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Review

Review of Bioplastics Characterisation by Terahertz Techniques in the View of Ensuring a Circular Economy

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Abstract: The increasing scarcity of natural resources, worsening global climate change, environmental degradation, and rising demand for food are forcing the biotechnology and plastics industries to seek and apply circular economy models that would lead to a sustainable transition in the production and use of bioplastics. Circular economy models can improve the economic productivity of bio-based plastics and have a positive impact on the environment by reducing conventional plastic waste and the consumption of petrochemical feedstocks for plastic production. In addition, some agricultural wastes that have the potential to be used as bioplastics can be reused. Terahertz (THz) systems are already used in the plastics and rubber industries for non-destructive testing, detection, imaging, and quality control. Several reports have highlighted the potential applications of THz spectroscopy and imaging in polymer analysis and plastics characterisation. This potential is even greater with chemometric methods and artificial intelligence algorithms. In this review, we focus on applications that support the transformation of the biotechnology sector to the circular economy, particularly via the transition from conventional plastics to bioplastics. In this review, we discuss the potential of THz systems for the characterisation and analysis of bioplastics and biopolymers. The results of previous studies on biopolymers in the THz frequency range are summarised. Furthermore, the potential of using artificial intelligence approaches such as machine learning as advanced analytical methods in THz spectroscopy and imaging, in addition to the conventionally used chemometric methods, is discussed. The results of this review highlight that THz technology can contribute to closed technological circles in important areas of biotechnology and the related plastics and rubber industries.

Keywords: terahertz spectroscopy; terahertz imaging; circular economy; biopolymer; biotechnology; bioplastics

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1. Introduction

Over the last 50 years, the production and consumption of plastics have grown faster than any other manufactured material. The production of plastics and other petrochemicals is expected to account for half of the world's oil demand by 2050 [1]. The widespread use of plastics is linked to marine pollution caused by microplastics and the carbon dioxide released in the production of plastics. This has led to a strong demand for environmentally friendly biomass-based plastics instead of petroleum-based plastics. While many polymer materials are used in daily life, using biopolymers in households is still less common. Using biopolymers and bioplastics can reduce many environmental problems associated with plastics and polymers, which raise concerns about potential impacts on marine, aquatic and terrestrial species, agricultural products and humans [2].

Polymer properties such as hardness, brittleness, processability and thermal stability depend not only on the chemical composition but also on the higher-order secondary and tertiary structures and their transitions related to crystallinity, molecular chain length and solid-state chain packing [3]. The properties of petroleum-based plastics are much more studied than those of biomass-based plastics, where the basis for understanding them is knowledge of their higher-order structure and physical properties. Non-destructive and non-invasive analytical techniques are needed to understand the functions and properties of bioplastics and their polymeric constituents. Common methods used for physiochemical properties analysis of this type of material are differential scanning calorimetry (DSC) to determine the glass transition temperature (the sample is usually destroyed), Fourier Transform Infra-Red (FTIR) spectroscopy to confirm the functional properties and molecular interactions, UV-Vis, Fluorescence spectroscopy, thermogravimetric analysis (TGA) to determine thermodynamic properties and X-ray diffraction (XRD), which requires lengthy measurements and has adverse effects on the human body [4–7]. Alternative non-destructive and non-invasive characterisation methods include those operating in the terahertz (THz) frequency range (0.1 THz to 20 THz), which lies between microwave and infrared light. THz spectroscopic and imaging techniques are widely used to assess polymer structures, dynamics and physiochemical properties and for structural analyses of various polymeric materials and composites [8–12].

