex shapes [403]. To achieve sustainable 3D printing, researchers are studying various biobased materials for use as potential candidates to replace petrol-based polymers [404,405].

Among various types of 3D printing techniques, fused deposition modeling (FDM) is the most common method due to its versatility, ease of use, and low cost [247]. It requires minimal technical knowledge that makes it an ideal option for many manufacturers [406]. Although many polymeric materials are available for FDM printing, the choice is very limited for use with eco-friendly and biodegradable products [407–409]. Accordingly, research and development of biobased filaments for FDM have received a significant amount of attention that is not only beneficial for the environment and reduces plastic usage but also decreases the cost of printing filaments.

Polylactic acid (PLA) is a major biopolymer in the market for 3D printing processes, and many studies have tried to develop novel methods to improve its mechanical properties, particularly its brittleness [410,411]. In recent years, researchers have reported on the development of other biopolymers for 3D printing process, such as polybutylene succinate (PBS) [412], polybutylene adipate-coterephthalate (PBAT) [413,414], Polyhydroxyalkanoates (PHA) [415], or other aliphatic polyesters [416,417]. PBS blends in particular have shown excellent capability in 3D printing of fully bio-based products. For example, Qahtani et al. [418] investigated the printability of the PLA-PBS blend using FDM printing. First, they produced the filament through extrusion and then used an FDM printer to fabricate tensile samples using various sets of parameters, as shown in Fig. 37a and b. They found that the printing temperature has a significant effect on the flowability of the filament on the nozzle and, consequently, on the layer adhesion of the printed parts. Therefore, they reported on the influence that printing temperature has on the viscoelastic behavior of the filament. Fig. 37c illustrates the results of the viscosity test for the PLA-PBS 70/30 blend using various printing temperatures between 180 and 270 °C.



Fig. 36. The most common processing techniques used for polymeric materials. (a) The screw used in extrusion process, (b) Injection moulding, (c) Extrusion blown film, (d) Cast film and sheet, (e) Thermoforming, and (f) Electrospinning. [400], copyright 2008. Reproduced with permission from Elsevier Science Ltd.

This graph shows that the complex viscosity of this blend decreases by raising the temperature. The highest amount of viscosity (around 1000 Pa.s) is recorded for a temperature of 180 °C which has poor flowability during 3D printing. In contrast, the viscosity dropped considerably at a high printing temperature (270 °C), and this results in the deterioration of the polymer chains. The effect of this phenomenon is uncontrollable filament leakage due to gravity, which is not an ideal printing condition. Finding the optimized temperature also has an impact on the adhesion between the layers, and consequently on the mechanical properties of the printed sample. As shown in Fig. 37d and e, the sample printed at 250 °C has a better dimensional accuracy and adhesion between the layers compared to the other one printed at 220 °C.

Di Lorenzo [419] investigated the printability of PLA/PBS blends using FDM printing in biomedical applications and in scaffolds for tissue engineering. They determined that the increase of PBS in the blend can produce a filament that is more ductile with improved mechanical properties. However, shrinkage might occur during printing. They found that the blend including 40–60% of PBS has optimal properties as the printing filament with minimum shrinkage. Ou-Yang et al. [420] also investigated the printability of PBS/PLA Blend Filaments at various rates (20–80%) using an FDM printer. They found the blend with more than 40% wt. PLA has a better printing surface without any detachment or distortion, and the mechanical properties, including tensile modulus, strength, and melt viscosity, are better and more suitable for FDM printing. Fig. 38a shows the results of samples printed with different PBS rates. As can be seen, there is a serious distortion when the weight ratio of PBS is higher than 80%. This distortion may cause thermal stress and, consequently, column shrinkage in the samples during cooling. Fig. 38b and c also demonstrate two printed objects using FDM printed with PBS60/PLA40 and PBS40/PLA60, respectively.

