We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter

New High-Performance Materials: Bio-Based, Eco-Friendly Polyimides

Radu Dan Rusu and Marc J.M. Abadie

Abstract

The development of high-performance bio-based polyimides (PIs) seems a difficult task due to the incompatibility between petrochemical-derived, aromatic monomers and renewable, natural resources. Moreover, their production usually implies less eco-friendly experimental conditions, especially in terms of solvents and thermal conditions. In this chapter, we touch some of the most significant research endeavors that were devoted in the last decade to engineering naturally derived PI building blocks based on nontoxic, bio-renewable feedstocks. In most cases, the structural motifs of natural products are modified toward amine functionalities that are then used in classical or nonconventional methods for PI synthesis. We follow their evolution as viable alternatives to traditional starting compounds and prove they are able to generate eco-friendly PI materials that retain a combination of high-performance characteristics, or even bring some novel, enhanced features to the field. At the same time, serious progress has been made in the field of nonconventional synthetic and processing options for the development of PI-based materials. Greener experimental conditions such as ionic liquids, supercritical fluids, microwaves, and geothermal techniques represent feasible routes and reduce the negative environmental footprint of PIs' development. We also approach some insights regarding the sustainability, degradation, and recycling of PI-based materials.

Keywords: bio-based polyimides, renewable monomers, polyimide recycling, ionic liquids, supercritical fluids, microwave synthesis, geothermal synthesis

1. Introduction

Long-established, commercial or innovative, tailor-made, functional polyimides (PIs) represent a benchmark for high-performance polymers and demonstrate many advantages, which include excellent thermo-oxidative stability, chemical inertness, high mechanical resistance, high dielectric strength, as well as a remarkable combination of thermal, mechanical, and electrical insulating properties [1–4]. Therefore, these heterocyclic polymers have found applications in many advanced technology industries, such as aviation, spaceflight, microelectronics (printed and integrated circuit board, flexible chip carriers) [5], composite materials [6], automotive, packaging industries, or separation membranes [7]. Moreover, PIs' biocompatibility was heavily explored in the last two decades and polyimide-based materials entered the high-demanding area of biomedical applications, such as cell

substrates, retina stimulation implants, cortical recordings, neural stimulation devices, and others [8].

This outstanding collection of traits mainly comes from their highly symmetrical backbones, extreme structural rigidity, and intra- and inter-chain hydrogen bonding. However, these features also imply some intrinsic weaknesses such as poor solubility in organic media, low thermal coefficient, poor corona resistance, relatively high thermal expansivity and, very important from the industrial point of view, difficult and expensive processability, which therefore restrict some of their potential applications [9–11].

PIs usually consist of linear, planar, (fully or partially) aromatic architectures that contain several flexible (bulky or pendant), heteroaliphatic structural elements which can provide additional features [12–14]. Completely aliphatic and cross-linked versions are also available.

Traditionally, linear PIs are prepared by a classical, two-step polycondensation method via a soluble poly(amic acid) (PAA) intermediate [15, 16].

The overall process displays a stepwise mechanism (a polyaddition alternative is also scarcely used in some labs) and runs at a rate dictated by the reactivity of the starting compounds. The formation of the PAA precursor is usually performed in common dipolar amidic solvents such as DMF (N, N-dimethylformamide), DMAc (N, N-dimethylacetamide), NMP (N-methyl-2-pyrrolidinone), TMU (1,1,3,3-tetramethylurea) which act as Lewis "bases," or in other nonamidic solvents such as DMSO (dimethyl sulfoxide) and m-cresol at low temperatures (from room temperature up to 80–100°C, depending on the basicity of the aromatic amines).

The cyclodehydration is conducted either by thermal or chemical imidization, both pathways being effective for either soluble or insoluble PIs. The former implies the stepwise heating of PAAs at various temperatures (usually from 100°C up to 250°C, depending on the polyimide's structure and the solvent used during synthesis) for various periods (mainly 1 h at each temperature). The latter involves the use of a chemical dehydrating agent of acidic (acetic anhydride, trifluoroacetic anhydride, and formic acid) or aminic (pyridine and trialkyl amines) nature to promote ring closure at temperatures between 20 and 80°C [17].

A one-step synthetic pathway is also used for the small-scale, in-house preparation of soluble polyimidic materials. This is based on the polycondensation of the monomers at high temperatures without the isolation of the PAA precursor [18].

Besides the widely employed reaction of (at least) a dianhydride with (at least) a diamine, an alternative that uses a dianhydride and diisocyanate is also known [19–21].

In the case of cross-linked PIs, the synthesis follows the same routes as above, with the usual additional presence of a diamine or triamine as a cross-linker in the PAA preparation stage [22].

Other functions may be also used in the development of cross-linked PIs, such as a diphenylethynylene structure along the main chain [23], or the use of a benzoxazine-containing monomer [24]. However, it must be noted that the three-dimensional, cross-linked structures cannot be recycled.

Given the experimental conditions employed in the synthesis of heterocyclic polymers in general, PIs included, it is difficult to envisage synthetic pathways or experimental conditions obeying the strict criteria of green chemistry, ecological synthesis, or eco-friendly polymers.

However, due to their specific macromolecular architectures, linearity, and rigid arrangement, PIs can be already considered as long-life, and therefore sustainable materials, that are however not produced by eco-friendly methods, especially in terms of solvents (some of them are not so green) and thermal conditions (which imply a high energy intake).

At this point, a special comment must be inscribed to the starting building blocks. The majority of dianhydride- and diamine-type monomers used in the synthesis of PIs are produced using petroleum-based chemicals as the raw materials. Furthermore, some of these monomers (especially some diamines like methylene dianiline, or the less used isocyanates) and their intermediates are highly toxic, carcinogenic, or endocrine-disrupting [25]. Therefore, considerable research endeavors have been devoted to achieving benign polyimide building blocks based on nontoxic, bio-renewable feedstocks. At the same time, long-term efforts were (and still are, as it will be detailed later on) dedicated to finding less toxic experimental conditions and synthetic pathways.

Considering all of the above, it seems difficult at first to come close to the Holy Grail of bio-based and/or green polyimide chemistry. However, in this chapter, we seek to demonstrate that there are some viable, strong alternatives to the traditional polyimide building blocks or classical experimental conditions. Moreover, these can unlock more eco-friendly, bio-based PI materials (even by using green chemistry routes) which maintain the same combination of high-performance characteristics and even bring some new or enhanced features to the field. We will mainly focus on bio-based polyimides developed in the last 10 years from natural, renewable resources and will also touch the basics of some less harmful synthetic platforms like synthesis in ionic liquids, supercritical fluids, microwave conditions, and other nonconventional methods. Some interesting insights regarding the sustainability, degradation, and recycling of PI-based materials are also provided.

2. Bio-based polyimides

A plethora of reliable studies and publications on bio-based, green polymers have been extensively produced in the last 10 years, some of the most solid reviews on the topic being cited herein [26–28].

Various natural, eco-friendly chemical structures have been produced and used after several modifications of their chemical function to access sustainable and eco-friendly polymers. These include vanillin [29] or bio-succinic acid [30] for semi-aromatic polyesters, lignins for phenolic oligomers [31], epoxidized castor oils for thermosetting architectures [32], catechol-based moieties for highly adhesive polymers [33], biodegradable copolymers from SO2, renewable eugenol for biodegradable materials [34] or cashew nut shell liquid for various systems [35].

The development of high-performance bio-based polymers such as PIs is currently indispensable to establish the sustainable and green objective of the research society. However, its accomplishment proves a difficult task due to the incompatibility of their aromatic monomers with renewable, natural resources. PIs were built for a long time from petrochemical-derived monomers, but some recent attempts to synthesize them from bio-based monomers are chancing this trend. Among eco-polymers, PIs' synthesis starting from natural and renewable resources is not to be outdone. As in the case of already well-developed eco-friendly polymers, the chemical functions present in natural products have been modified to obtain, in the majority of cases, amine functions. Several attempts have been made to prepare partially or completely biopolyimides using bio-based aromatic diamines and various dianhydrides.

After thoroughly sweeping the available studies, we were able to find a handful of biopolyimide systems (bioPIs) based on different green or eco-friendly diamines. Some of the most important ones are described below.

2.1 PIs derived from natural phenols and polyols

2.1.1 PIs derived from cardanol

Cardanol is a phenolic lipid obtained from an anacardic acid, the main component of cashew nutshell liquid, and the starting point in the development of many interesting organic building blocks [36].

A partially bio-based aromatic diamine, namely 1,1-bis(4-aminophenyl)-3-pentadecylcyclohexane, was synthesized starting from cardanol via a 3-pentadecylcyclohexanone intermediate in the presence of aniline and aniline hydrochloride under reflux conditions.

This bulky, unsymmetrical diamine was used in the development of processable PIs with reasonably high molar masses in the range of 15–32 kDa [36].

The obtained polyimides and copolyimides were soluble in common organic solvents and maintained high thermal stability, with a glass transition temperature (Tg) in the 160–250°C framework (depending on the dianhydride partner) and a 10% mass loss temperature (Td10) recorded above 500°C.

2.1.2 PIs derived from isomannide

- Another approach used biomass isomannide to develop both bio-based diamine and dianhydride monomers and optically transparent bioPIs therefrom [37]. The two hydroxylic groups of isomannide were used as the starting points of various chemical transformations to obtain one cycloaliphatic and two semi-aromatic diamines, together with a flexible dianhydride.

The diamines were used in combination with the bio-based isomannide anhydride or with the commercial 4,4-oxydiphthalic anhydride (ODPA) to produce completely or partially bio-based PIs through the classic two-step method. The ordered arrangement of the isomannide heterocycle conveyed a certain degree of crystallization in the PI framework and afforded materials only soluble in common, high boiling point solvents.

The relatively rigid alicyclic isomannide imparted good optical transparency (transmittances above 80% at 450 nm), reasonably high thermal resistance (Tg between 227 and 264°C, Td10 greater than 430°C in nitrogen) and outstanding mechanical features (tensile strength above 90 MPa, elongation at break over 6%). Surprisingly, the use of the fully alicyclic monomer generated PIs of superior thermal stability when compared to the ones containing the semi-aromatic bio-based diamines.

Two of the isomannide-based diamines were further used in both their isomeric forms in combination with other six commercial dianhydrides. As expected, similar results were obtained: soluble, processable bioPIs with thermo-mechanical stability comparable with those of analogous petroleum-based PIs. They also provide the additional features of optical transparency and optical activity which qualify them for applications like liquid crystal alignment and solar cells [38, 39].

2.1.3 PIs derived from myo-inositol (MI)

Myo-inositol or cyclohexanehexol is a naturally occurring cyclohexane decorated with six hydroxylic groups that is widely encountered in animals and plants. One of the many stereoisomers of inositol, it is the most commonly used biologically active isomer [40].

Until now, a large number of bioactive molecules bearing inositol-derived components were used as building blocks in developing macromolecular backbones

containing diols, like polyurethanes [41] or polyamides [42]. It was a matter of time until it would have been used to prepare polyimidic architectures through its incorporation in diamines [15, 16, 28, 40].

For example, myo-inositol was treated with 1,1-dimethoxycyclohexane to yield a heterocyclic compound with three alicyclic units, the central one bearing two free hydroxyl groups [42]. These hydroxyl moieties are further used to introduce two aromatic amine functions through substitution and subsequent reduction reactions [40].

The target diamine readily underwent polycondensation with widely used, commercial dianhydrides in microwave conditions [40].

The resulting bioPIs, whose main chains inherited the bulky 6-5-6-5-6 polyalicyclic system from the diamine monomers, are soluble in common organic solvents at room temperature, even in chloroform, dichloromethane, and acetone. They displayed quite respectable molar masses, between 40 and 99 kDa, and relatively narrow polydispersities, with PDI values below 1.6. All bioPI films displayed characteristic thermal stability and outstanding mechanical features (tensile modulus above 3.5 GPa), even higher than those of most petroleum-based PIs. Their most important traits are the optical ones (light coloration and high transmittance values [for a PI], above 82%) and are also derived from the voluminous cycloaliphatic segment and its ability to hamper the charge-transfer complex usually found in PI materials.

2.2 PIs derived from anethole

Anethole is a natural styrene analog that is widely found in various in essential oils from plants and can be used in a peculiar preparation protocol (polymerization of Wagner-Jauregg type monomers containing preformed imide rings) of bio-based PIs [43].

Starting from this phenylpropene derivative, a new multicyclic monomer containing Wagner-Jauregg type imide motifs was synthesized via cascade, double Diels-Alder reaction. The polycondensation reaction of this diphenol-type monomer between and decafluorobiphenyl yielded a colorless and transparent (86% transmittance at 450 nm) poly(ether imide) film.

The partial bioPI showed reasonably high molar mass (72 kDa, 1.6 dispersity), sound thermal stability (5% weight loss [Td5] starting above 410°C, Tg higher than 360°C) and above reasonable mechanical characteristics (1.90 GPa tensile strength, 53.3 MPa elastic modulus, 5.4% elongation). These traits make them eligible for various optoelectronic applications in harsh conditions.

2.3 PIs derived from vanillin and its derivatives

Vanillin is one of the few commercially available, bio-based, aromatic compounds, and therefore, it is widely used in the polymer community dealing with bio-based macromolecular materials, PIs included [44, 45].