Terahertz spectroscopy and imaging are already being used to analyse the chemical composition of drugs and their active ingredients in the pharmaceutical industry [13–15]. In the field of biomedical research, THz technology is used to investigate and analyse the structure, dynamics and properties of biological molecules such as proteins [16–18], DNA [19–21] and even cells and tissues [22–24]. This approach contributes to explaining the mechanisms of various diseases and helps develop new diagnostic tools and therapies to ensure human health [25–28]. Recently, other areas of the industry have started to benefit from these advantages of THz systems. THz technology has already shown its potential in applications in various areas of agriculture [29–31], the construction and building industry [32,33], the food industry [30,34–37] and biotechnology [38,39]. The food industry uses THz spectroscopy as a non-destructive method to determine the quality and safety of food products [34]. It can be used, for example, to detect foreign bodies [35] and contaminants such as pesticides [40] in food samples. In agriculture, this technology is used to study the properties of plant tissues [41] and to detect the presence of pathogens and pests in crops [42]. It makes an important contribution to improving crop quality and reducing crop losses due to the timely detection of diseases and pests. At this point, we can already talk about the contribution of THz technologies to the circular economy in agriculture. However, biotechnology regarding the bioplastics characterisation still lags, although THz technology already showed great potential in the applications of polymer analysis [8,43,44] and plastic materials characterisation [45,46].

THz systems are already widely used for biosensing and biomedical analysis [47–51]. These applications are not covered in this review, which focuses on the role of biotechnology in the transition from traditional plastics to bioplastics. In this review, we discuss the potential of THz systems for characterising and analysing bioplastics and biopolymers. In this paper, we focus on key building blocks of bioplastic polymers that have already been studied by THz spectroscopy. We have summarised the results of previous studies on biopolymers in the THz frequency range. In addition, we also present the potential of using artificial intelligence approaches such as machine learning and deep learning as advanced analytical methods in THz spectroscopy and imaging in addition to the conventionally used chemometric methods.

2. Biopolymers as a Solution to Environmental Plastic Pollution

A polymer material can be considered bioplastic if it is bio-based or made from renewable materials with biodegradable potential and represents an alternative to conventional petrochemical plastics [52]. Bioplastics have important advantages compared to petroleum-based plastics, such as lower consumption of non-renewable raw materials and reduced greenhouse gas emissions (i.e., lower carbon footprint), better functionality and additional waste management options (e.g., organic recycling). In addition to the positive aspects, the production and use of bioplastics must also consider other environmental aspects, such as the exploitation of land used for intensive cereal cultivation for source materials, which threatens agricultural food production and natural habitats and local ecosystems, with possible consequences for fauna and flora. In addition, the material properties of bioplastics and their composites in terms of biodegradability, durability, rigidity and strength are also of concern, as they lose their functional properties under certain environmental conditions, i.e., abiotic (humidity, temperature) and biotic (enrichment in microorganisms) factors [53–55]. The type of bioplastics considering its origin and biodegradability is shown in Figure 1.