Badouard et al. [421] explored the applicability of flax fibers and shives in the PLA/PBS blend in order to produce fully biodegradable filaments. They reported that the choice of the matrix has a direct impact on the mechanical properties of the final printed parts. The study showed that plant fibers reinforcing 3D printed products exhibit promising printability and performance, and these could be used as candidates to fabricate fully compostable products. In another study, Zhou et al. [422] used talc in the blend of PBS to enhance the melt strength and performance during printing. For this purpose, they first produced a PBS/Talc filament via melt extrusion and then printed some tensile samples to investigate the mechanical properties of the fabricated



Fig. 37. (a) schematic of the FDM process, (b) for 3D printing of PLA-PBS tensile samples, (c) complex viscosity of the material in a different temperature ranges from 180 to 270 °C, and (d-e) layer adhesion of the printed samples at two different temperatures (220 and 250 °C). [418], copyright 2019. Reproduced with permission from American Chemical Society.



Fig. 38. (a) Schematic of PBS/PLA samples with different weight ratios, (b) Printed rabbit using PBS60/PLA40 filament, and (c) Printed tower using PBS40/PLA60 filament. [420], copyright 2018. Reproduced with permission from American Chemical Society.

parts. Fig. 39a–f show the filament production, printing, and final fabricated parts. The results proved that the application of talc to the PBS biopolymer increases the crystallization temperature and results in improved mechanical properties for the printed samples due to a distinct forming process. The printing temperature was 135 °C, which is much lower than the printing temperature of commercial PLA or ABS filaments. Also, a microscopic investigation shows that an increase in the talc concentration in the blend resulted in an improvement in the formability of the printing pro-

cess, which in turn results in a better surface quality in the printed parts as well.

6. Biodegradability and biomedical application of PBS based materials

Plastic materials can be obtained from raw materials derived from fossil sources, from bio-derivation with other feedstock, or directly in their bio-available form without special interventions.



Fig. 39. (a-f) Schematic of the preparation steps of PBS/Talc printing filaments and the final fabricated tensile samples. [422], Copyright 2019. Reproduced with permission from John Wiley & Sons Inc.

When plastics are derived from raw biological materials, we refer to them as bioplastics. Not all bioplastics are biodegradable, and some fossil-derived plastics can be biodegradable. A classification of plastic materials is shown in Fig. 40.

The biodegradability of polyesters is therefore of crucial importance to develop plastic materials with a low environmental impact for numerous industrial applications. Biodegradable plastics dissolve at different speeds depending on the conditions of the controlled or uncontrolled environment in which degradation takes place, leaving non-toxic residues, and, in many cases, reusable material. There are numerous standards and directives to regulate the biodegradation of plastics. Furthermore, the UNI EN 13,432:2000 standard has definitively clarified the difference between compostability and biodegradability, particularly in that compliant plastic materials must be compostable in an industrial environment or in a controlled environment.

According to the EN 13,432 standard, a material to be defined as compostable in an industrial environment must: (i) degrade by at least 90% in 6 months if subjected to an environment rich in carbon dioxide, in accordance with the standard method EN 14,046 (also called ISO 14,855); (ii) in contact with organic materials for a period of 3 months, the mass of the material must consist of at least 90% of fragments smaller than 2 mm, in accordance with the standard method EN 14,045; (iii) be such as not to induce negative effects on the composting process; (iv) have a low concentration of heavy metals added to the material; (v) have pH values within established limits; (vi) have a salt content within the established limits; (vii) have a concentration of volatile solids within the established limits; have a concentration of nitrogen, phosphorus, magnesium and potassium within the established limits. The compost thus produced can be used as a fertilizer or, more simply, for soil improvement in reclamation operations. On the other hand, there is no universally recognized standard or regulation for the compostability of such materials in a residential setting, such as in a garden composter, since it is not so easy to control the conditions of the composting process as well as can be done in an industrial composting. In particular, the composting process in a domestic environment normally takes place at temperatures of 10-30 °C lower than the composting process in an industrial environment, so it takes place more slowly.

However, there are some local regulations that define the characteristics that a plastic material must possess in order to be considered compostable in a domestic environment: (i) the Australian standard AS 5810 of 2010 relating to biodegradable plastics suitable for composting in the domestic environment; (ii) the French regulation NF T 51,800 of 2015 relating to the definition of the specifications for a plastic to be considered suitable for composting in a domestic environment; (iii) the European regulation prEN 174,267 of 2020 relating to the characteristics that a plastic bag must possess in order to be treated adequately in a domestic composter. Alongside the regulations on compostability in an industrial and domestic environment, specific directives are being disseminated to test the biodegradability of plastics in close-to-real conditions to establish what can happen in the event of accidental dispersion into the environment. Therefore, specific procedures have been defined and are aimed to test the biodegradability of plastics in a marine environment (ASTM D6691), on soil (ISO 17,556) or in an aquatic environment such as rivers, lakes or any source of fresh water (ISO 14,851 - aerobic environment; ISO 14,853 - anaerobic environment).