Vanillin was used as the starting point in the preparation of two dimers further used in two synthetic pathways for the development of bio-based aromatic diamines.

The first one involves three steps: phenol alkylation, oxidation of divanillin's aldehyde moieties, and subsequent reduction of the obtained oxime toward a methylated divanillylamine [46].

The second route uses the Curtius rearrangement and employs the synthesis of an acyl azide intermediate from divanillic acid, its transformation into a diisocyanate, and further hydrolysis toward another divanillin derivative decorated with two amino groups.

Another sequential synthetic scheme was used to prepare a diisocyanate starting from vanillic acid and its methylated dimer.

Therefore, these accessible synthetic transformations afford the preparation of a broad range of bio-based PI building blocks and corresponding polymers. One particularity of these procedures is that they unlock bio-based isocyanates which can be further used in combinations with dianhydrides to obtain bioPIs [45].

This series of partially bioPIs shows moderate molar masses (Mw from 49.5 to 75.8 kDa), characteristic polydispersity (2.0–2.5), acceptable solubility, and good thermal stability (Tg between 260 and 330°C, Td10 around 460°C).

The ability of vanillic acid to act as a versatile building block was explored even further together with another lignin-derivative, syringic acid, in the development of diacylhydrazides. These were then used in a two-step polycondensation procedure with aromatic anhydrides to generate partially bio-based poly(amide imide)s. The new materials provided transparent, flexible, and tough films with high thermal stability [47].

A simpler synthetic pathway can be also used to transform vanillin into an asymmetric diamine.

The aminic building block was then used to build partially bio-based PIs with four conventional, commercial dianhydrides and the results were compared with an analogous series based on a symmetric aromatic amine.

As expected, the use of the asymmetric structural moiety hampers the formation of charge-transfer complexes while vanillin's aromatic structure maintains backbone rigidity. This is translated into improved solubility, optical transparency, and hydrophobicity, without any negative impact upon thermal or mechanical stability [48].

The vanillin route was also pursued to develop a bio-based diamine containing aromatic, pyridine, and aliphatic structural moieties. This was used in combination with an alicyclic dianhydride, Epiclon, to obtain a semi-aromatic bioPI through the two-stage route.

The resulting flexible PI backbone afforded easily processable films with improved solubility and proper chemical and thermal stability (Td10 around 317°C). The PAA precursor was also employed to prepare a series of Ag nanocomposites by sonication. The casted films displayed a homogeneous dispersion of Ag nanoparticles within the bioPI matrix due to the high compatibility of the composites' elements. This resulted in Ag-induced, partial crystallinity, improved thermal properties (Td10 from 317°C up to 357°C, depending on the Ag amount), and antibacterial activity against *E. coli* [49].

2.4 PIs derived from camphor

Another bio-renewable, natural resource, camphor, a waxy, alicyclic forestry product was used in its (D) form to produce two diamine building blocks via an accessible synthetic route [50, 51]. The diamine was further condensed with two aromatic dianhydrides to prepare semi-alicyclic PIs with high solubility and optical transparency by the conventional two-step method.

The partially bio-based PIs were comparable to their fully aromatic counterparts (based on the combination of the similar rigid diamines with the same dianhydrides) in terms of solubility, optical features, thermal, and mechanical resilience. They provided transmittance values between 75 and 81% at 500 nm, Td10 from 390 to 519°C, tensile strength above 110 MPa, and elastic modulus in the range 2.4–3.24 GPa.

2.5 PIs derived from *Escherichia coli*

Bio-available aromatic diamines were derived from genetically manipulated *Escherichia coli*, through a photodimer of an aromatic amino acid, namely

4-aminocinnamic acid. This was produced by the fermentation and bioconversion of the genetically engineered microorganism from glucose via 4-aminophenylalanine [52].

The diamine displaying an alicyclic structure sandwiched between two aromatic rings was synthesized via a 4,4′-diamino-α-truxillic acid dihydrochloride, obtained through a [2+2] photocycloaddition of the microorganism-derived monoamine's hydrochloride salt.

This new building block was polycondensed afterward with different common dianhydrides following the two-stage procedure.

The bio-based PAAs displayed high molar masses, between 250 and 400 kDa, while the inadequate solubility of the thermally cyclized PIs precluded molecular mass determination. These bio-based PI films showed ultrahigh thermal resistance with Td10 values over 425°C and no Tg values below 350°C, which are the highest thermal features of all bio-based plastics reported thus far. They also showed high tensile strength and Young's moduli, excellent transparency, and high refractive indices, and adequate cell compatibility [53].

The transparent bioPI based on 1,2,3,4-cyclobutanetetracarboxylic dianhydride showed electrical insulative properties comparable to those of Kapton®, the most used PI dielectric. As in the case of the commercial PI, the volume resistivity proved to be directly connected to the annealing time and water uptake [54].

The precursor of this bioPI was used to prepare silica hybrids by sol-gel polycondensation with silicon alkoxide and in vacuo thermal annealing. The method generated transparent, thermo-mechanically robust films with excellent electrical stability [55].

The applicative potential of this bioPI was explored even further, by developing bionanohybrids through the sputtering of ITO nanolayers on the functionalized, reactive surface of a bioPI. The obtained materials displayed thermal, mechanical, electrical, optical, and adhesions performances comparable to or superior (especially in terms of optical transparency, ITO adherence, and device resistivity) to the extensively employed Kapton® PI film. This allowed the development of flexible, robust, and transparent electrodes for high tech electronic devices [56].

Other cycloaliphatic dianhydrides were also polymerized with the bio-based diamine coming from 4-aminocinnamic acid to draw a correlation between the PIs' solubility and the structural motifs belonging to the dianhydride.

The study concluded that a lower cycloaliphatic ring strain determines PI microstructures with improved flexibility and reduced Tg. All semi-aromatic bioPIs maintained relatively high molar masses (50–80 kDa) and displayed improved solubility and processability while preserving high thermal stability (Td10 temperatures above 375°C) [57, 58]. One of them was also used to develop highly transparent, flexible TiO2 and ZrO2 hybrid films that display the basic features of memory devices with tunable memory properties.

Ductile bioPI films were obtained from the same renewable semi-aromatic diamine by copolymerization with different binary mixtures of the aforementioned dianhydrides [59]. The copolymers displayed high-performance features comparable to those of the Kapton® film. For example, they maintained a high thermal resistance (Td10 values above 406°C and Tg over 208°C), improved tensile strength and elongation at break, and a Young's modulus around 4 GPa. Also, the copolymers showed adhesion strength to the carbon plate in the range of 0.22–4.47 MPa, which is similar to that of cyanoacrylate-based superglues [59].

The same bio-based, exotic building block, 4-aminocinnamic acid, was employed to develop two other diamines, 4, 4′-diaminostylbene and its hydrogenated version, by using Grubb's olefin metathesis as a key step.

The two diamines were further polymerized via two-stage polycondensation with the same dianhydrides as the photodimer ester coming from 4-aminocinnamic acid. High molecular masses PAAs were obtained both as films and fibrils and their thermal imidization afforded partially bio-based PIs with high thermal stability and mechanical properties superior to Kapton® [60].

2.6 PIs derived from peptides and amino acids

A monoamine-substituted version of the above-mentioned, microorganism-derived building tool was used to develop an aromatic amino acid, 4-amino-L-phenylalanine. This was used as a core to build a cyclic dipeptide, 3,6-di(4-aminophenylmethyl)-2,5-diketopiperazine through iterative protection/coupling/deprotection protocols [61].

Several bioPIs incorporating the diketopiperazine heterocyclic structure in the backbone were prepared by polycondensation of the peptide with commercially available aromatic dianhydrides.

Through a judicious design, the cyclic dipeptide monomer contains a centrosymmetric amide functionality in the diketopiperazine ring adjoined by two aromatic rings through a methylenic bridge. This type of architecture is able to induce auto-aggregation of the corresponding polymer chains through hydrogen bonding and π-π interactions. As a consequence, these bioPIs and their PAAs can self-assemble into nanosized conglomerates of various shapes (spheres, spiky balls, flakes, and rods), as observed by scanning electron microscopy (SEM) investigation. This particular feature (and its combination with the innate characteristics of any PI) enables these PIs suitable for applications such as fillers, heat-resistant superhydrophobic coatings, and ultralow-dielectric-constant films.

In addition, the peptide-based PIs display a high thermal resistance, particularly the one derived from pyromellitic dianhydride (PMDA), which showed the highest Td10 (around 432°C) and a Tg value above the decomposition temperature.

The literature provides few examples of other amino acids used as building blocks for bioPIs. For instance, isoleucine, valine, methionine, and phenylalanine were used together with benzimidazole pendant units to build four chiral diamines.

The diamines were polymerized with a particular dianhydride containing a pendant trifluoromethyl segment to attain optically active, aromatic bioPIs.

This resulted in amorphous, versatile PIs with improved solubility and molar masses above 124 kDa. The materials showed accessible Tg (142–165°C), suitable mechanical resilience (97 MPa ultimate strength), and a rather lower thermal stability (Td10 around 255°C) as compared to the PIs presented herein. They were further involved in sol-gel procedures to produce Ti bionanocomposites with improved UV absorption and enhanced gas permeability [62].

2.7 PIs derived from bio-based adenine

Adenine, as an amine-substituted purine, is one of the four building blocks of the DNA's double helix supramolecular structure and therefore an important naturally abundant structural framework for multiple hydrogen bonds [63].

An adenine-containing diamine was synthesized through the nucleophilic substitution of biomass adenine with 4-chloronitrobenzene and the subsequent reduction of the nitro groups. The adenine-containing diamine was then polycondensed in a single-step reaction with the widely used 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) to obtain a new bioPI.

The unique conjugated heterocyclic structure of adenine and its propensity toward hydrogen-bonding interactions generated a bioPI with excellent solubility and outstanding combined (thermal and mechanical) performance. The Tg value was higher than 350°C and the Td10 over 500°C (both in nitrogen and air). The tensile strength was up to 144 MPa, and the elastic modulus exceeded 4.1 GPa. A low dielectric constant of 2.8 (measured at 10 MHz) adds an important feature to this bio-based high-performance material. Similar results were obtained when the diamine was combined with another widely employed commercial dianhydride, ODPA [64].

The same adenine-based diamine was used together with PMDA to obtain a new bioPI and study its thermal expansion conduct along the in-plane direction. The PI films proved a rare in-plane thermal contraction feature which maintained its negative nature even above Tg. Infrared spectroscopy studies showed a mutation of the adenine-powered hydrogen bonding from a purine type to carbonyl-based interactions [65].

2.8 PIs derived from fatty diamines

Many of the PIs' characteristics are an outcome of the hard blocks coming from both the dianhydride and diamine segment. By replacing one of them with a softer block of natural origin, bio-based PIs with interesting traits are obtained. For example, a long, branched, cycloaliphatic, fatty diamine was employed as the soft block together with several, flexible or rigid, hard aromatic dianhydrides in the construction of some PIs, and the effect of the soft-hard combination was investigated [66].

The integration of flexible (or bulky) hard segments containing various spacers provided amorphous PIs, while the use of a highly rigid dianhydride segment yielded a semicrystalline polymer with separated nanophases after annealing.

The soft-hard combination resulted in highly soluble, processable, thermoplastic PIs of moderate molecular mass, with Tg values near room temperature, yet relatively thermal stability. They display superior processability as compared to most polyimides and are also available for recycling without significant changes in their outstanding mechanical features.

The four materials displayed high elongations (especially the one containing the highly rigid hard segment) and qualify as trustworthy candidates for applications that require high damping characteristics in ambient conditions (shock absorbers, noise, or vibration insulating materials, sealants).

Further studies revealed a self-healing capacity of these materials at room temperature. Rheological and tensile investigations proved the two-step kinetics and physical characteristic of the healing process and its dependency on the particular relaxation behavior of the PIs during stepwise healing. Mechanical integrity is maintained during healing due to the interplay of primary and secondary interactions between the soft and hard structural motifs [67, 68].

Another fatty diamine, the commercial Priamine™ 1074 coming from vegetable extracts (tall oil and soybean oil), was used as a starting material in the synthesis of partially bio-based fluorinated PIs.

The dimer containing fully renewable C36 enabled the preparation of highly soluble, thermally resistant PIs with a high content of biomass (up to 48.9%). During the two-stage polycondensation process, additional building blocks were used to ensure double-bond terminal groups which were further employed in the preparation of UV-cross-linked coatings. The obtained materials can satisfy some key requirements of microelectronics photoresists, like high optical transparency, adequate thermal stability, low water absorption, and suitable adhesion [69].

3. Green and nonconventional synthesis and processing of polyimides

As mentioned earlier, PIs are not usually produced by eco-friendly synthetic methods, especially in terms of solvents and thermal conditions. As detailed in the previous section, the production of some bioPIs starting from renewable building blocks involves the use of heavy-duty, rather toxic solvents (cresols in particular), with a negative environmental impact. This is a drawback which needs further research dedicated to greener experimental conditions.

On the other side, a large number of research studies were dedicated in the last two decades to the progress of nonconventional synthetic platforms or experimental conditions which can be used with some undeniable success in the development of PI-based materials. These come quite close to the strict criteria of green or sustainable chemistry based on ecological synthesis.