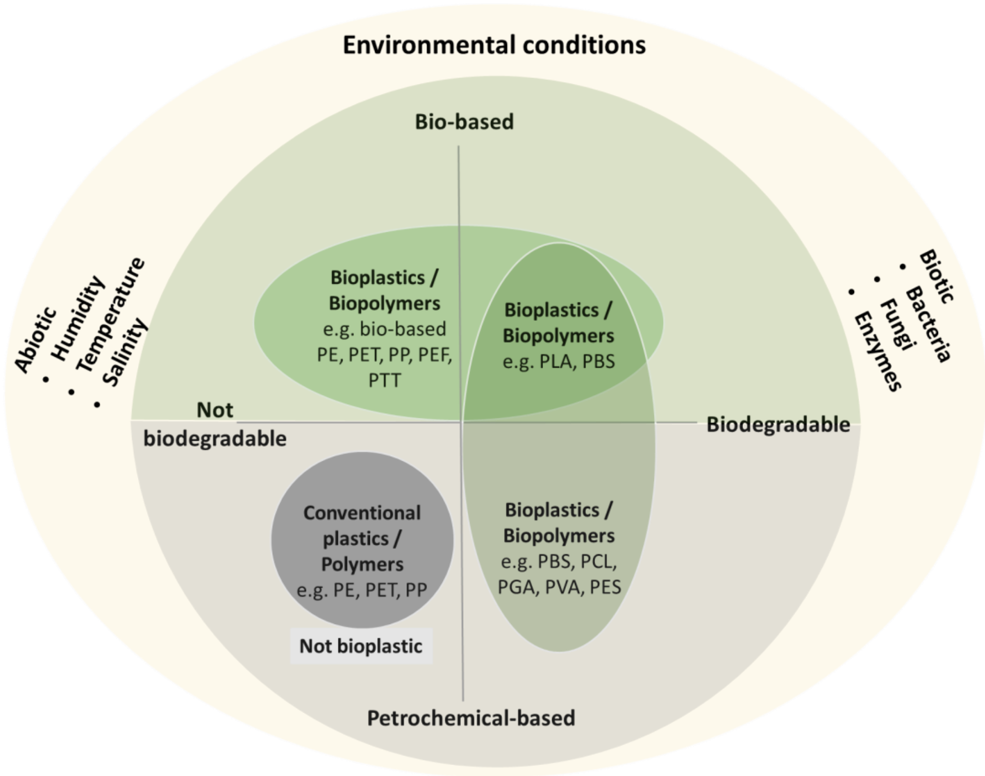


Figure 1. The type of bioplastics and the abiotic and biotic factors causing their environmental degradation.

Bioplastics like petroleum-based plastics include materials composed of polymers. The term 'bioplastics' refers to plastics whose organic carbon is derived in whole or in part from renewable biomass feedstocks such as agricultural plants, other plants, animals, forest materials, algae or other microorganisms and fungi [52]. Biobased plastics thus refer to the source of the polymer's organic carbon and therefore have a much lower environmental impact. Materials of biological origin, such as biopolymers, play a key role in the sustainability/life cycle as they are part of the organic carbon cycle [56]. The ratio of biobased to total carbon in biobased plastics shall comply with ASTM (D6866) and ISO (ISO 16,620 series) standards [2]. Biopolymers can also be obtained from renewable waste from agriculture [57]. Bioplastics as an innovative material are one of the branches of the bioeconomy that represents a pathway to the closed-loop model of the circular economy. In line with these approaches, biodegradable plastics are mainly mentioned as a solution to plastic pollution of water and land [58]. However, their biodegradability by microorganisms depends on the physicochemical properties of the polymer and the biochemical nature of the system, i.e., the environmental conditions under which biodegradation takes place (e.g., temperature, humidity, oxygen percentage, and pH). However, it is very important to distinguish between biological interactions with the plastic that lead to physical or chemical degradation and those that lead to biodegradation and thus to complete removal from the environment [2].

3. THz Spectroscopic and Imaging Techniques for (Bio) Polymer and Plastics Characterisation

Polymer spectroscopy has long been an important technique for studying the structural, physical, and chemical properties as well as dynamics and reactions of polymers. Polymer spectroscopic techniques are mainly based on optical spectroscopy, which includes spectroscopy in the ultraviolet, visible, and infrared (IR) regions. The latter, including THz spectroscopy, are vibrational spectroscopic techniques, which are divided into near-IR (NIR), mid-IR (MIR) and far-IR (FIR) spectroscopy, depending on the frequency of the incident light [59,60]. Vibrational spectroscopy is mainly used to study the thermodynamic properties and structure of molecules. The vibrational motions of a molecule in its ground electronic state result in a characteristic absorption spectrum in the IR region. Strongly localised stretching vibrations have resonant frequencies in the MIR range, while out-of-plane or torsional vibrations involving many atoms are resonant in the FIR range. The FIR also reflects the conformation and structure of the molecule and its surrounding environment, so in addition to internal motions within the molecule, intermolecular interactions or lattice vibrations in crystalline samples may also contribute to the FIR absorption spectrum [61]. This shows the importance of the THz spectral region, which provides a unique fingerprint of the molecules. THz technology has shown great potential for the analysis of polymers and plastic materials, including composites where plastic particles are embedded in other materials such as wood or paper [62,63]. For this reason, it can be concluded that THz radiation can also be applied for the characterisation of biopolymers and bioplastics as a non-destructive method for the analysis of the molecular structure and dynamics of these materials. THz waves can penetrate many materials, such as plastics, wood, polymer foams, paper and even bioplastics. This characteristic of THz radiation can be used for non-destructive imaging of the internal structure of a sample to reveal defects, inclusions, homogeneity, porosity and other structural characteristics of the material [8,9,64].