Narancic et al. carried out an interesting and extensive study on the biodegradability of plastic materials [423]. In particular, the researchers investigated the biodegradability in multiple conditions of PLA, PHB, (polyhydroxyoctanoate) PHO, PBS, TPS, PCL and some blends obtained from them. The results of the tests that were conducted are summarized in Fig. 41. Note how all polymers mentioned are compostable in an industrial environment. On the other hand, PLA, PBS and PHO are not compostable in a home environment, so many blends that involve them continue not to be compostable in a home environment, such as the particularly relevant case of PLA/PBS blends (20 wt.%). Finally, most of the tested polymers are not biodegradable in marine and aquatic environments, with the exception of PHB and TPS. PC joins PHB and TPS as the only biodegradable high polymer on soil.

Fig. 42a-d show, in this sense, a quantitative summary of the results obtained by conducting biodegradation tests in different environments of PLA, PHB, PHO, PBS, TPS, PCL and some blend ob-

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Fig. 40. Classification of bioplastics.

tained from them. Note the 90% line (red dotted line) that corresponds to the minimum target to be reached during execution of the standardized test in order to consider it to have successfully passed and the 100% line (green dotted line) that corresponds to the total biodegradability of the material tested under the conditions tested. The most widely used materials on the market, namely PLA and PBS, are both characterized by extremely limited biodegradability both in marine and aquatic environments and on soil, which in fact significantly limits their possible industrial applications.

Biodegradable and compostable plastics are used in many industrial sectors, such as food packaging, agriculture, and fishing sectors. However, they are also important to use in biomedical and pharmaceutical sectors. Cho et al. investigated the biodegradability and biodegradation rate of PBS compared to PCL, both in an aerobic and an anaerobic environment [424]. The researchers found that PBS in an aerobic environment has a biodegradation rate of just 0.01 day⁻¹ while PCL produced an estimated value of 0.007 day⁻¹, that is, seven times higher. Under anaerobic conditions, PBS showed a very low biodegradability, with a mass loss of 2% in 100 days. On the other hand, the PCL lost 83% over 139 days despite having a biodegradation rate equal to half that obtained for cellulose. Mao et al. studied the biodegradation of PBS due to the bacterial strain fusarium FS 1301 [425]. This strain was found to be effective in the biodegradation of both the amorphous phase and the crystalline phase of PBS. The main degradation products of depolimerasi of PBS were identified as 1,4-succinate, succinate-butanediol, succinate-butanediol-succinate and succinate- butanediol-succinate- butandiol. Strains from the genus fusarium solani were also studied [426,427], and these consistently showed that the biodegradation rate of the polymer depends strictly on the degree of crystallinity. In particular, a lower crystallinity of the plastic material resulted in a higher expected biodegradation rate, although the degradation mechanism is simultaneously active on the amorphous and crystalline fractions. The degradation of PBS was observed to occur in a layer-by-layer mechanism, with the molecular weight of the PBS remaining substantially unchanged before and after degradation. Jbilou et al. assessed the biodegradability of PBSA/starch blends [428] and observed that the starchy part effectively degrades due to the effect of the amylolytic enzymes, whose function is progressively hindered as the PBSA concentration increases, especially when the latter forms a co-continuous phase with starch. However, the addition of lipase to hydrolyze the PBSA ester bonds tends to restore the rate of starch degradation due to effect of amylolytic enzymes, which become efficient again. Kundys et al. studied the biodegradability of PBS / TPS blends [429] in the presence of α -amylase and an unpurified amylase of bacterial origin. A significant difference was confirmed in the gravimetric weight loss between the degraded mixtures in the two different solutions tested. The unpurified microbial enzymes produced by rhizopus oryzaecultures decomposed the materials more efficiently than their purified commercial counterparts. Kuo et al. studied the biodegradation of PBSA blends reinforced with hexadecylamine-modified zinc phenylphosphonate (m-PPZn) produced with a single-screw extruder [430]. The examina-



Fig. 41. Synthesis of the biodegradation tests. [423], copyright 2018. Reproduced with permission from American Chemical Society.