In this section, we will focus on some less harmful experimental conditions like synthesis (and processing) in ionic liquids, supercritical fluids, microwave conditions, and other nonconventional methods, as depicted by the scientific literature of the last 10 years.

3.1 Synthesis and processing of PIs in supercritical fluids

A supercritical fluid can be largely defined as a substance whose temperature and pressure are above its critical values. Above the critical temperature and pressure, a substance has the density of a liquid and the rheological properties of a gas. The characteristic density of a liquid allows the supercritical fluid to dissolve the substances, while the flowing features of the gas offer the advantage of lower reaction times [70].

This unique combination of physical traits offers several benefits in the use of supercritical fluids, both in macromolecular chemistry and materials science, but also in areas such as fine organic synthesis, catalysis, coordinative chemistry, and biochemistry.

Supercritical fluids and especially carbon dioxide (scCO2) have been successfully used in the last decade as solvents, antisolvents, or plasticizers in the synthesis and processing of PI-type materials. The synthetic procedure offers some chemical, ecological and economic conveniences. scCO2 is inert, nontoxic, nonflammable, relatively inexpensive, and, as an ambient gas, the solvent's removal after usage and depressurization is quite easy and hampers any ecological drawbacks. In some cases, the improved quality of the obtained products is an important factor in choosing supercritical liquids to the detriment of conventional organic solvents [70–78].

On the other hand, the use of supercritical fluids requires relatively high pressures and special equipment, and these considerations must be carefully balanced with the perceived advantages for a particular application.

The behavior of PI systems in the presence of scCO2 strongly depends on several parameters: the structural elements of the polymer, its physico-chemical characteristics (Tg, degree of crystallinity, cross-linking), the properties of pure scCO2 (molecular structure, critical points), the nature of the interactions between scCO2 and the polymer, and, obviously, the external temperature and pressure [72, 73].

Solubility is the crucial factor in the synthesis of polymers in scCO2. While scCO2 is a good solvent for low molecular mass, polar and nonpolar molecules, it is a very weak solvent for most high molecular mass polymers in mild conditions (below 100°C and 1000 bar). In some cases, a mixture of scCO2 and a common organic solvent provides satisfying results [74, 75].

The majority of research dealing with the synthesis of PIs in scCO2 focuses on the polycondensation of common, commercial monomers. 6FDA or similar fluorine-containing monomers are the preferred building blocks in this regard because most fluorinated polyimides seem to have a higher solubility in scCO2 [76–78].

Most studies report reactions with good yields and products with variable inherent viscosities, depending on the monomers' structure and reaction conditions. The molecular mass of the resulting PIs is influenced both by the concentration of monomers, by the reaction time and temperature, and by the scCO2 pressure. Some articles report a catalytic effect of scCO2, since the reaction rate increases in the presence of traces of water. Subsequently, the small water amounts can lead to the formation of cyclization products of lower molecular mass. At the same time, the employment of scCO2 in the synthesis of polymers leads to a small decrease in the Tg and dielectric constant values, due to a plasticizing effect. This can be an important advantage when it comes to the processability possibilities of the final material [79–82].

An increasing trend regarding the processing of polyimide materials using scCO2 was also observed in the last decade. The scCO2 dissolved in a condensed phase causes various changes in the microstructure of the polymer and a considerable reduction of its viscosity due to the increase in the free volume of the polymer matrix. This leads to severe modifications in the transport properties of the polymer, the permeability, and selectivity coefficients growing several times [83, 84]. As a consequence, scCO2 is largely used in the production of nanoparticles, foams, aerogels, and membranes based on linear [85–87] or cross-linked [88–92] PIs. These materials have interesting features (high porosity, tunable shrinkage, nano- and micro-cavities, high surface area, ultralow dielectric constant, and mechanical resilience) that open up new possibilities in the applicability of PI-based systems such as catalytic systems, separation membranes, aviation, aerospace, construction, and others [93–97].

For a rational design and optimization of these processes, it is essential to know the solubility, diffusibility, density, and permeability of the imidic macromolecular compound.

Nevertheless, despite the advantages and promising results attained so far, supercritical fluid technology has little chance to replace conventional methods for the time being. This is due to the limitations imposed by the solubility issue, the viscosity and molecular mass of the reaction products, as well as by the special equipment required by the supercritical conditions.

3.2 Synthesis and processing of PIs in ionic liquids

Ionic liquids had a cutting edge impact in the last two decades in polymer chemistry and materials science. They are widely used in both academia and industrial research and are considered a new class of ecologically compatible, green solvents, which can reduce or even replace the often dangerous, polluting, classic organic solvents.

The ionic liquids term generally implies different types of salts with a structure similar to ordinary salts like NaCl. However, while common salts melt at high temperatures, most ionic liquids remain liquid in a temperature range between room temperature and 200°C. They are usually formed by highly polar combinations of organic, voluminous, and asymmetric cations, decorated with aliphatic residues, and inorganic anions of symmetrical, regular shape, this chemical composition resulting in a low melting point. Poor packaging and poor coordination of ions in the structure of ionic liquids is the reason why they remain liquid at room temperature [98–100].

This peculiar structural composition unlocks a unique range of physicochemical features that make them environmentally compatible and suitable for various applications. They can dissolve different types of organic, inorganic, and organometallic materials, and their solvent properties can be modified to satisfy a particular application, by varying the combinations of anions and cations. They have high thermal conductivity, are liquid on a broad temperature range, and thermally stable up to 300°C, which allows the kinetic control of a reaction within wide limits. In addition, they possess extremely low vapor pressures (and hence do not evaporate) and are immiscible with many organic solvents [98, 101].

The benefits of ionic liquids were widely applied at first in the synthesis of classical PIs by the two-stage polycondensation reaction of common commercial diamines and dianhydrides [102]. Nevertheless, the solubilizing capacity of ionic liquids enables their usage in the polycondensation of more exotic building blocks with special features [103–107]. The method usually results in satisfying yields, without further addition of other catalysts. The obtained compounds show high molecular masses and inherent viscosities, enhanced thermal stability, and proper mechanical resistance.

Some studies also evidence an activating or catalytic effect of ionic liquids that boost the monomers' reactivity and unlock PIs with high molecular mass [102, 108].

The polycondensation of said monomers is usually performed in hydrophobic ionic liquids. Otherwise, the retained water will cause a decrease in the monomers' reactivity and hamper the formation of cyclization products with high molecular masses. The procedure generally involves easy work-up and solvent reusability and provides the potential for further scale-up attempts.

The innate immiscibility of ionic liquids with organic solvents was also explored in the green, interfacial polymerization of cross-linked PIs to obtain composite osmotic membranes [109].

In the early stages of their usage, ionic liquids were criticized for "sticking" to the PI material, even after various purification attempts. A small quantity of ionic liquid within the microstructure of a PI film or membrane would interfere with its thermo-mechanical features.

In the last decade, this issue was transformed into a benefit, through the advantageous combination of the versatility of both PIs and ionic liquids. The synthesis of these materials is usually performed by polycondensation of classical PI building blocks with ionic monomers (especially diamines) or via commercial PI modification. The resulting macromolecular species is called polyimidic ionenes or imidic poly(ionic liquid)s. The strategy uses ionic liquids' strong affinity to CO2 with the high-performance characteristics of PIs for the development of new materials for gas membrane separation [110–113].

3.3 Synthesis of PIs in microwave conditions

As it can be easily observed from the previous sections of this chapter, classical heating remains the primary means of stimulating chemical reactions that are difficult to carry out under ambient conditions, such as those used in PIs chemistry. In recent years, this technique is strongly rivaled by several modern heating techniques, the most important being microwave heating [114].

The main advantages of using microwaves in the synthesis of PIs are the rapid completion of polycondensation, high purity of final products, uniform temperature rise, and overall greener energy balance. Some small drawbacks refer to the less accessible upscale and the need to re-dissolve the final product to prepare PI films or membranes [115, 116].

The outstanding downsizing of reaction time is the strongest point of this experimental technique. Microwave-assisted polycondensation reactions proceed very rapidly, requiring only a few minutes of irradiation to obtain binary or ternary soluble polyimides with more than acceptable inherent viscosity (up to 1.2 dL/g) and molecular masses (up to 200 kDa) [117]. The irradiation time is a key parameter that can easily turn from a benefit to a drawback. Too long irradiation times or too high irradiation powers are many times translated into PIs of lower molecular mass, due to the partial degradation of the polymer [118].

The polycondensation proceeds through a one-stage mechanism, the imidization being performed employing microwave heating [119] or with the help of additional chemical initiators [120]. At the same time, microwaves can be used only to perform the cyclization of the PAA precursors obtained by conventional methods. This procedure is able to generate PI films with improved mechanical features as compared to their thermally cyclized counterparts [121].

The reaction can be easily extended to a wide range of building blocks (common monomers' salts included [122, 123]) and even to the direct production of various composites [114, 116, 124]. The viscosity value of the final products usually depends on the solubility of the final compound in the reaction medium. The initial amount of solvent or overall monomer concentration thus plays an important role in the characteristics of the final material.

The most used solvents in microwave-assisted PI synthesis are the polar ones, with a high dielectric constant and high boiling point like NMP, DMF, and alike. Under microwave irradiation, these solvents increase their temperature extremely fast and reach the boiling point in a short time. Although nonpolar solvents do not absorb microwaves, they can be still be used in combination with small amounts of polar solvent or salts.

Some reactions are solvent-free and only require pertinent microwave-absorbing monomers [125] or additives (CuO is an efficient example) [126]. The latter are used to quickly raise the reaction temperature to the melting of (at least one of) the monomers, thus empowering melt polycondensation. Such a strategy eliminates the usual, tedious washing process and the use of any (potentially) toxic organic reagents, further increasing the green character of the technique.

The one-stage polycondensation mechanism, combined with a small heating time and reduced (if any) contact with solvent usually translates in higher optical transparencies as compared to PI analogs obtained by the classical method [118].

Several studies compared the classical, thermal-, and microwave-assisted polycondensation procedures applied on the same common starting compounds in terms of order degree within polymeric backbones, imidization level, thermal and mechanical properties of resulting films. Microwaves assured a higher order level of the final products and proved to be more efficient and, of course, faster in reaching imidization [115, 122]. The imidization degree attained by microwaves was double the size of the one obtained by common thermal cyclization at 200°C and was almost complete at 250°C. Moreover, the PIs obtained by microwaves displayed higher thermal stability and superior mechanical resilience (even up to 30% higher) as compared to their thermally imidized counterparts [115, 117, 127].

Even if the method comes with some technological limitations regarding upscale and industrial use, the results obtained so far are quite impressive and, together with their obvious green character, require extensive research on the topic.

3.4 Other green and non-conventional synthetic procedures

A new, alternative method for PI synthesis appeared roughly 25 years ago, involving the use of the ultimate green solvent, water, in special temperature, and pressure

conditions [128, 129]. The method is now generally known as hydrothermal polymerization (HTP) due to its resemblance to the geomimetic conditions of silicates' forming by condensation in the hydrothermal veins of the Earth's crust [129, 130].

HTP uses the same building blocks as the conventional PI synthesis: a dianhydride (usually, the original, more stable, tetracarboxylic acid is employed since the dianhydride will automatically hydrolyze in water) and a diamine. They form a nylon-type AB monomer salt intermediate which is subjected to polycondensation in water, at elevated temperatures and pressures accessible through a steel pressure vessel [131–133].

Since the monomer salt formation was undeniably proven by separate studies [128, 131, 132], one version of the method begins with the separate synthesis and purification (washing and filtration) of the monomer salt as the starting building block. Although not mandatory, this will provide the (almost) perfect stoichiometry required by any polycondensation reaction to ensure high yields.

Typical HTP experimental conditions for high monomer conversion are a 200°C temperature, a 16.7 bar pressure, and a reaction time between 6 and 24 h. The imidic product precipitates on cooling in aqueous residues of low toxicity. There are small amounts of residual solvent and no volatile impurities trapped in the final product.

At first glance, the reaction seems remarkable or even paradoxical, since it appears to contradict Le Chatelier's principle and the formation of PIs by polycondensation. A reversible reaction, with water as a side product, leading to products that cannot be (classically) obtained systematically unless firm absence or removal of water, feels inappropriate to be carried in water. Nevertheless, it works with noteworthy results. First, the salt formation increases hydrolytic stability, prevents the reverse reaction, and leads to increased imidization rates. Second, the aforementioned principle is still followed, the (theoretically) reversible polycondensation reaction being generally driven by the innate insolubility of the synthesized imide products.

The reaction follows a classical stepwise polymerization with a three-fold mechanism strongly depending on the temperature (TR) (reaction time and monomer concentration must be also considered) [132]. In the sub-hydrothermal regime, sHTP, the polymerization takes place in solution and leads to amorphous, short, low oligomeric PIS of a zwitterionic nature that coexists with unreacted, less soluble monomers. Between 100 and 130°C, longer macromolecular chains start to form in an ordered fashion, leading to semicrystalline PIs. When the reaction temperature comes to close to 200°C, the order degree and overall morphological homogeneity rise considerably and crystalline imidic products are generated. Solid-state polymerization (SSP) takes place in the high-temperature regime and is correlated to the polymerization temperature of any given monomer. If sHTP and SSP are mostly suppressed by judicious selection of starting compounds and reaction parameters, (almost) completely cyclized, highly crystalline PIs with particular morphological features are accessible by this method.