Since the first published reports, in which THz generators and detectors appeared [65–67], continuous research and development in photonics and electronics over the last 30 years have contributed to the development and design of THz spectroscopic systems, which open the possibility of new applications of electromagnetic waves in various fields. The wide bandwidth in the THz range, even up to 20 THz [68], allows insight into the structure of materials with micrometre resolution. Based on THz spectroscopy, THz imaging modalities were also developed. The first optoelectronic THz transmission image was produced already in 1995 by Hu and Nuss [69]. Since then, most research and applied THz imaging systems have used pulsed lasers to generate THz images.

Most THz time-domain spectroscopy (THz-TDS) systems are based on (i) optical rectification as a second-order nonlinear optical effect (NLO) in nonlinear inorganic and organic crystals [70–72] or (ii) photoconductive antennas that generate THz pulses with transient photovoltages induced by femtosecond pulses [73–77]. Optoelectronic spectroscopic methods have also been extended into THz imaging techniques based on the optoelectronic generation and detection of THz radiation from pulsed or CW lasers using photoconductive antennas or nonlinear crystals. Thus, THz imaging can be divided into pulsed and CW imaging. There have also been developed completely electronic approaches to THz imaging where both the generation and detection of the THz waveform are electronic. This approach can be further divided into passive and active THz imaging. The working principle of these systems is described in detail in several studies and reviews [78–85], which categorise THz imaging systems in different ways, such as active vs passive, electronic vs optical, continuous wave vs pulsed, transmission vs reflection, near-field vs far-field, or single-pixeled vs multi-pixeled.

Several THz techniques can be used for polymer and plastics characterization. Some of the most commonly used techniques are:

- Fourier transform infrared (FTIR) spectroscopy: This technique was the most applied for materials characterisation in the far infrared band before the introduction of THz-TDS. It is used quite simply to obtain a high-quality spectrum between the near-infrared to the visible frequency band. In comparison to THz-TDS, its use is limited, especially due to the cooling system, which is usually needed for spectroscopic measurement. After the measurement, an interferogram is obtained, where it is difficult to distinguish any physical features of the sample directly from the interferogram; a Fourier transformation is necessary for analysis. FTIR typically has a better signal-to-noise ratio than THz-TDS systems above 5 THz. Below 3 THz, their signal-to-noise ratio is lower by a few orders of magnitude. In comparison to THz-TDS, one major drawback is that the FTIR system measures only the intensity of the THz waves and does not capture the phase information. Therefore, Kramers-Kronig analysis is needed for extracting the complex-valued refractive index of the sample [86–88]. FTIR spectroscopy can provide information on the chemical composition of the molecular structure and functional groups in biopolymers and bioplastics. By analysing the absorption spectra of a sample, FTIR can determine the types of chemical bonds present, such as C-H, O-H, C=O, C-O and N-H [89]. This information can be used to identify the biopolymer or bioplastic and its purity and degree of crystallinity [90]. FTIR can also be used to monitor the composting and degradation of biopolymers and bioplastics over time, as changes in the spectra can indicate the formation of new functional groups or the loss of existing ones [91]. In addition, FTIR can provide information on the thermal properties and conformational changes of macromolecules, e.g., biopolymers in bioplastics, from which glass transition temperature and melting point can be determined [92,93].
- Terahertz Time-Domain Spectroscopy (THz-TDS): This technique involves the generation/detection of short THz pulses and the measurement of the electric field of the transmitted or reflected signal as a function of time after they pass through the sample. The same short optical pulse is used both to produce (pump) and detect (probe) the THz radiation. Thus, THz-TDS allows simultaneous measurement of the THz field amplitude and phase or, in other words, real and imaginary optical constants, i.e., absorption coefficient and the refractive index [94]. The basic principle of operation with electrooptic crystals is shown in Figure 2a. The transmitted or reflected signal is analysed to obtain information about the sample's properties, such as refractive index, absorption coefficient, and dielectric constant. Using the THz-TDS, the time delay between the THz pulse sent through the material sample and the reflected pulse can be measured. In general, each THz-TDS measurement starts with a measurement of the reference spectrum. The reference can be an empty spectrometer sample compartment in a particular atmosphere (ambient air, nitrogen, dry air) or a sample before the treatment under study has been performed. This is followed by the measurement of the sample under study. The ratio of these two spectra gives the expression from which the refractive index and the absorption coefficient can be determined, as well as the thickness of the sample [95]. By Fourier transform of the recorded signal to the frequency domain, the technique can provide information about the molecular structure of the polymer, including the presence of functional groups, the degree of crystallinity, and the orientation of the biopolymer chains [96]. In addition, THz-TDS can be used to study the dynamics of polymers, such as their relaxation times and diffusion coefficients. This information can be used to understand the behaviour of polymers under different conditions, such as temperature and humidity, and to optimise their properties for specific applications. Biological polymers show low spectral features in the THz region corresponding to functionally relevant, global and subglobal collective modes with periods on the picosecond timescale. THz spectroscopy can also be used to analyse the dynamics of biopolymers in water [97]. Compared to FTIR spectroscopy, THz spectroscopy can provide information on the low-frequency vibrational modes of