Fig. 42. Biodegradation of PLA, PHB, PCL, PBS, PHO, PHB, TPS and some of their blends in water, marine environments and on soil. [423], copyright 2018. Reproduced with permission from American Chemical Society.

tion of the morphology of the blend revealed the presence of partially intercalated and partially exfoliated m-PPZn particles within the PBSA matrix, in the absence of a clear phase separation between the two constituents of the composite. The rate of biodegradation was measured by employing d or lipase from Pseudomonas sp., showing an increase in biodegradability in the presence of higher levels of m-PPZn. This result, which can be ascribed to a lower crystallinity of the polymeric phase and to a lower thickness of the lamellae as the m-PPZn content increases also allows to modulate the biodegradation rate of the material simply by varying the amount of reinforcing phase. The biodegradation rate of the composite, in fact, varies almost linearly with the concentration of the reinforcement. Shi et al., instead, investigated the biodegradability of PLA/PBS blends through an enzymatic route in the presence of cutinase and K-proteinase [431]. The results in terms of the weight loss of PBS/PLA blends degraded by the cutinase and the proteinase K suggest that PLA hinders the degradation of PBS catalyzed by cutinase. The addition of PBS in the mixtures accelerates the degradation of the PLA within a specific ratio of PBS/PLA up to 50 wt.%. The change in the crystallinity after degradation is closely related to the different degradation kinetics of the two constituents of the blend. The characterization of the PBS/PLA mixtures shows that after degradation, the pores formed by proteinase K within the polymeric material were more uniform and larger than those formed from cutinase. Delamarche et al. studied the biodegradability of PLA/PBS blends (60 wt.%) in the presence of 1 wt.% of deep eutectic solvents (DESs), in particular of a mixture of choline chloride/glycerol (1:2 mole ratio), which can act as a compatibilizing agent for the mixture [432]. The researchers have shown that the addition of DESs inside the blende favours the formation of phases dispersed in it by each constituent. Although this does not involve significant changes in the thermo-mechanical properties of the blend, the presence of DESs appears to promote the biodegradation rate of the blend, reducing the temperature at which the material disintegrates and generates smaller fragments. It seems that PLA is the most sensitive to the addition of DESs, also showing a reduction in the melting temperature and a faster reduction in the mass fraction of PLA inside the blend. Han et al. studied the biodegradability of PBS/Ramie fiber composites (RFF, 50 wt.%), with the latter modified on the surface with amino functionalities [433]. The composites thus obtained show excellent mechanical properties (tensile strength, elongation at break, flexural strength, flexural modulus, interlaminar shear strength (ILSS) and impact strength, respectively, equal to 72.4 MPa, 19.4%, 100.5 MPa, 4.9 GPa, 3.3 MPa and 67.5 kJ/m²). fiber content above 50 wt.% determines the decay of all mechanical properties of the composite. Furthermore, the biodegradation rate is significantly accelerated in the presence of the fiber. Tolga et al. studied the biodegradation process of PLA/PBS blends (30 wt.%) in the presence of talc (5 or 15 wt.%, fine and coarse grained) or gypsum (5 or 15 wt.%) in industrial composting conditions [434]. The disintegration studies show how talc disfavours the degradation process of the blend which, on the other hand, is favoured in the presence of gypsum which is more hydrophilic. Therefore, it is possible to control the biodegradation rate of the PLA/PBS blend by adding mineral phases. For example, plastic films are used in agriculture to retard the growth of weeds and to allow the retention of water in soil. After harvesting, these films must be disposed of, posing a huge environmental problem, given that the material is very dirty and deteriorated and therefore extremely difficult to revalue. For this reason, this material is often sent to a landfill or is thermovalorised. The use of biodegradable