The potential usage of the method was recently broadened by the successful PI synthesis in various protic polar solvents (ethanol, isopropanol, and glycerin) or several aqueous mixtures therefrom. This unlocks the employment of new building blocks and fine tuning of reaction conditions toward desired PI morphologies [134].

Most HTP reactions performed so far used various aromatic dianhydrides/tetracarboxylic acids and commercial diamines and reproduced the structure of common or commercially available polyimides. The obtained molecular masses were in most cases significantly close to those of the PIs prepared by the classical method. Other basic properties (aspect, optical transparency, thermal, and

mechanical features) are strongly dependent on the starting monomers and crystallinity degree of the polycondensation product.

Nevertheless, the method allows the synthesis of new PI structures [135] and composites [136], which can also be assisted by microwaves [137] or extended toward the production of PI fibers by green electrospinning or application-driven materials [133, 138].

Although only in its infancy and not easily accessible due to the special reaction setup, HTP delivers interesting results which require extension toward new building blocks and structures. Most importantly, the method is close to achieving all the strict criteria imposed by an ideal green chemical industry: high efficiency, economy, low (if any) toxicity, and benign environmental impact.

4. Recycling of polyimides

Polymer recycling is (or should be) a vital criterion to be taken into account in the life cycle of a product, especially when it comes to PIs. They represent key, reliable, long-life materials for a wide range of high-tech applications, but their recycling is a major challenge. Several technological and economic hurdles hamper the progress in this field.

On one side, recycling should enable the reintegration of discarded PI materials in the technological cycle or the production of new PI materials from recycled ones (especially since PIs represent materials of high-end value). On the other, it implies the quest for real sustainable solutions for the PI wastes issue, even if they represent a very small percent of the total polymer volume in use/to be recycled. Last but not least, it also means cutting down the dependence on oil-based raw materials, this matter being (at least partially) treated in the previous sections.

As in the case of most materials, mechanical and chemical recycling and combustion are the most common polymers' recycling methods, PIs included.

When it comes to the recycling or reuse of PI-based materials, two options are available, depending on whether you are dealing with a thermoplastic or thermoset. Important constraints are met in both cases.

Only a low percent (between 5 and 8%) of thermoplastic PIs is prone to recycling by reuse. There is no clear, general answer to the dilemma regarding the faith of the more than 92% left.

In the case of PI thermosets, the problem is even more complex, since the three-dimensional structure impedes easy changes in the physical state, especially to the molten state. Cross-linked PIs cannot be melted, molded, or extruded and therefore suffer from severe limitations in terms of recycling or require complicated or energy-intensive recycling methods. One easy example would be their reuse as additives in composites. If such, the problem of the matrix-reinforcement interface will arise from the homogeneity of the composite.

4.1 Degradation of polyimides

At this point, a separate discussion must be dedicated to the degradation of PI materials. Degradation (commonly known as aging) usually encompasses any modification of the initial polymeric material's features due to one or several external factors like light, heat, or chemicals. This is a major concern when it comes to the application of PI-based materials. Moreover, degradation is a key process when it comes to the reuse or recycling of a PI-based product to meet green environmental criteria. Its importance is also crucial when considering the final disposal or destruction/decomposition of the envisaged material and its environmental impact.

Assisted degradation of polymeric materials is an intricate procedure due to multifaceted mechanisms involving highly reactive macro- and micro-radicals and a plethora of degradation and decomposition products. These mechanisms are strongly dependent on the environment, more precisely on the presence or absence of oxygen. In the particular case of the highly stable PIs, there are also strongly time-dependent mechanisms [139–141].

The degradation of PI-based materials can be the subject of various pathways that will be briefly approached below.

4.1.1 Thermal (oxidative) degradation

As repeatedly mentioned in this chapter, PIs and PI-based materials display outstanding thermal stability, both in air or inert atmosphere. Degradation starts at very high temperatures, usually above 350°C for aromatic PIs, depending on the polymer's structure. Naturally, decomposition follows at much higher temperature regimes.

The thermal degradation of the widely used Kapton® film mainly generates CO2 from various sources (initial hydrolysis of the imidic units, followed by decarboxylation of the resulting acidic group), CO, and other volatiles from further transformations of imidic and aromatic moieties (a total of five degradation steps with variable activation energies) [141–144].

Several studies investigated the exact origin and nature of the volatiles resulting from the thermally induced degradation of common thermoplastic PIs: CO2, HCN, NH3, N2, H2O, CH4, and HCs. The presence of F- or S-rich structural motifs determines other, usually toxic volatiles. The decomposition process follows several pathways: depolymerization, pyrolytic reformation, successive homolytic and hydrolytic cleavages, hydrogen ablation, progressive molecular rearrangements, and loss of organic functionality through radical scission [140, 145, 146]. In every pathway, CO2 remains the main degradation product, while the nature of the other volatiles is dictated by the chemical structure of the polymer.

The resulting carbon-rich materials display improved compatibility between the organic (PI) and inorganic (carbon) parts which are mixed at the molecular level and enable several features that can be tuned by thermal treatment. Such materials can find various applications as fillers for gas purification membranes, dielectric composite films, coatings for electronic devices, and others.

Naturally, the degradation of cross-linked PIs has a more puzzling nature due to the three-dimensional architecture of the materials and requires different temperature and activation energy ranges [8]. Nevertheless, the pyrolysis of such thermosets can be used to form new reticulated structures. For example, a PI bearing cross-links of anhydride nature formed new reticulation points during thermal treatment at 430°C, which finally resulted in microporous membranes with potential gas transport properties [147].

In the presence of oxygen, the mechanisms of thermal polymer degradation become even more complex due to the formation of highly reactive peroxide macroradicals which enable a cascade of degradation reactions [148–150].

4.1.2 Hydrolytic degradation

Several experimental and computational studies were also dedicated to the chemical (especially hydrolytic) degradation or aging of common or less conventional PIs and model compounds [143, 151–153]. Two main mechanisms were evidenced: hydrolytic degradation and water-induced plasticization, both of them

being thermally activated and severely time-dependent (long exposure times [month scale] are usually involved).

In its early stages, plasticization can be cautiously reversed with no significant impact upon thermal or mechanical features. Further on, water induces irreversible hydrothermal defects like blistering and/or delamination [153]. The process is stronger when high temperatures or pressures are involved [152, 154].

The mechanism is usually based on the hydrolysis-activated chain scission of PI macromolecules through the attack of water molecules on carbonyl groups or other humidity labile structural motifs [155, 156].

4.1.3 Radiation degradation

Several studies on this issue were performed due to the employment of Kapton® and other commercial PIs in aircraft and aerospace applications. Kapton® in particular is renowned for its outstanding resilience to ionizing irradiation, as compared to other widely used PIs.

The photodegradation of PIs results in macro- and micro-cracks coming from the scission of macromolecular backbones and low molecular mass volatiles such as CO and CO2 (and CHF3 in the case of 6FDA-containing PIs). The resulting oligomeric or polymeric chains display phenol, amine, isocyanate, and carboxylic acid terminal groups [157, 158]. Most UV irradiation experiments showed biexponential degradation kinetics [159].

In the case of beam-induced degradation processes, CO and CO2 are the major volatile fragments, with an additional significant contribution of short hydrocarbons like CxHy [160–162]. The degradation requires heavy energetic conditions and can be inhibited by the addition of various fillers [157]. Additionally, the process is accelerated by air exposure, which quickly determines a significant loss of radicals.

When the aging experiments mimicked low earth orbit, space-flight conditions (temperatures between 10 and 300 K, ultra-high vacuum [10–11 Torr], and high concentration of electronically excited atoms [108 atoms•cm^{-3} of atomic O]), the degradation proceeded through chain scission and generated H2, CO, and CO2 [163, 164]. Similar experiments mimicking geostationary orbit conditions (involving high energy [90 keV] electrons) showed a board range of radiation-induced damage (breakage of chemical bonds and formation of new ones) and a strong effect on optical (lower transmittance) and charge transport (higher conductivity) features [165].

Most ion- or radiation-induced degradation studies have been performed at room temperature, and very little is known about degradation effects determined by irradiation experiments performed at extreme (very low [cryogenic] or high) temperatures [160].

4.1.4 Biodegradation

PIs are generally known to be biostable and bioinert, a very useful trait when it comes to biomedical applications (implantable devices, especially) [8]. However, the biodegradation of some PI-based materials would prove an advantageous feature in terms of recyclability and environmental impact. However, this requires specially designed building blocks and very strict control of the overall synthetic procedure.

One successful example in this regard is the two-stage synthesis of a biodegradable PI starting from an aliphatic amine derived from poly(propylene fumarate) and two commercial aromatic dianhydrides [166].

Both the PAA precursor and the cyclized PI proved biodegradable in a buffer solution, with a weight loss between 20 and 40% after 60 days of exposure, depending on the amount of amine used.

This represents a good starting point for a new research topic in the field of bioPIs. Similar studies are currently considering some of the partially or completely bio-based PIs described in the second section of this chapter.

4.2 Recycling of polyimides

Generally, two recycling technologies apply to PI materials: chemical and mechanical. The chemical recycling is a viable solution since it allows the maximum output of the final products (starting monomers, partially imidized powders) with a high degree of purity. Its main disadvantages are the long duration (multistage process) and energetic intensity.

In recent years, mechano-chemistry (e.g., ball milling) has proved its advantages over conventional chemical methods (fly ash modification, rubber, and plastic recycling), which lead to its intensive application in polymer recycling, PIs included. The process is simpler, economically favorable, and more eco-friendly (no solvents or intermediate fusion are used). Moreover, it allows attaining final products in a metastable state, which is not easily accessible by other conventional recycling methods.

Solid-state mecano-chemistry can be successfully applied in the recycling of PI film wastes with the purpose to develop thermostable blends and multicomponent tribocompositions. To gain applicative potential, these can be prepared in combination with other high-performance polymers, carbon black, diamond powder, and Al-Cu-Fe crystals [167].

The recycling treatment method depends on the physical form of the PI waste. PI-based powder compositions are obtained through low-energy planetary ball mill, PI film wastes are treated by high-energy planetary ball mill, while bulk samples are obtained by compression molding.

Multicomponent systems with a "multiscaled structure" based on PI waste and fluorinated ethylene propylene were obtained by the above methods. The resulting composites displayed an increased wear resistance and a smaller friction coefficient as compared to the raw propylenic material.

As mentioned before, a disadvantage of recycled PI usage in the development of composite materials is the lack of control of the interface and cohesion between composite elements. This results in a composite with unsatisfying integrity and poor mechanical features.

One solution to this issue is the use of polymer wastes of the same nature and proper tuning of the milling process. For example, common PMDA-ODA (pyromellitic dianhydride-4,4′-oxydianiline) PI films were grinded to powders and mixed with another commercial PI powder (BTDA [3,3′,4,4′-benzophenonetetracarboxylic dianhydride]-ODA) and a liquid, BTDA-based, commercial PI resin [168].

Several adjustments were performed to the high energy ball milling process, especially in terms of duration. The milling time strongly influences the average size and the particle-size distribution of the PI powder and the corresponding mechanical features of the resulting PI composites. Finally, bulk samples were obtained by compression molding at 400°C. The technique provided access to homogeneous materials with a flexural strength of 87 MPa, deformation at failure around 4.2%, and linear elastic modulus between 50and 350°C.

The milling duration also influences the chemical structure of the resulting recycled PI and its cohesion with the other two components of the composite material. Shorter milling times (45 min and 65 min) create larger particles that are

strongly reinforced through links provided by the PI resin during compression molding. On the other side, longer milling times (90 min and 180 min) provide smaller particles that are more compatible with and reinforced by the other powdered component (BTDA-ODA commercial PI).

Another mechanical recycling method is the application of uniaxial stretching on PI films to control and reduce the coefficient of thermal expansion of the recycled material [169]. The resulting PI material is stretchable at a certain operating temperature regime and draw ratios. Increased stretching stress (performed in the machine's direction) leads to recycled films with higher birefringence and Young's modulus and lower thermal expansion, mostly independent of temperature.

A very useful recycling procedure was proposed for gelled PAAs, a common issue for researchers dealing with PI synthesis. PAAs frequently form gels during synthesis or storage due to various intermolecular and intramolecular interactions, the entanglement of long, high mass chains, partial imidization, or even undesired cross-linking. The formed PAA gels are usually discarded both in research and industry, which translates into time and economic loss and, more importantly, to negative environmental impact.

The recycling method was applied for a broad range of conventional PI building blocks and is based on the conversion of PAA gels to homogeneous solutions by using common microwave irradiation for a short time at room temperature. In some random cases, similar results can be obtained by less green conditions: heating the gelled PAA at 135°C for at least an hour [170].

The resulting PAA solutions can be successfully converted to the corresponding PIs. The resulting materials maintain the original film-forming features and show superior thermal (Tg values included), mechanical, and dielectric features as compared to the original PIs (obtained from the ordinary, homogeneous PAA solutions).