biopolymers, such as the collective vibrational modes of amino acids, proteins and carbohydrates, which are not accessible with FTIR spectroscopy [60].

- Terahertz Pulsed Imaging (TPI): This is an imaging technique that uses THz radiation to create images of objects. It is based on the principle that THz radiation can penetrate many materials, including polymers, and is sensitive to the differences in the refractive index and absorption properties of different materials. The transmitted or reflected pulse is then detected at a detector and analysed to obtain information about the sample's structure and composition. The time delay between the transmitted and reflected signals is used to determine the position of the object, while the amplitude of the signal provides information about the object's properties, including the presence of defects or inhomogeneities. This technique has been used to perform 2D and 3D imaging of materials. The amplitude image is recorded by sitting at the peak of the THz pulse and then doing the raster scan of the object. Thus, only the detection is possible without the identification and classification needed. Recording the pulse profile at each selected point on a sample can lead to enormous information on the image in the frequency domain, allowing also identification and classification of materials and compounds since various substances exhibit unique spectral responses in the THz frequency range, some with distinct spectral peaks. By analysing the frequency-dependent amplitudes and phases of the transmitted or reflected THz pulse, we can obtain information on the dielectric and optical properties of the bioplastic samples, which can be related to their molecular structure as well as intermolecular interactions [98]. Using multispectral THz imaging, where the entire frequency spectrum is recorded at each point on the sample, it is also possible to identify foreign bodies inside or below the surface of the material in addition to detecting them [41]. The principle of generation and detection of THz radiation using photoconductive antennas are described in [73] and organic electro-optic crystals in [99].
- THz Time-Domain Ellipsometry: Compared to THz transmission measurements, this method is applicable to highly absorbing substrates and thin layers on opaque substrates. In contrast to reflectometry measurements, ellipsometry does not require reference measurements and avoids phase detection problems due to layout errors. Ellipsometry is self-referential and allows simultaneous estimation of the complex refractive index and the layer thickness. THz TDS ellipsometry is used to characterise the anisotropic properties of materials, especially optical properties of thin films, multilayer systems and complex substrates in the THz frequency range [85,100–102]. An example of such a system setup is shown in Figure 2b.
- THz tomography: This is an imaging technique that uses THz radiation to create cross-sectional images of a target and allow the internal detail to be observed in three-dimensional (3D) images of objects. It is based on the principle that THz radiation can penetrate many materials, including polymers, and is sensitive to the differences in the refractive index and absorption properties of different materials. THz tomography involves various approaches, which were well described by Guillet et al., who emphasised the advantages, drawbacks and limitations of 3D imaging of the internal structure of an object by THz radiation [103]. Here the most interesting is THz computed tomography (CT) in Figure 2c since this technique is comparative to well-known X-ray CT, which has already been transferred from medical applications to various industrial applications. Usually, a THz beam is used to illuminate the object from multiple angles, and a detector measures the transmitted or reflected THz signal. The data obtained from these measurements are then used to reconstruct a 3D image of the object. The technique can provide information about the internal structure and composition of the polymer. THz CT can be used for spectral analysis of samples, providing identification or comparison of different substances and their localisation in a non-destructive way. The main limitation is the absorption in the material under investigation, which limits the thickness of the sample to be imaged, and the high absorption in an industrial environment due to dust particles and atmospheric moisture.