plastic films would be of fundamental importance since it would simplify their disposal. In particular, the compostable films could be collected to be sent to a suitable composting process to obtain compost for use on the same fields, favouring a logic of reuse that is fully compliant with the paradigms of the circular economy. The plastic films, if biodegradable on soil, could be left in the field without the need to be collected, even without impacting the environment in the least. Abe et al. investigated the use of PBS for mulch film manufacturing [435]. The researchers studied soil degradation mechanisms using fungal strains of the fusarium solani class, and they determined a degradation rate of 2.8% in 14 days in sterile soil. They also noted a synergistic effect on the biodegradability of PBS in the presence of the bacterial strain stenotrophomonas maltophilia. However, in the presence of non-sterile soil, the degradation mechanisms in question were less efficient due to competition with other micro-organisms that slowed down the process. Phua et al. studied soil biodegradation of montmorillonite-reinforced PBS [436]. The presence of montmorillonite caused a significant slowdown in the biodegradation of PBS (- 15% of CO₂ released after 180 days in the presence of 2 wt.% of montmorillonite), probably due to greater impermeability of the composite compared to as-is PBS. The use of PBS conjugated with maleic anhydride PBS-g-MA instead determines the almost total restoration of the biodegradation capacity of the PBS, with small differences in the presence or absence of 2 wt.% montmorillonite. Zheng et al. observed that PBS and PLA exhibit the same degradation rate on soil [437]. Huang et al. studied the biodegradability on soil of PBS-based composites reinforced with sugar cane fiber [223]. The results showed that adding 5 wt.% of bio-derived fiber within the composite material resulted in a significant increase in the biodegradation rate, especially by treating the fiber with an alkaline surface treatment that causes an increase in the surface roughness of the fiber itself and a higher hydrophilicity. Palai et al. compared the biodegradability on soil of films obtained by blown extrusion in PLA, PLA/PBSA (5 wt.%), and PLA/TPS (20 wt.%) [438]. Adding PBSA to PLA accelerated the biodegradation process. In fact, the tensile strength of the degraded film drops by 60.32% in the case of the PLA film and by as much as 71.28% in the case of the PLA/PBSA film. However, the PLA/TPS film has the greatest biodegradability with a decrease in the tensile strength of the corresponding film of 75.31%. Chen et al. studied the biodegradability of PCL/PBS blends [293], aiming to form a suitable system to control the release of anti-vegetative species for marine applications. They noted that as the concentration of PBS increases, the PCL spherulites decrease in size. This causes an increase in the total amorphous area between the PCL and PBS spherulites, and therefore biodegradation is favoured. This mechanism allows to regulate the biodegradation rate of PCL/PBS blends in the marine environment, and therefore, to control the release of anti-vegetative species. Biodegradability in seawater is also the subject of the study [439]. The researchers investigated marine biodegradation of polyhydroxybutyrate-co-hexanoate PHB-HHx and its blends with numerous polyesters, such as PBAT, PBS and PLA, using the biological oxygen demand (BOD) methodology. The biodegradability of PHBHHx over a 28-day trial was excellent. The blends show biodegradability as a function of PHBHHx content in the blend itself. The biodegradability of PBS in the marine environment is considered to be irrelevant (1%). Blended PHBHHx/PBS (20 wt.%) shows, however, a percentage of biodegradation of 41% in a marine environment, with the PBS content in blend at the end of the test increasing from 20 to 24 wt.%. However, PBS blended with PHBHHx proved to be more degradable in a marine environment than blends with similar characteristics but based on PLA (PHB-HHx/PLA - 20 wt.%) and PBAT (PHBHHx/PBAT - 20 wt.%). These blends, respectively, showed a percentage of biodegradation in the marine environment of 33 and 19 wt.%.