Recyclability can be also attained by finding new applications for already established, commercial PI materials, as to ensure a longer product lifetime. For example, the Kapton PI film was used to build an efficient, active particulate matter air filter which, very important, is also recyclable. Patterned through-holes were developed by ion etching on the common film (15 μm hole diameter; 30 μm interhole distance) [171]. These holes are combined with the strong electrostatic forces coming from Kapton®'s high work function to capture particulate matter. The device was tested under real working conditions and proved efficient in long-term filtration of dust particles with dimensions ranging from 0.3 up to 10 μm.

Moreover, the highly flexible, thermally stable filter is easily recyclable and reusable by simple washing (with tap water), which makes it suitable for various air filter-based applications (air purifiers, air conditioners, humidifiers, and industrial filtration systems).

4.3 Recyclable PIs by design

Another strategic approach in the field of recycling PI-based materials is to ensure recyclability through judicious design, a tactic inspired by applications based on cyclic operations.

One example in this direction is the development of highly hydrophilic, composite recyclable PI adsorbents for wastewater treatment and removal of heavy metal ions [172]. These can be easily attained by the common sol-gel process which leads to hybrid PI/silica materials with Cu2+ adsorption yields comparable to those of common activated carbon adsorbents. The innate resilience of PIs affords adsorbents with stable adsorption performance over 50 recycling processes.

A more complex concept for hybrid, recyclable PIs is the development of intricate, green, poly(imide imine) thermosets that combine the mechanical resilience of

rigid PIs with the on-demand degradation and recyclability of flexible polyimines through dynamic covalent chemistry [173]. The greenness of the approach comes from the ability of imine units to provide heat- or water-triggered reversibility in the absence of expensive, environmentally unfriendly (transition metal) catalysts. The hybrid architecture is based on various ratios of an aromatic bisimide developed from widely used, commercial PI building blocks, a common aldehyde, and some aliphatic triamines or tetraamines as cross-linkers. The strategy affords thermosets with thermal and mechanical features comparable to common polyimides.

The key characteristic of these hybrid structures resides in the use of the primary amine as a catalyst to generate interchain imine exchange reactions at the interface of ruptured film strips. This feature leads to the conversation of mechanical properties and promotes a high healing output. The mechanical features of the (re) healed material are comparable or slightly superior to the original material up to the third generation.

The dynamic covalent chemistry concept unlocks novel pathways in the design of smart, high-performance PI-based materials able to lay out rehealability, repairability, and recyclability.

Another pathway to develop recyclable PIs is based on the introduction of flexible spacer units within and pendant to the macromolecular backbone. For example, the highly flexible 4,4′-diamino-3,3′-dimethyldiphenyl methane was polycondensed with BTDA to generate recyclable, PI-based, nanofiltration membranes. These are fabricated by phase inversion and retain a skinned asymmetric architecture [174].

The optimized membranes are efficient in rejecting Rose Bengal, PEG 1000, and typical salts with yields above 91%. They successfully corroborated their recyclability and display stable, longtime performance.

5. Conclusion

The development of high-performance, PI-based materials by following the rigid prerequisites of environmentally benign, green, or sustainable chemistry may still seem an arduous or eccentric task to the research society, especially to the industry-related part of it. The illusive incompatibility with the petrochemical-derived starting compounds and the usually harsh experimental conditions involved in their synthesis contribute to this stance. Nevertheless, judging by the firm advances made in the field in the last decade, the concept of bio-based or green PIs is not to be outdone.

Significant research endeavors have been devoted to engineer naturally derived building blocks based on nontoxic, bio-renewable feedstocks. These have evolved as viable and accessible alternatives to the traditional starting compounds and can be subjected to the classical experimental conditions of PI synthesis or even to greener ones. In most cases, the structural motifs of natural products are tailored to attain amine functionalities, while bio-based dianhydrides are still in their infancy.

Moreover, these building blocks can unlock eco-friendly, bio-based PI materials that maintain the same combination of high-performance characteristics and even bring some new or enhanced features to the field. There is a handful of high molar mass, soluble bioPIs with thermal stability, and mechanical features comparable with (and in a couple of cases even higher than) those of analogous petroleum-based PIs. They can be processed both as films and fibrils and provide industry-appealing features such as high optical transparency, optical activity, stable dielectric character, or tailorable hydrophilicity, without any negative impact upon thermal or mechanical resilience. Therefore, green polyimide chemistry exceeds the

fading trend aura and already has the solid starting points of a long-term strategy. Based on the plethora of yet unexploited, renewable reagents available, the Holy Grail of high-performance, fully bio-based PIs is not unreachable.

At the same time, serious progress has been made in the field of nonconventional synthetic and processing platforms for the development of PI-based materials. Less harmful experimental conditions such as ionic liquids, supercritical fluids, microwaves, and geothermal-inspired setups represent workable options and further reduce the negative environmental footprint of PIs' production. While still undeveloped and with some technological limitations regarding upscale and industrial use, these methods deliver sound results and provide access to novel, impressive PI materials such as nanoparticles, foams, aerogels, and membranes.

Last, but not least, the status quo has slightly shifted from the constant investigation of the outstanding stability of PIs to the evaluation of several recycling strategies. The mechano-chemical pathway is the lead runner in the field, since it is economically favorable, more eco-friendly, and paves the way for new, interesting materials. Therefore, this represents the third valid point of departure for new research topics in the field of high-performance, bio-based PIs.

Author details

Radu Dan Rusu[1*] and Marc J.M. Abadie[1,2]

1 Petru Poni Institute of Macromolecular Chemistry, Romanian Academy, Iasi, Romania

2 Institute Charles Gerhardt Montpellier, University of Montpellier, Montpellier, France

*Address all correspondence to: radu.rusu@icmpp.ro

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

References

[1] Abadie MJM, editor. High Performance Polymers—Polyimides Based. From Chemistry to Applications. Rijeka: Intech Europe; 2012. p. 256. DOI: 10.5772/2834

[2] Bruma M, Damaceanu MD, Rusu RD. Study of thin films made from aromatic polymers containing six-member imide rings. High Performance Polymers. 2012;**24**:31-39. DOI: 10.1177/0954008311431115

[3] Damaceanu MD, Rusu RD, Musteata VE, Bruma M. Dielectric behavior of thin films made from poly (oxadiazole-naphthylimide)s. Soft Materials. 2011;**9**:44-63. DOI: 10.1080/1539445x.2010.525445

[4] Rusu RD, Damaceanu MD, Bruma M, Ronova IA. Effect of conformational parameters on thermal properties of some poly(oxadiazole-naphthylimide)s. Iranian Polymer Journal. 2011;**20**:29-40

[5] Shin HI, Chang JH. Transparent polyimide/organoclay nanocomposite films containing different diamine monomers. Polymers. 2020;**12**:135-153. DOI: 10.3390/polym12010135

[6] Nalwa HS, editor. Supramolecular Photosensitive and Electroactive Materials. San Diego: Academic Press; 2001. p. 970

[7] Escorihuela S, Tena A, Shishatskiy S, Escolá Stico S, Brinkmann T, Serra JM, et al. Gas separation properties of polyimide thin films on ceramic supports for high temperature applications. Membranes. 2018;**8**:16. DOI: 10.3390/membranes8010016

[8] Constantin CP, Aflori M, Damian RF, Rusu RD. Biocompatibility of polyimides: A mini-review. Materials. 2019;**12**:3166. DOI: 10.3390/ma12193166

[9] Rusu RD, Damaceanu MD, Bruma M. Aromatic copolyimides containing perylene units. Macromolecular Symposia. 2010;**296**:399-406. DOI: 10.1002/masy.201051055

[10] Damaceanu MD, Rusu RD, Bruma M. Six-member polyimides incorporating redox chromophores. Journal of Materials Science. 2012;**47**: 6179-6188. DOI: 10.1007/s10853-012-6542-8

[11] Rusu RD, Damaceanu MD, Bruma M. Comparative study of soluble poly(keto-naphthylimide)s. Revue Roumaine de Chimie. 2009;**54**: 1015-1022

[12] Damaceanu MD, Rusu RD, Bruma M, Rusanov AL. New thermally stable and organosoluble heterocyclic poly(naphthaleneimide)s. Polymers for Advanced Technologies. 2011;**22**: 420-429. DOI: 10.1002/pat.1519

[13] Damaceanu MD, Rusu RD, Bruma M. Copolyimides containing perylene and hexafluoroisopropylidene moieties. High Performance Polymers. 2012;**24**:50-57. DOI: 10.1177/0954008311431112

[14] Belomoina NM, Bulycheva EG, Rusanov AL, Rusu RD, Damaceanu MD, Bruma M. Polynaphthylimides based on isomeric 2,5-bis[(aminophenoxy) phenylen]-1,3,4-oxadiazoles. Polymer Science, Series B. 2011;**22**:420-429. DOI: 10.1134/S156009041009006X

[15] Sroog CE. Polyimides. Progress in Polymer Science. 1991;**16**:561-694. DOI: 10.1016/0079-6700(91)90010-I

[16] Rusu RD, Damaceanu MD, Bruma M. Copoly(1,3,4-oxadiazole-naphthylimide)s containing siloxane units in the main chain: Synthesis and properties. High Performance Polymers.

2011;**23**:384-393. DOI: 10.1177/0954008311409784

[17] Kricheldorf HR, editor. Progress in Polyimide Chemistry I. Berlin Heidelberg: Springer-Verlag; 1999. DOI: 10.1007/3-540-49815-X

[18] Damaceanu MD, Rusu RD, Musteata VE, Bruma M. Insulating polyimide films containing n-type perylenediimide moieties. Polymer International. 2012;**61**:1582-1591. DOI: 10.1002/pi.4253

[19] Barikani M. Polyimides derived from diisocyanates. Iranian Polymer Journal. 2002;**11**:215-236

[20] Yu F, Wang K, Liu XY, Zhan MS. Preparation and properties of rigid polyimide foams derived from dianhydride and isocyanate. Journal of Applied Polymer Science. 2013;**127**: 5075-5081. DOI: 10.1002/app.38121

[21] Paraskevopoulou P, Chriti D, Raptopoulos G, Anyfantis GC. Synthetic polymer aerogels in particulate form. Materials. 2019;**12**:1543. DOI: 10.3390/ma12091543

[22] Deligoz H, Ozgumus S, Yalcınyuva T, Yıldırım S, Deger D, Ulutas K. A novel cross-linked polyimide film: Synthesis and dielectric properties. Polymer. 2005;**46**: 3720-3729. DOI: 10.1016/j.polymer.2005.02.097

[23] Ando S, Harada M, Okada T, Ishige R. Effective reduction of volumetric thermal expansion of aromatic polyimide films by incorporating interchain crosslinking. Polymers. 2018;**10**:761

[24] Zhang K, Liu J, Ishida H. High performance crosslinked polyimide based on main-chain type polybenzoxazine. RSC Advances. 2014; **4**:62550-62556. DOI: 10.1039/c4ra12015a

[25] Pohanish RP. Sitting's Handbook of Toxic and Hazardous Chemicals and Carcinogens. 6th ed. Norwich: William Andrew Publishing; 2012. pp. 873-875

[26] Zhu Y, Romain C, Williams CK. Sustainable polymers from renewable resources. Nature. 2016;**540**:354-362. DOI: 10.1038/nature21001

[27] Schneiderman DK, Hillmyer MA. 50th anniversary perspective: There is a great future in sustainable polymers. Macromolecules. 2017;**50**:3733-3749. DOI: 10.1021/acs.macromol.7b00293

[28] Nguyen HTH, Qi PX, Rostagno M, Feteha A, Miller SA. The quest for high glass transition temperature bioplastics. Journal of Materials Chemistry A. 2018; **6**:9298-9331. DOI: 10.1039/c8ta00377g

[29] Llevot A, Grau E, Carlotti S, Grelier S, Cramail H. Renewable (semi) aromatic polyesters from symmetrical vanillin-based dimers. Polymer Chemistry. 2015;**6**:6058-6066. DOI: 10.1039/c5py00824g

[30] Short GN, Nguyen HTH, Scheurle PI, Miller SA. Aromatic polyesters from biosuccinic acid. Polymer Chemistry. 2018;**9**:4113-4119. DOI: 10.1039/c8py00862k

[31] Llevot A, Grau E, Carlotti S, Grelier S, Cramail H. Selective laccase-catalyzed dimerization of phenolic compounds derived from lignin: Towards originalsymmetrical bio-based (bis) aromatic monomers. Journal of Molecular Catalysis B: Enzymatic. 2016; **125**:34-41. DOI: 10.1016/j.molcatb.2015.12.006

[32] Noe C, Malburet S, Bouvet-Marchand A, Graillot A, Sangermano M. Cationic photopolymerization of bio-renewable epoxidized monomers. Progress in Organic Coating. 2019;**133**: 131-138. DOI: 10.1016/j.porgcoat.2019.03.054

[33] Faure E, Falentin-Daudré C, Jerome C, Lyskawa J, Fournier D, Woisel P, et al. Catechols as versatile platforms in polymer chemistry. Progress in Polymer Science. 2014;**38**: 236-270. DOI: 10.1016/j.progpolymsci.2012.06.004

[34] Liu LM, Ni YH, Zhi YF, Zhao WB, Pudukudy M, Jia QM, et al. Sustainable and biodegradable copolymers from SO2 and renewable eugenol: A novel urea fertilizer coating material with superior slow release performance. Macromolecules. 2020;**53**:936-945. DOI: 10.1021/acs.macromol.9b02202