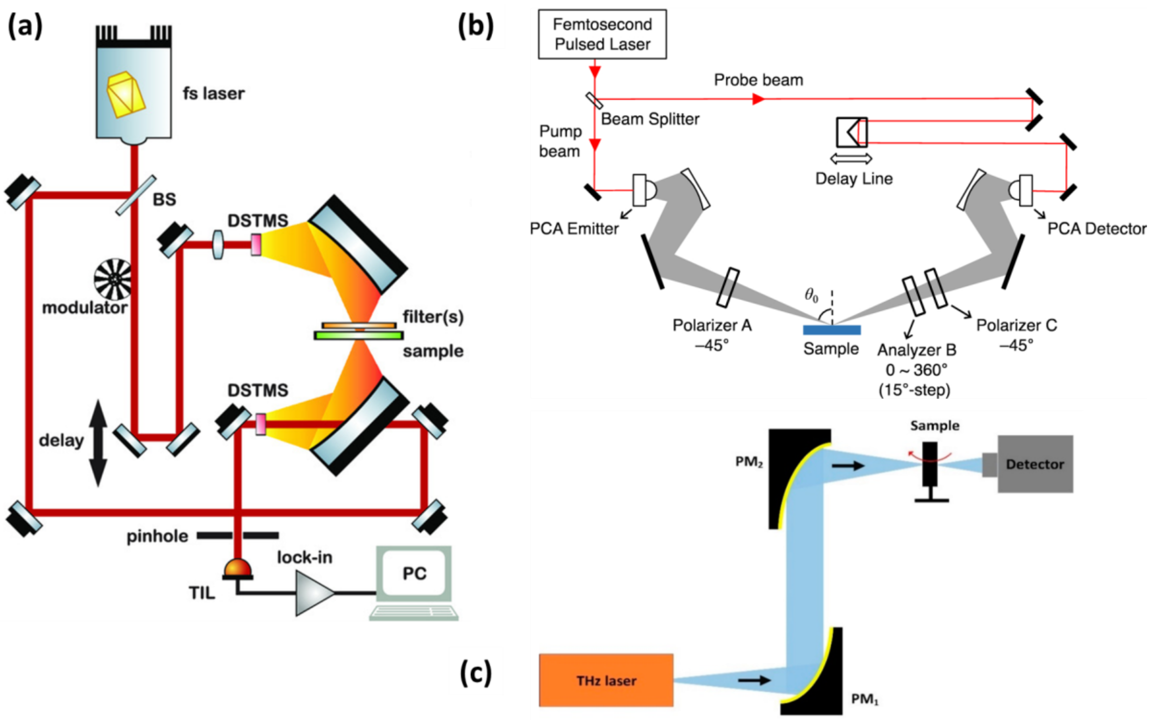


Figure 2. Varios THz system for polymeric materials characterisation: (**a**) THz-TDS in transmission geometry operating with DSTMS electro-optic crystals (Reprinted (adapted) with permission from Ref. [68]. Copyright 2022, American Chemical Society (**b**) THz time-domain ellipsometry setup [104] and (**c**) THz-computed tomography (CT) imaging system [105].

Despite some advantages of THz imaging, such as high quality, efficient, and reliable operation at room temperature, researchers and developers face several technological challenges. Valušis et al. emphasised the following key challenges [78]:

- compactness,
- low power consumption,
- powerful and tunable THz emitters,
- fast response,
- high sensitivity detectors,
- operating over a broad frequency range,
- system integration,
- incorporation of artificial intelligence in THz image processing.