Among various types of biomaterials, aliphatic polyesters have been utilized in various biomedical applications since they are biodegradable and easy to synthesize in combination with other materials [305]. In particular, PBS biopolymer is an excellent aliphatic biopolymer with many promising biomedical applications mainly due to its excellent chemical resistance, melt processability, biodegradability, good biocompatibility, and thermal properties that make it an ideal candidate compared to other aliphatic polymers [48,440-442]. These characteristics also make PBS a great candidate for temporary use products. For example, the biodegradability of the PBS biopolymer can be used to fabricate bioimplants so that additional surgery to remove implants from the body can be avoided since these bioimplants can be degraded or absorbed in the body. It is notable that the degradation ratio has a direct impact on cellular processes, such as tissue regeneration, cell growth, and host response [443]. Hence, the degradation of the PBS polymers needs to be investigated in a physiological environment to evaluate the potential for use in tissue engineering.

Besides their degradation, biomaterials should also demonstrate proper biocompatibility in physiological environments to be successfully implanted in the body. Indeed, biocompatibility is related to the behavior of the body cells, as well as the cell morphology, adhesion, and proliferation, in contact with the biomaterial [43]. Gigli et al. reported that PBS-based copolymers and composites have good *in vivo* and *in vitro* biocompatibility according to various experimental conditions [1]. As a result, they can be applied in different areas of tissue engineering, ranging from bone tissue replacement to myocardial applications.

In the following, some publications discuss the benefits of the PBS biopolymer in the design and fabrication of biomedical products. For example, Gigli et al. [1] reported that PBS biopolymers have excellent potential to produce bone marrow stem cells. The results of the study showed that PBS has a better capability and higher tendency than PLA or Polyvinyl Chloride (PVC) polymers to generate new tissue growth. In another study, Li et al. [43] investigated the degradation of a PBS biopolymer. The degradation rate indicates the potential for use of PBS in biomedical applications and tissue engineering [444,445]. Therefore, it should have the appropriate molecular weight and

Fig. 43. Osteoblast proliferation on the PBS biopolymer during 7 days. [43], copyright 2005. Reproduced with permission from John Wiley & Sons Inc.

mechanical properties for use in tissue replacement. They found that the physiological environments have a significant impact on the growing process of new tissue. Fig. 43 shows osteoblast proliferation on a PBS sample for 7 days. As can be seen, the number of osteoblast cells increased quickly, and the surface of the PBS plates is fully covered by cells for only 7 days [446].

The PBS polymer can be applied in the fabrication of various medical devices. However, there are some limitations in its applicability in terms of the mechanical properties, surface quality, and thermal degradation. Consequently, blending PBS with other polymers or fillers can help overcome these restrictions [447]. Some studies have suggested blending PBS with other materials in order to improve various properties, e.g., the thermo-mechanical properties, of the material that help in cellular interactions, adhesion, and damage repair [448]. For example, blending PBS with chitosan results in quick cell growth and better protein absorption for bone repair [449-452]. A PBS and hydroxyapatite (HA) composite can also be applied for this purpose [1,453]. Likewise, a combination of PBS with Poly(glycerol sebacate) and dilinoleate (PGS/PBS-DLA) proved to have great capability to fabricate fibrous scaffolds that can be applied in cardiac tissue engineering [454]. PBS-based polymers or composites have potential for use in drug delivery applications as well. In particular, drugs can be released through the polymer matrix mainly by changing the environmental conditions (temperature or pH) and diffusion-controlled release [1,455-458]. Fig. 44a-c demonstrate the three main drug delivery mechanisms based on various release methods. For example, Mohanraj et al. used PBS biopolymer to produce microcapsules loaded with anti-Parkinson's medicine. They reported a high encapsulation efficiency so that the drug releases smoothly during delivery [459].

Besides the many advantages of the PBS biopolymer for tissue engineering, it also has a few challenges, including susceptibility to bacterial infection and inadequate osteocompatibility after implanting in the body. Consequently, it requires a surface treatment or modification to improve this issue [48]. To this end, Domínguez-Robles et al. [230] applied a blend of Lignin (LIG) and PBS biopolymer due to the antioxidant and antibacterial properties suitable for biomedical applications and to prevent infection in the fabricated parts. *S. aureus* is a common infection in medical devices, and the PBS/LIG composite can reduce the adherent bacteria significantly to up to 90%. Fig. 45 illustrates that the PBS/LIG composite is an extremely promising anti-infective material for wide use in biomedical applications.