[35] Chatterjee D, Sadavarte NV, Shingte RD, More AS, Tawade BV, Kulkarni AD, et al. Step-growth polymers from cashew nut shell liquid (CNSL)-based aromatic difunctional monomers. In: Anilkumar P, editor. Cashew Nut Shell Liquid: A Goldfield for Functional Materials. 1st ed. New York: Springer; 2017. pp. 163-214. DOI: 10.1007/978-3-319-47455-7_9

[36] Shingte RD, Tawade BV, Wadgaonkar PP. Partially bio-based processable polyimides based on aromatic diamine derived from cardanol. Green Materials. 2017;**5**:74-84. DOI: 10.1680/jgrma.17.00010

[37] Yang G, Zhang R, Huang H, Liu L, Wang L, Chen Y. Synthesis of novel biobased polyimides derived from isomannide with good optical transparency, solubility and thermal stability. RSC Advances. 2015;**5**: 67574-67582. DOI: 10.1039/C5RA14526K

[38] Ji XD, Yan JL, Liu XJ, Wang ZK, Wang Z. Synthesis and properties of polyimides derived from bis(4-aminophenyl)isohexides. High Performance Polymers. 2017;**29**: 197-204. DOI: 10.1177/0954008316634443

[39] Ji XD, Wang ZK, Yan JL, Wang Z. Partially bio-based polyimides from isohexide-derived diamines. Polymer. 2015;**74**:38-45. DOI: 10.1016/j.polymer.2015.07.051

[40] Zhang R, Li T, Zhou H, Huang H, Chen Y. Biobased transparent polyimides with excellent solubility and mechanical properties using myo-inositol derived diamines. Reactive and Functional Polymers. 2018;**128**:91-96. DOI: 10.1016/j.reactfunctpolym.2018.05.006

[41] Okamoto S, Onou S, Kobayashi M, Sudo A. Rigid triol and diol with adamantane-like core derived from naturally occurring myo-inositol and their polyaddition with diisocyanates. Journal of Polymer Science, Part A: Polymer Chemistry. 2014;**52**:3498-3505. DOI: 10.1002/pola.27414

[42] Sudo A, Sugita S. A highly rigid diamine monomer derived from naturally occurring myo-inositol and its use for polyamide synthesis. Journal of Polymer Science, Part A: Polymer Chemistry. 2016;**54**:3436-3443. DOI: 10.1002/pola.28231

[43] Wang C, Sun J, Tao Y, Fang L, Zhou J, Dai M, et al. Biomass materials derived from anethole: Conversion and application. Polymer Chemistry. 2020; **11**:954-963. DOI: 10.1039/c9py01513b

[44] Kuhire S, Ichake A, Grau E, Cramail H, Wadgaonkar P. Synthesis and characterization of partially bio-based polyimides based on biphenylene-containing diisocyanate derived from vanillic acid. European Polymer Journal. 2018;**109**:257-264. DOI: 10.1016/j.eurpolymj.2018.09.054

[45] Fache M, Boutevin B, Caillol S. Vanillin production from lignin and its use as a renewable chemical. ACS Sustainable Chemistry & Engineering. 2016;**4**:35-46. DOI: 10.1021/acssuschemeng.5b01344

[46] Savonnet E, Le Croz C, Grau E, Grelier S, Defoort B, Cramail H.

Divanillin-based aromatic amines: Synthesis and use as curing agents for fully vanillin-based epoxy thermosets. Frontiers in Chemistry. 2019;**7**:606. DOI: 10.3389/fchem.2019.00606

[47] Kuhire SS, Sharma P, Chakrabarty S, Wandgaonkar PP. Partially bio-based poly(amide imide)s by polycondensation of aromatic diacylhydrazides based on lignin-derived phenolic acids and aromatic dianhydrides: Synthesis, characterization, and computational studies. Journal of Polymer Science, Part A: Polymer Chemistry. 2017;**55**: 3636-3645. DOI: 10.1002/pola.28748

[48] Wang ZK, Li YJ, Zhu TS, Xiong L, Liu F, Qi HX. Conversion of renewable vanillin into high performance polyimides via an asymmetric aromatic diamine derivation. Polymer Degradation and Stability. 2019;**167**:67-76. DOI: 10.1016/j.polymdegradstab. 2019.06.002

[49] Mirzakhanian Z, Faghihi K, Geravi HA, Mahdies M. Semi-aromatic polyimide/Ag nanocomposite derived from vanillin. Journal of Applied Polymer Science. 2016;**133**:44001. DOI: 10.1002/app.44001

[50] Wu Y, Tian Z, Liu Z, Xiong Z, Liu F. Semi-alicyclic polyimides from bio-renewable natural-(D)-camphor with high solubility and optical transparency. In: Abadie MJM, editor. Proceedings of the 11th Polyimides & High Performance Polymers Conference, STEPI 11; 2–5 June 2019. Montpellier: U. Montpellier; 2020. pp. 26-42

[51] Zhang HS, Li J, Tian ZL, Liu F. Synthesis and properties of novel alicyclic-functionalized polyimides prepared from natural-(D)-camphor. Journal of Applied Polymer Science. 2013;**129**:3333-3340. DOI: 10.1002/app.39053

[52] Minakawa H, Masuo S, Takaya N. Fermentation and purification of microbial monomer 4-amminocinnamic acid to produce ultra-high performance bioplastics. Process Biochemistry. 2019; **77**:100-105. DOI: 10.1016/j.procbio.2018.11.021

[53] Suvannasara P, Tateyama S, Miyasato A, Matsumura K, Shimoda T, Ito T, et al. Bio-based polyimides from 4-aminocinnamic acid photodimer. Macromolecules. 2014;**47**:1586-1593. DOI: 10.1021/ma402499m

[54] Kato S, Yusof FAA, Harimoto T, Takada K, Kaneko T, Kawai M, et al. Electric volume resistivity for biopolyimide using 4,4′-diamino-α-truxillic acid and 1,2,3,4-cyclobutanetetracarboxylic dianhydride. Polymers. 2019;**11**:1552. DOI: 10.3390/polym11101552

[55] Dwivedi S, Sakamoto S, Kato S, Mitsumata T, Kaneko T. Effects of biopolyimide molecular design on their silica hybrids thermo-mechanical, optical and electrical properties. RSC Advances. 2018;**8**:14009-14016. DOI: 10.1039/c8ra01965g

[56] Dwivedi S, Kaneko T. Robustification of ITO nanolayer by surface-functionalization of transparent biopolyimide substrates. Journal of Applied Polymer Science. 2018;**135**: 46709. DOI: 10.1002/app.46709

[57] Dwivedi S, Kaneko T. Molecular design of soluble biopolyimide with high rigidity. Polymers. 2018;**10**:368. DOI: 10.3390/polym10040368

[58] Huang TT, Tsai CL, Tateyama S, Kaneko T, Liou GS. Highly transparent and flexible bio-based polyimide.TiO2 and ZrO2 hybrid films with tunable refractive index, Abbe number, and memory properties. Nanoscale. 2016;**8**: 12793-12802. DOI: 10.1039/c6nr03963d

[59] Shin H, Wang S, Tateyama S, Kaneko D, Kaneko T. Preparation of a ductile biopolyimide film by

copolymerization. Industrial and Engineering Chemistry Research. 2016; **55**:8761-8766. DOI: 10.1021/acs.iecr.6b02221

[60] Kumar A, Tateyama S, Yasaki K, Ali MA, Takaya N, Singh R, et al. Ultrahigh performance bio-based polyimides from 4,4′-diaminostilbene. Polymer. 2016;**83**:182-189. DOI: 10.1016/j.polymer.2015.12.008

[61] Hirayama T, Kumar A, Takada K, Kaneko T. Morphology-controlled self-assembly and synthesis of biopolyimide particles from 4-amino-l-phenylalanine. ACS Omega. 2020;**5**:2187-2195. DOI: 10.1021/acsomega.9b03231

[62] Ahmadizadegan H, Ranjbar M. Synthesis and characterization of green membranes polyimide/titania bionanocomposites containing amino acid and benzimidazole moieties for gas transport properties. Polymer Engineering and Science. 2018;**58**: 1666-1677. DOI: 10.1002/pen.24757

[63] Hu J, Wang Z, Lu Z, Chen C, Shi M, Wang J, et al. Bio-based adenine-containing high performance polyimide. Polymer. 2017;**119**:59-65. DOI: 10.1016/j.polymer.2017.05.012

[64] Li RK, Lu Z, Liu Y, Zeng K, Hu JH, Yang G. The retarding effects and structural evolution of a bio-based high-performance polyimide during thermal imidization. Journal of Applied Polymer Science. 2019;**136**:46953. DOI: 10.1002/app.46953

[65] Hu JH, Li RK, Chen C, Lu Z, Zeng K, Yang G. New insights into mechanism of negative in-plane CTE based on bio-based adenine-containing polyimide film. Polymer. 2018;**146**:133-141. DOI: 10.1016/j.polymer.2018.05.001

[66] Susa A, Bijleveld J, Hernandez M, Garcia SJ. Understanding the effect of the dianhydride structure on the properties of semiaromatic polyimides containing a bio-based fatty diamine. ACS Sustainable Chemistry & Engineering. 2018;**6**:668-678. DOI: 10.1021/acssuschemeng.7b03026

[67] Susa A, Mordvinkin A, Saalwachter K, van der Zwaag S, Garcia SJ. Identifying the role of primary and secondary interactions on the mechanical properties and healing of densely branched polyimides. Macromolecules. 2018;**51**:8333-8345. DOI: 10.1021/acs.macromol.8b01396

[68] Susa A, Bose RK, Grande AM, van der Zwaag S, Garcia SJ. Effect of the dianhydride/branched diamine ratio on the architecture and room temperature healing behavior of polyetherimides. ACS Applied Materials & Interfaces. 2016;**8**:34068-34079. DOI: 10.1021/acsami.6b10433

[69] Liu JC, Wang K, Xie YZ, Gao F, Zeng QT, Yuan Y, et al. Novel partially bio-based fluorinated polyimides from dimer fatty diamine for UV-cured coating. Journal of Coating Technology and Research. 2017;**14**:1325-1334. DOI: 10.1007/s11998-017-9931-8

[70] Kiran E. Supercritical fluids and polymers. The year in review: 2014. Journal of Supercritical Fluids. 2016;**110**: 126-153. DOI: 10.1016/j.supflu.2015.11.011

[71] Kratochvil AM, Koros WJ. Effects of supercritical CO2 conditioning on cross-linked polyimide membranes. Macromolecules. 2010;**43**:4679-4687. DOI: 10.1021/ma100535h

[72] Haruki M, Hasegawa Y, Fukui N, Kihara S, Takishima S. Deposition of aromatic polyimide thin films in supercritical carbon dioxide. Journal of Supercritical Fluids. 2014;**94**:147-153. DOI: 10.1016/j.supflu.2014.07.010

[73] Ishizaka T, Ishigaki A, Suzuki TM, Chatterjee M, Kawanami H. Green synthetic method and simple

size-control of polyimide nanoparticles in scCO2. Chemistry Letters. 2011;**40**: 849-851. DOI: 10.1246/cl.2011.849

[74] Haruki M, Fukui N, Kihara S, Takishima S. Measurement and prediction of the solubilities of aromatic polyimide monomers in supercritical carbon dioxide with acetone. The Journal of Chemical Thermodynamics. 2012;**54**:261-265. DOI: 10.1016/j.jct.2012.04.013

[75] Haruki M, Fukui N, Kobayashi F, Kihara S, Takishima S. Entrainer effect of N,N-dimethylformamide on solubility of monomers for aromatic polyimide in supercritical carbon dioxide. Industrial and Engineering Chemistry Research. 2011;**50**: 11942-11949. DOI: 10.1021/ie2013289

[76] Haruki M, Wasada A, Hosokama Y, Kihara S, Takishima S. Deposition of PMDA-TFDB type polyimide onto microscale trenches patterned on silicon wafer using supercritical carbon dioxide. Journal of Supercritical Fluids. 2017;**127**:200-207. DOI: 10.1016/j.supflu.2017.03.008

[77] Haruki M, Oda A, Wasada A, Kihara S, Takishima S. Deposition of fluorinated polyimide consisting of 6FDA and TFDB into microscale trenches using supercritical carbon dioxide. Journal of Supercritical Fluids. 2017;**119**:238-244. DOI: 10.1016/j.supflu.2016.10.001

[78] Haruki M, Oda A, Wasada A, Hasegawa Y, Kihara S, Takishima S. Phase appearance during polymerization of fluorinated polyimide monomers and deposition into the microscopic-scale trenches in supercritical carbon dioxide. Journal of Applied Polymer Science. 2016;**133**: 43334. DOI: 10.1002/APP.43334

[79] Ronova IA, Sinitsyna OV, Abramchuck SS, Nikolaev AY, Chisca S, Sava I, et al. Study of porous structure of polyimide films resulting by using various methods. Journal of Supercritical Fluids. 2012;**70**:146-155. DOI: 10.1016/j.supflu.2012.06.018