The cost of THz spectroscopy and imaging systems is still high, so they are mainly used in laboratories for scientific research. It is expected that the cost of these systems will come down in the future, allowing for wider use also in an industrial environment. Moreover, for industrial applications, especially spectro-terahertz imaging will probably be an emerging and efficient tool, allowing room-temperature, short-distance, real-time and video-rate multipixel imaging [78,85].

4. Biopolymers Analysis by THz Spectroscopy

Many polymers forming petroleum-based plastics are transparent to THz waves, so the first research on polymers was mainly carried out for the purpose of making optical components for THz systems [106–108]. For this reason, the first studies were focused on the characterisation of their dielectric properties (refractive index and absorption coefficient), and later morphological studies, such as the determination of macromolecular origin, temperature dependence, glass transition temperature, etc., have also emerged. Despite the transparency of polymers to THz radiation, it is quite difficult to distinguish them using optical techniques, as there are few or no spectral features in the THz spectral range by which they can be distinguished and classified. However, by using chemometric methods such as principal component analysis (PCA), it is possible to distinguish between polymers [44]. Due to the pulsed nature and the coherent detection, THz spectroscopy allows simultaneous extraction of the dielectric material properties, i.e., permittivity and refractive index, as well as the thickness of the sample. This fact is exploited when determining the glass transition of polymer samples.

The polymers' internal structure is relatively complex. Therefore, its morphology can be described as semi-crystalline, where both crystalline and amorphous domains are present in the investigated samples. Consequently, the THz absorption spectral features of polymers are very broad. Non-polar polymers, e.g., polyethylene (PE) and polypropylene (PP), containing non-polar covalent bonds, exhibit very high transparency and a refractive index below 1.55 at lower THz frequencies. In contrast, polymers with polar bonds without symmetric dipole moments exhibit a relatively high refractive index, typically above 1.60. Polar polymers also show an anomalous dispersion in the THz frequency range [8]. In the last few years, the industrial potential of THz spectroscopy for polymer studies in plastics manufacturing has also become apparent [109–112]. THz-TDS can characterise polymers for in-line monitoring (composition, defects, inclusions, additives, impurities, joints, water content) by exploiting dielectric contrast mechanisms.

Some of the key building blocks of bioplastic polymers are polyhydroxyalkanoate (PHA) [113], polylactic acid (PLA) [114], poly-3-hydroxybutyrate (PHB) [115], polyamide 11 [116], polyhydroxyurethanes, [117] and cellulose- [118], starch- [119], protein- [120] and lipid-based [121] biopolymers (Figure 3). Their responses in the THz frequency range are discussed in the following subsections. Some other types of bioplastics are bio-based PET, bio-epoxy, polyethylene furanoate (PEF), polybutylene succinate (PBS), polytrimethylene terephthalate (PTT), furfural and others, which are not addressed in this review as they belong to the type of biopolymers that are not bio-based and biodegradable (Figure 1). THz studies of biopolymers and related compounds or precursors are summarised in Table 1 at the end of this chapter.