7. Future trends

PBS is a biodegradable polymer that is suitable to fabricate a wide range of applications that can substitute plastic materials and overcome environmental concerns. Therefore, it would have a great impact on global plastic production and can be used as a future reference. Also, the cost and availability of PBS must be taken into account to successfully utilize it instead of conventional plastic polymers. As discussed, PBS biopolymer has specific physical and mechanical properties and can be easily synthesized via melt polycondensation at a reasonable cost. The major characteristic of this polymer is its full biodegradability that is obtained from a renewable source, which makes it a unique material to fabricate

Fig. 44. The mechanism of the drug release process including (a) diffusion-controlled release, (b) triggered release, and (c) erosion-controlled release. [1], copyright 2016. Reproduced with permission from Elsevier Science Ltd.

Fig. 45. Bacterial adhesion reduction based on LIG content (%) in the PBS/LIG composite. [230], copyright 2019. Adapted with permission from Elsevier Science Ltd.

bio-derived products. However, it must exhibit some major characteristics, such as adequate biocompatibility, biodegradability, and mechanical properties, to be reliable to produce a wide range of bio-derive products, from biomedical devices to packaging applications. PBS itself cannot be used in certain applications. The brittleness of PBS is its principal drawback that limits the mechanical strength and elongation of PBS products. Therefore, blending and copolymerization can be applied as a solution to improve the PBS characteristics for future applications in various domains [1]. Furthermore, the PBS bio-composites could provide additional reinforcements by adding natural fibers to the structure without losing processability [48].

So far, different experimental techniques and fabrication methods have been employed to produce biodegradable and compatible PBS-based composites and copolymers. PBS and its copolymers have branched structures and consequently high weight, which makes them suitable to produce films for product packaging. Therefore, blown film extrusion has major demand in the market, particularly for packaging processes [460]. However, due to the limitations of pure PBS, PBS blends with other biomaterials, such as starch and PLA, will be used to improve the strength of the final products, and the material will also be cheaper by further development of fermentation technologies and by exploring novel fabrication techniques [461]. Fig. 46 demonstrates the future trends and applications of PBS biopolymers. As shown, PBS currently has various applications that are mainly related to the fabrication of bioderived products, such as agricultural films, food packaging, and fabrics. Recent development there will be more studies on biomedical applications of PBS biopolymers and composites, particularly in the fields of tissue engineering and drug delivery where the controlled release of drugs from thin films, micro/nanocarriers, or scaffolds will be a major topic. Thus, more research is needed through clinical trials and in vivo tests for biomedical PBS products and devices before being commercially advertised and employed in the market.

The future of PBS polymers depends on further development in various aspects. First, low-cost manufacturing, mass production, and increased customer demand can have a direct impact on the final cost and availability of cheaper biopolymers. Second, the application of new additive natural fibers, with different ratios, shapes, and varieties will help improve the material properties and functionality of the fabricated products. Finally, future studies will open up novel applications of PBS in industry through the integration of nanomaterials into the blend, providing new functionalities for PBS-based products. There are still many potential applications that are yet to be discovered as medical products, food packaging, thin films, and so on. Thus, these numerous applications of PBS will attract further use by industry and consumers in the future.

The designing of PBS copolymers to fit the different applications is another trend which need to be considered when the future works of PBS polymers are discussed. This comes from the importance of molecular architecture and the nature of co-monomer to control the various properties, including crystallinity, mechanical properties and biodegradation, of the final copolymer. Here, in addition to the PBS copolymers discussed in this review, new types of copolymers should be considered in future, and that is for broadening the applicability of PBS polymers. For example, due to the good biocompatibility and biodegradability of PBS, the micellization of PBS-based copolymers can be an important topic for further investigations in the fields of molecular brushes and drug delivery,

Fig. 46. Future trends and applications of PBS biopolymers.

Fig. 47. Triboelectric nanogenerator (TENG) based on multilayered MXene/PLA composites. [463], copyright 2021. Reproduced with permission from Elsevier Science Ltd.

where the monomer to be co-polymerized with PBS should be selected carefully to reach an optimized micellization behavior.

The recyclability of PBS blends with non-biodegradable polymers, like PE, is also another direction, which should be investigated more broadly in future works. In this regard, starting from the very few works reported on the compostability of biodegradable/non-biodegradable polymer blends, a general finding showed that the biodegradability of the blend is higher than the neat non-biodegradable polymer, and this, in turn, was simply figured out based on the presence of the biodegradable polymer. On the other hand, even these blends exhibited some levels of biodegradability; they are still far away from being considered as a solution for plastic waste accumulation. Accordingly, the future efforts in this field should be more orientted to study the recyclability and/or re-formability of these systems. In addition, when handling the fully biodegradable PBS-based materials, it will be worth asking whether the recycling is still required.