[80] Ronova IA, Bruma M, Kuznetsov AA, Nikolaev AY. Lowering the dielectric constant of polyimide thin films by swelling with supercritical carbon dioxide. Polymers for Advanced Technologies. 2013;**24**:615-622. DOI: 10.1002/pat.3123

[81] Li L, Chang KC, Lin XN, Zhang R, Lou JH. Insulating property improvement of polyimide in devices by low-temperature supercritical fluids. Advanced Electronic Materials. 2019;**5**: 1900580. DOI: 10.1002/aelm.201900580

[82] Haruki M, Hasegawa Y, Fukui N, Kihara S, Takishima S. Production of polyamic acid in supercritical carbon dioxide with N, N-dimethylformamide. Journal of Applied Polymer Science. 2014;**131**:39878. DOI: 10.1002/app.39878

[83] Ronova IA, Alentiev AY, Chisca S, Sava I, Bruma M, Nikolaev AY, et al. Change of microstructure of polyimide thin films under the action of supercritical carbon dioxide and its influence on the transport properties. Structural Chemistry. 2014;**25**:301-310. DOI: 10.1007/s11224-013-0282-5

[84] Scholes CA, Kanehashi S. Polymeric membrane gas separation performance improvements through supercritical CO2 treatment. Journal of Membrane Science. 2018;**566**:239-248. DOI: 10.1016/j.memsci.2018.09.014

[85] Lin HW, Tan CS. Preparation of polyamic acid and polyimide nanoparticles by compressed fluid antisolvent and thermal imidization. Journal of Supercritical Fluids. 2015;**99**: 103-111. DOI: 10.1016/j.supflu.2015.01.028

[86] Zhai WT, Feng WW, Ling JQ, Zheng WG. Fabrication of lightweight microcellular polyimide foams with three-dimensional shape by CO2 foaming and compression molding. Industrial and Engineering Chemistry Research. 2012;**51**:12827-12834. DOI: 10.1021/ie3017658

[87] Wu S, Du A, Huang SM, Sun W, Xiang YL, Zhou B. Solution-processable polyimide aerogels with high hydrophobicity. Materials Letters. 2016; **176**:118-121. DOI: 10.1016/j.matlet.2016.04.099

[88] Kuiper S, Embrechts A, Every HA, de Vries T, de Smet LCPM. Matrimid aerogels by temperature-controlled, solution-based crosslinking. Macromolecular Materials and Engineering. 2013;**298**:868-875. DOI: 10.1002/mame.201200335

[89] Fei ZF, Yang ZC, Chen GB, Li KF. Preparation of tetraethoxysilane-based silica aerogels with polyimide cross-linking from 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride and 4, 4′-oxydianiline. Journal of Sol-Gel Science and Technology. 2018;**3**: 506-513. DOI: 10.1007/s10971-017-4566-x

[90] Kim M, Eo K, Lim HJ, Kwon YK. Low shrinkage, mechanically strong polyimide hybrid aerogels containing hollow mesoporous silica nanospheres. Composites Science and Technology. 2018;**165**:355-361. DOI: 10.1016/j.compscitech.2018.07.021

[91] Zhang TY, Zhao Y, Wang K. Polyimide aerogels cross-linked with aminated Ag nanowires: Mechanically strong and tough. Polymers. 2017;**9**:530. DOI: 10.3390/polym9100530

[92] Teo N, Gu ZP, Jana SC. Polyimide-based aerogel foams via emulsion-templating. Polymer. 2018;**157**:95-102. DOI: 10.1016/j.polymer.2018.10.030

[93] Zhai CH, Jana SC. Tuning porous networks in polyimide aerogels for airborne nanoparticle filtration. ACS Applied Materials & Interfaces. 2017;**9**: 34068-34079. DOI: 10.1021/acsami.7b09345

[94] Fanf GQ, Li H, Liu JG, Ni HJ, Yang HX, Yang SY. Intrinsically atomic-oxygen-resistant POSS-containing polyimide aerogels: Synthesis and characterization. Chemistry Letters. 2015;**44**:1083-1085. DOI: 10.1246/cl.150396

[95] Shen DX, Liu FG, Yang HX, Yang SY. Intrinsically highly hydrophobic semi-alicyclic fluorinated polyimide aerogel with ultralow dielectric constants. Chemistry Letters. 2013;**42**:1230-1232. DOI: 10.1246/cl.130623

[96] Zhang TY, Zhao Y, Muhetaer M, Wang K. Silver nanoparticles cross-linked polyimide aerogels with improved high temperature microstructure stabilities and high mechanical performances. Microporous and Mesoporous Materials. 2020;**297**: 110035. DOI: 10.1016/j.micromeso.2020.110035

[97] Feng JZ, Wang X, Jiang YG, Du DX, Feng J. Study on thermal conductivities of aromatic polyimide aerogels. ACS Applied Materials & Interfaces. 2016;**8**: 12992-12996. DOI: 10.1021/acsami.6b02183

[98] Singh SK, Savoy AW. Ionic liquids synthesis and applications. An overview. Journal of Molecular Liquids. 2020;**297**:112038. DOI: 10.1016/j.molliq.2019.112038

[99] Villa R, Alvarez E, Porcar R, Garcia-Verdugo E, Luis SV, Lozano P. Ionic liquids as an enabling tool to integrate reaction and separation processes. Green Chemistry. 2019;**21**:6527-6544. DOI: 10.1039/c9gc02553g

[100] Sinha AK, Singh R, Kumar R. Towards an understanding of the

ambiphilic character of ionic liquids for green synthesis of chemically diverse architectures. Asian Journal of Organic Chemistry. 2020;**9**:706-720. DOI: 10.1002/ajoc.202000065

[101] Xing DY, Chan SY, Sung TS. Fabrication of porous and interconnected PBI/P84 ultrafiltration membranes using [EMIM]OAc as the green solvent. Chemical Engineering Science. 2013;**87**:194-203. DOI: 10.1016/j.ces.2012.10.004

[102] Chen M, Wang SL. Non-thermal polyimidization reaction using base-ionic liquid medium as a dual catalyst-solvent. RSC Advances. 2016; **6**:96914-96917. DOI: 10.1039/c6ra23162d

[103] Mallakpour S, Zadehnazari A. Tailored synthesis of nanostructured polymer thin films from optically active and thermally stable poly(amide-co-imide)s containing hydroxyl pendant groups in a green ionic solvent. Polymer-Plastics Technology and Engineering. 2012;**51**:1097-1105. DOI: 10.1080/03602559.2012.689060

[104] Mallakpour S, Zarei M. Novel, thermally stable and chiral poly(amide-imide)s derived from a new diamine containing pyridine ring and various amino acid-based diacids: Fabrication and characterization. High Performance Polymers. 2013;**25**:245-253. DOI: 10.1177/0954008312461658

[105] Gharekhani E, Mehdipour-Ataei S, Taghi-Ganji M. Soluble and thermally stable new pyridine-based poly(ether imide)s synthesized through conventional and ionic liquid methods. Iranian Polymer Journal. 2011;**20**: 491-502

[106] Mansoori Y, Atghia SV, Sanaei SS, Zamanloo MR, Imanzadeh G, Eskandari H. New, organo-soluble, thermally stable aromatic polyimides and poly(amide-imide) based on 2-[5-(3,5-dinitrophenyl)-1,3, 4-oxadiazole-2-yl] pyridine. Polymer International. 2012;**61**: 1213-1220. DOI: 10.1002/pi.4234

[107] Akbarian-Feizi L, Mehdipour-Ataei S, Yeganeh H. Investigation on the preparation of new sulfonated polyimide fuel cell membranes in organic and ionic liquid media. International Journal of Polymeric Materials and Polymeric Biomaterials. 2014;**63**:149-160. DOI: 10.1080/00914037.2013.812086

[108] Akbarian-Feizi L, Mehdipour-Ataei S, Yeganeh H. Synthesis of new sulfonated copolyimides in organic and ionic liquid media for fuel cell application. Journal of Applied Polymer Science. 2012;**124**:1981-1992. DOI: 10.1002/app.35136

[109] Hartanto Y, Corvilain M, Marien H, Janssesn J, Vankelecom IFJ. Interfacial polymerization of thin-film composite forward osmosis membranes using ionic liquids as organic reagent phase. Journal of Membrane Science. 2020;**601**:117869. DOI: 10.1016/j.memsci.2020.117869

[110] Li P, Coleman MR. Synthesis of room temperature ionic liquids based random copolyimides for gas separation applications. European Polymer Journal. 2013;**49**:482-491. DOI: 10.1016/j.eurpolymj.2012.11.016

[111] O'Harra KE, Kammakakam I, Bara JE, Jackson EM. Understanding the effects of backbone chemistry and anion type on the structure and thermal behaviors of imidazolium polyimide-ionenes. Polymer International. 2019;**68**: 1547-1556. DOI: 10.1002/pi.5825

[112] Shaplov AS, Morozova SM, Lozinskaya EI, Vlasov PS, Gouveia ASL, Tome LC, et al. Turning into poly(ionic liquid)s as a tool for polyimide modification. Synthesis, characterization and CO2 separation

properties. Polym. Chem. 2016;**7**: 580-591. DOI: 10.1039/c5py01553g

[113] O'Harra KE, Kammakakam I, Devriese EM, Doll DM, Bara JE, Jackson EM. Synthesis and performance of 6FDA-based polyimide-ionenes and composites with ionic liquids as gas separation membranes. Membranes. 2019;**9**:79. DOI: 10.3390/membranes9070079

[114] Govindaraj B, Sarojadevi M. Microwave-assisted synthesis and characterization of polyimide/functionalized MWCNT nanocomposites containing quinolyl moiety. Polymer Composites. 2016;**37**: 2417-2424. DOI: 10.1002/pc.23426

[115] Zhou LR, Li YZ, Wang ZQ, Zhang MY, Wang XD, Niu HQ, et al. Preparation of polyimide films via microwave-assisted thermal imidization. RSC Advances. 2019;**9**: 7314-7320. DOI: 10.1039/c9ra00355j

[116] Govindaraj B, Sarojadevi M. Microwave-assisted synthesis of nanocomposites from polyimides chemically cross-linked with functionalized carbon nanotubes for aerospace applications. Polymers for Advanced Technologies. 2016;**29**: 1718-1726. DOI: 10.1002/pat.4275

[117] Wang Y, Huang MY, Lei Y. Improved synthesis and properties of BTDA-TDI/MDI ternary copolyimides via microwave-assisted polycondensation. High Performance Polymers. 2020;**32**: UNSP0954008320908635. DOI: 10.1177/0954008320908635

[118] Cheng K, Hu JP, Wu YC, Shi CQ, Chen ZG, Liu SM, et al. Microwave-assisted synthesis of high thermal stability and colourless polyimides containing pyridine. Royal Society Open Science. 2019;**6**:190196. DOI: 10.1098/rsos.190196

[119] Li TY, Liu JJ, Zhao SS, Chen ZQ, Huang HH, Guo RL, et al. Microporous polyimides containing bulky tetra-o-isopropyl and naphthalene groups for gas separation membranes. Journal of Membrane Science. 2019;**585**:282-288. DOI: 10.1016/j.memsci.2019.05.003

[120] Li TY, Huang HH, Wang L, Chen YM. High performance polyimides with good solubility and optical transparency formed by the introduction of alkyl and naphthalene groups into diamine monomers. RSC Advances. 2017;**7**:40996-41003. DOI: 10.1039/c7ra07142f

[121] Choi JY, Jin SW, Kim DM, Song IH, Nam KN, Park HJ, et al. Enhancement of the mechanical properties of polyimide film by microwave irradiation. Polymers. 2019;**11**:477. DOI: 10.3390/polym11030477

[122] Xiao JD, Qiu LG, Yuan YP, Jiang X, Xie AJ, Shane YH. Ultrafast microwave-enhanced ionothermal synthesis of luminescent crystalline polyimide nanosheets for highly selective sensing of chromium ions. Inorganic Chemistry Communications. 2013;**29**:128-130. DOI: 10.1016/j.inoche.2012.12.028

[123] Seckin T, Kivilcim N, Koytepe S. Synthesis of triazine-based polyimide nanocomposites with flower-like ZnO by microwave-assisted solvothermal technique. Polymer-Plastics Technology and Engineering. 2013;**52**:1368-1375. DOI: 10.1080/03602559.2013.820747

[124] Fujii S, Kawamura S, Mochizuki D, Maitani MM, Suzuki E, Wada Y. Microwave sintering of Ag-nanoparticle thin films on a polyimide substrate. AIP Advances. 2015;**5**:127226. DOI: 10.1063/1.4939095

[125] Dasgupta J, Sikder J, Chakraborty S, Adhikari U, Reddy BVP, Mondal A, et al. Microwave-assisted modified polyimide synthesis. A facile route to the enhancement of visible-

light-induced photocatalytic performance for dye degradation. ACS Sustainable Chemistry & Engineering. 2017;**5**:6817-6826. DOI: 10.1021/acssuschemeng.7b01044

[126] Lin L, Ye P, Cao C, Jin Q, Xu GS, Shen YH, et al. Rapid microwave-assisted green production of a crystalline polyimide for enhanced visible-light-induced photocatalytic hydrogen production. Journal of Materials Chemistry A. 2015;**3**: 10205-10208. DOI: 10.1039/c5ta01078k