The energy related applications of PBS-based materials are also of importance in future works, where flexible or/and stretchable electronic materials are needed for these applications. In general, petroleum-derived non-biodegradable polymers, like polyurethan (PU), are usually used, and in order to enhance its electrical conductivity, composites based on these polymers are fabricated, like graphene nanoplatelets-contained composites [462]. On the other hand, the employment of these polymers (petroleum-derived) comes with a disadvantage related to their non-degradability nature. As an alternative, biodegradable polymers can be used in these applications, where the mentioned disadvantage can be avoided. In this regard, PLA was recently employed in such applications, where a triboelectric nanogenerator (TENG) based on multilayered MXene/PLA composites were fabricated using electrospinning technique [463], as shown by Fig. 47, and this nanogenerator exhibited a good performance which was comparable with nonbiodegradable-based TENGs.

Finally, it is also important to focus more on the employment of PBS based materials to fabricate hierarchically porous materials, which have a high potential in biomedical applications, like tissue scaffolding. In general, the porous structures, for this application, consist of pores with bimodal distributions, where fine pores (submicrometer scale) are distributed in the walls of coarser pores (micrometer scale). Here, micrometer-scale pores can significantly enhance the tissue growth, whereas cell differentiation can be assisted by the finer ones in the submicrometer scale. Generally, binary polymer blends with a co-continuous morphology are used to fabricate porous materials, and in this case, a unimodal distribution is obtained, where one phase is extracted by a selective solvent. On the other hand, for fabricating the hierarchically porous structure, ternary blends with specific morphologies should be prepared, and here, solvents are selected carefully to extract the phases, leaving behind the required hierarchically porous structure of the targeted polymer [387,393]. It is well known that the morphologies evolved during polymer blending are mainly related to the blending conditions (mixing technology, time, temperature and compatibilizers) and blended polymer characteristics (rheological and mechanical behaviors). Accordingly, to fabricate porous PBS materials successfully, the processing conditions and the two polymers to be blended with PBS should be selected carefully, and the presence of a co-solvent should be considered as well.

8. Conclusions

The present review was conducted to summarize the materials chemistry, properties, processing, and applications of PBS. For this purpose, the recently reported works on the preparation of PBS polymer and copolymers, properties of PBS and its blends, 3D printing of PBS, and finally, the biodegradability and biomedical applications of PBS-based materials were collected and critically discussed. The following findings were reached in the present work.

- (1) As compared to some other biodegradable polymers, PBS shows a well balance between the cost, mechanical performance, thermal stability, biodegradability, and processability, making it suitable candidate in a wide range of fields from biomedical devices to packaging applications.
- (2) The various properties of PBS, such as mechanical and thermal properties, could be improved significantly using the copolymerization strategy. For example, it was found that the thermal stability of PBS could be enhanced though a copolymerization with terephthalate to form poly(butylene succinate-coterephthalate). The electrospinning-ability was also found to be improved in poly(butylene succinate-co-dilinoleic succinate).
- (3) The blending technique was also used to tune the properties and processability of this polymer, where the fabrication, processing, and performance of various PBS blends, such as PBS/PLA, PBS/TPS, PBS/PBAT, and PBS/PCL, were reviewed. Additionally, it was found that the addition of compatibilizers can highly enhance the properties of the blends, especially in those with low miscibility, where these compatibilizers were mostly found to enhance the intermolecular interactions, and thus, to reduce the interfacial tension between the different phases in the blend. The selection of the suitable compatibilizer is mainly related to the blended polymer, whether it has functional groups or not, and the type of these groups.
- (4) PBS and its materials showed high processibility using the 3D printing technology, where they could be fabricated using this technology to form fully bio-based products.
- (5) Future work should be focused on improving the recyclability of PBS-based materials. In addition, the application of this polymer to fabricate hierarchically porous materials for biomedical applications should receive more interest in the future works.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.progpolymsci.2022. 101579.

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