[127] Wang K, Yuan XJ, Zhan MS. Comparison between microwave and thermal curing of a polyimide adhesive end-caped with phenylethynyl groups. International Journal of Adhesion and Adhesives. 2017;**74**:28-34. DOI: 10.1016/j.ijadhadh.2016.12.008

[128] Imai Y. Recent progress in synthesis of polyimides. Journal of Photopolymer Science and Technology. 1994;**7**:251-256. DOI: 10.2494/photopolymer.7.251

[129] Baumgartner B, Bojdys MJ, Unterlass MM. Geomimetics for green polymer synthesis: Highly ordered polyimides via hydrothermal techniques. Polymer Chemistry. 2014;**5**: 3771-3776. DOI: 10.1039/c4py00263f

[130] Baumgartner B, Puchberger M, Unterlass MM. Towards a general understanding of hydrothermal polymerization of polyimides. Polymer Chemistry. 2015;**6**:5773-5781. DOI: 10.1039/c5py00231a

[131] Unterlass MM, Kopetzki D, Antonietti M, Weber J. Mechanistic study of hydrothermal synthesis of aromatic polyimides. Polymer Chemistry. 2011;**2**:1744-1753. DOI: 10.1039/c1py00109d

[132] Baumgartner B, Bojdys MJ, Skrinjar P, Unterlass MM. Design strategies in hydrothermal polymerization of polyimides. Macromoecular Chemistry and Physics. 2016;**217**:485-500. DOI: 10.1002/macp.201500287

[133] Unterlass MM, Emmerling F, Antonietti M, Weber J. From dense monomer salt crystals to CO2 selective microporous polyimides via solid-state polymerization. Chemical Communications. 2014;**50**:430-432. DOI: 10.1039/c3cc47674j

[134] Taublaender MJ, Reiter M, Unterlass MM. Highly crystalline, nanostructured polyimide microparticles via green and tunable solvothermal polymerization. Macromolecules. 2019;**52**:6318-6329. DOI: 10.1021/acs.macromol.9b00985

[135] Cui ZW, Zhou J, Liu T, Wang YC, Hu Y, Wang Y, et al. Porphyrin-containing polyimide with enhanced light absorption and photocatalysis activity. Chemistry, an Asian Journal. 2019;**14**:2138-2148. DOI: 10.1002/asia.201900261

[136] Leimhofer L, Baumgartner B, Puchberger M, Prochaska T, Konegger T, Unterlass MM. Green one-pot synthesis and processing of polyimide–silica hybrid materials. Journal of Materials Chemistry A. 2017; **5**:16326-16335. DOI: 10.1039/c7ta02498c

[137] Zhuo LH, Tang SL, Zhao KY, Xie F, Bai Y. Green facile fabrication of polyimide by microwave-assisted hydrothermal method and its decomposition dynamics. Journal of Applied Polymer Science. 2020;**137**: 48484. DOI: 10.1002/app.48484

[138] Jiang SH, Hou HQ, Agarwal S, Greiner A. Polyimide nanofibers by "green" electrospinning via aqueous solution for filtration applications. ACS Sustainable Chemistry & Engineering. 2016;**4**:4797-4804. DOI: 10.1021/acssuschemeng.6b01031

[139] Abadie MJM, Marchal J. Dégradation oxydante du polystyrène à 25°C. II. Étude du mécanisme par amorçage radiochimique en solution chloroformique diluée. Die Makromolekulare Chemie. 1971;**14**: 299-316. DOI: 10.1002/macp.1971.021410123

[140] Ferreira FAS, Battirola LC, Lewicki JP, Worsley MA, Pereira-da-Silva MA, Amaral T, et al. Influence of thermal treatment time on structural and physical properties of polyimide films at beginning of carbonization. Polymer Degradation and Stability. 2016;**129**:399-407. DOI: 10.1016/j.polymdegradstab. 2016.05.001

[141] Hondred PR, Yoon S, Bowler N, Moukhina E, Kessler MR. Degradation kinetics of polyimide film. High Performance Polymers. 2011;**23**: 335-342. DOI: 10.1177/0954008311409262

[142] Hondred PR, Bowler N, Kessler MR. Electrothermal lifetime prediction of polyimide wire insulation with application to aircraft. Journal of Applied Polymer Science. 2013;**130**: 1639-1644. DOI: 10.1002/app.39304

[143] Lin L, Bowler N, Hondred PR, Kessler MR. Influence of thermal degradation and saline exposure on dielectric permittivity of polyimide. Journal of Physics and Chemistry of Solids. 2011;**72**:875-881. DOI: 10.1016/j.jpcs.2011.04.004

[144] Dine-Hart RA, Parker DBV, Wright WW. Oxidative degradation of a polyimide film: I. initial studies. British Polymer Journal. 1971;**3**:222-225. DOI: 10.1002/pi.4980030504

[145] Su X, Xu Y, Li L, Song C. Characterization and thermal degradation kinetics of thermoplastic polyimide based on BAPP. High Performance Polymers. 2017;**30**:787-793. DOI: 10.1177/0954008317729741

[146] Liu Y, Xu X, Mo S, Lan B, Zhu C, Xu J, et al. Kinetic study of the multistep thermo-oxidative degradation of thermosetting siloxane-containing polyimide and unmodified polyimide. Journal of Applied Polymer Science. 2020:e49021. DOI: 10.1002/app.49021

[147] Huertas RM, Tena A, Lozano AE, de Abajo J, de la Campa JG, Maya EM. Thermal degradation of crosslinked copolyimide membranes to obtain productive gas separation membranes. Polymer Degradation and Stability. 2013;**98**:743-750. DOI: 10.1016/j.polymdegradstab. 2012.12.017

[148] Li X, Miyauchi M, Gonzalez C, Nutt S. Thermal oxidation of PEPA-terminated polyimide. High Performance Polymers. 2018;**31**:707-718. DOI: 10.1177/0954008318787852

[149] Hamciuc C, Lisa G, Hamciuc E, Tudorachi N. Thermal decomposition study of some polyimide-polydimethylsiloxane copolymers. Journal of Analytical and Applied Pyrolysis. 2018;**129**:204-214. DOI: 10.1016/j.jaap.2017.11.011

[150] Khazaka R, Locatelli ML, Diaham S, Bidan P. Effects of mechanical stresses, thickness and atmosphere on aging of polyimide thin films at high temperature. Polymer Degradation and Stability. 2013;**98**: 361-367. DOI: 10.1016/j.polymdegradstab. 2012.09.005

[151] Perrota C, Gonona L, Marestinb C, Gebela G. Hydrolytic degradation of sulfonated polyimide membranes for fuel cells. Journal of Membrane Science. 2011;**379**:207-214. DOI: 10.1016/j.memsci.2011.05.063

[152] Xu Y, Zehnder AT. Moisture degradation effects on the mechanical properties of HFPE-II-52 polyimide: Experiments and modeling. Experimental Mechanics. 2017;**57**:857-869. DOI: 10.1007/s11340-017-0281-3

[153] Xu Y, Zehnder AT. Pressure, hydrolytic degradation and plasticization drive high temperature blistering failure in moisture saturated polyimides. Extreme Mechanics Letters. 2017;**16**:49-55. DOI: 10.1016/j.eml.2017.09.002

[154] Sili E, Cambronne JP, Naude N, Khazaka R. Polyimide lifetime under partial discharge aging: Effects of temperature, pressure and humidity. IEEE Transactions on Dielectrics and Electrical Insulation. 2013;**20**:435. DOI: 10.1109/TDEI.2013.6508745

[155] Campbell FJ, Brewer AK, Orr RJ, Janicke TA, Brunining AM. Hydrolytic deterioration of polyimide insulation on naval aircraft wiring. In: Proceeding of the IEEE Conference on Electrical Insulation and Dielectric Phenomena; 16–20 October 1988. Ottawa, New York: IEEE; 1988. pp. 180-188. DOI: 10.1109/CEIDP.1988.26329

[156] Huang X, Pu Y, Zhou Y, Zhang Y, Zhang H. In-situ and ex-situ degradation of sulfonated polyimide membrane for vanadium redox flow battery application. Journal of Membrane Science. 2017;**526**:281-292. DOI: 10.1016/j.memsci.2016.09.053

[157] Harito C, Bavykin DV, Yuliarto B, Dipojono HK, Walsh FC. Inhibition of polyimide photodegradation by incorporation of titanate nanotubes into a composite. Journal of Polymers and the Environment. 2019;**27**:1505-1515. DOI: 10.1007/s10924-019-01443-w

[158] Rusu RD, Constantin CP, Drobota M, Gradinaru LM, Butnaru M, Pislaru M. Polyimide films tailored by UV irradiation: Surface evaluation and structure-properties relationship. Polymer Degradation and Stability. 2020;**177**:109182. DOI: 10.1016/j.polymdegradstab. 2020.109182

[159] Rasmussen K, Grampp G, van Eesbeek M, Rohr T. Thermal and UV degradation of polymer films studied in situ with ESR spectroscopy. ACS Applied Materials & Interfaces. 2010;**2**:1879-1883. DOI: 10.1021/am100219z

[160] Severin D, Balanzat E, Ensinger W, Trautmann C. Outgassing and degradation of polyimide induced by swift heavy ion irradiation at cryogenic temperature. Journal of Applied Physics. 2010;**108**:024901. DOI: 10.1063/1.3457846

[161] Damaceanu MD, Rusu RD, Olaru MA, Timpu D, Bruma M. KrF pulsed laser ablation of thin films made from fluorinated heterocyclic poly (naphthyl-imide)s. Microscopy and Microanalysis. 2012;**18**:545-557. DOI: 10.1017/S1431927612000165

[162] Damaceanu MD, Rusu RD, Olaru M, Stoica I, Bruma M. Nanostructured polyimide films by UV excimer laser irradiation. Romanian Journal of Information Science and Technology. 2010;**13**:368-377

[163] Ennis CP, Kaiser RI. Mechanistical studies on the electron-induced degradation of polymethylmethacrylate and Kapton. Physical Chemistry Chemical Physics. 2010;**12**:14902-14915. DOI: 10.1039/c0cp01130d

[164] Dong SS, Shao WZ, Yang L, Ye HJ, Zhena L. Surface characterization and degradation behavior of polyimide films induced by coupling irradiation treatment. RSC Advances. 2018;**8**:28152. DOI: 10.1039/c8ra05744c

[165] Plis E, Engelhart DP, Barton D, Cooper R, Ferguson D, Hoffmann R. Degradation of polyimide under exposure to 90 keV electrons. Physica Status Solidi B: Basic Solid State Physics. 2017;**254**:1600819. DOI: 10.1002/pssb.201600819

[166] Lin RH, Wang WM, Chen YH, Ho TH. Preparation and characterization of biodegradable

condensation polyimide. Polymer Degradation and Stability. 2012;**97**: 1534-1544. DOI: 10.1016/j.polymdegradstab. 2012.04.012

[167] Olifirov LK, Kaloshkin SD, Ergin KS, Tcherdyntsev VV, Danilov VD. Solid-state recycling of polyimide film waste. Journal of Applied Polymer Science. 2012;**127**:2960-2968. DOI: 10.1002/APP.37964

[168] L Olifirov LK, Kaloshkin SD, Zadorozhnyy MY, Zadorozhnyy VY, Tcherdyntsev VV, Danilov VD. Recycled moulded polyimide materials obtained by high-energy ball milling. Journal of Applied Polymer Science. 2018;**135**:46733. DOI: 10.1002/app.46733

[169] Wang HY, Liu TJ, Liu SF, Jeng JL, Guan CE. Thermal and mechanical properties of stretched recyclable polyimide film. Journal of Applied Polymer Science. 2011;**122**:210-219. DOI: 10.1002/app.34139

[170] Yu HC, Choi JY, Jeong JW, Kim BJ, Chung CM. Simple and easy recycling of poly(amic acid) gels through microwave irradiation. Journal of Polymer Science, Part A: Polymer Chemistry. 2017;**55**: 981-987. DOI: 10.1002/pola.28458

[171] Choi SJ, Kim KH, Kim HJ, Yoon JS, Lee M, Choi KS, et al. Highly efficient, flexible, and recyclable air filters using polyimide films with patterned thru-holes fabricated by ion milling. Applied Sciences. 2019;**9**:235. DOI: 10.3390/app9020235

[172] Huang J, Zheng Y, Luo L, Feng Y, Zhang C, Wang X, et al. Facile preparation of highly hydrophilic, recyclable high-performance polyimide adsorbents for the removal of heavy metal ions. Journal of Hazardous Materials. 2016;**306**:210-219. DOI: 10.1016/j.jhazmat.2015.12.023

[173] Lei XF, Jin YH, Sun HL, Zhang W. Rehealable imide-imine hybrid polymers with full recyclability. Journal of Materials Chemistry A. 2017;**5**: 21140-21145. DOI: 10.1039/c7ta07076d

[174] Wei CJ, Cheng Q, Lin LG, He ZF, Huang K, Ma SS, et al. One-step fabrication of recyclable polyimide nanofiltration membranes with high selectivity and performance stability by a phase inversion-based process. Journal of Materials Science. 2018;**53**: 11104-11115. DOI: 10.1007/s10853-018-2369-2