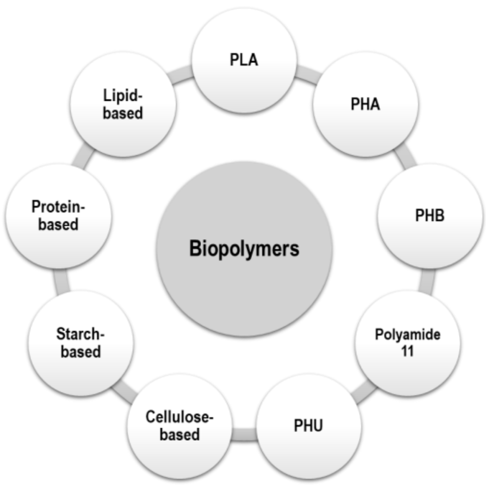
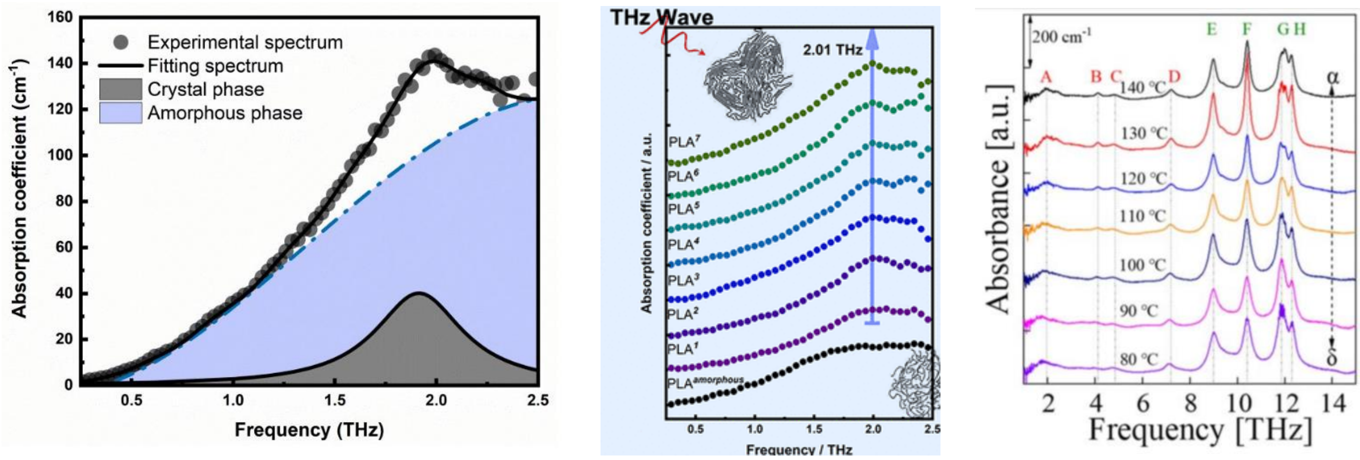


Figure 3. Commonly used bio-based and biodegradable plastic polymers are discussed in this review (summarised from [52]).

4.1. Polylactic Acid (PLA)

PLA is a typical polymer with homogeneous polymorphism. It has specific properties due to its different crystalline forms. The structure and crystallisation behaviour have been studied by THz spectroscopy. Ariyoshi et al. observed clear THz absorption peaks in their studies, which can be attributed to the higher-order structure of one of the biopolymers, i.e., poly(L-lactide). They performed broadband THz spectroscopic analysis of PLA with different polymer crystal structures [122]. Based on the differences in absorption peaks in the THz spectra, they found differences in the higher-order structure that are difficult to reveal by conventional methods such as X-ray diffraction. PLA with different crystal structures showed a clear correlation in terms of peak intensities in the range of 4 to 5 THz. The THz absorption peaks thus facilitated the assessment of higher-order structures, which is important for further understanding the higher-order structures of different biomass-based plastics and their functions. The results show that THz spectroscopy can characterise the crystalline changes of PLA polymers and effectively study the kinetics of polymer crystallisation [123]. Ariyoshi research work continues to focus on the potential of THz spectroscopy to investigate the properties of bioplastics, in particular, the analysis of stereocomplexes and enantiomers, which are the origin of the functional properties of biomass-based plastics and determine their biodegradability and microbial degradation.

THz spectroscopy shows strong responses to crystalline poly(lactic acid) at 2.01 THz (Figure 4a,b), indicating that THz spectroscopy can be used to determine the crystallinity of PLA. The peak at 2.01 THz also shows conformational and interaction sensitivity, most likely due to the effect of the dipole-dipole interactions between the carbonyl groups [124]. Ohnishi et al. have recognised eight spectral peaks (Figure 4c) in the frequency band between 1–15 THz [125]. Polylactic acid is a thermoplastic polymer consisting of basic building blocks of lactides or monomers of lactic acid, which are further polymerised to produce polylactic acid. Due to its mechanical properties, polylactic acid is an alternative material to synthetic polymers such as polyethylene terephthalate and polystyrene [55].



(a) (b) (c)

Figure 4. (**a**) Experimental THz spectrum and calculated THz spectrum for PLA film (a grey area represents the contribution of lattice vibrations, blue area represents the contribution of the amorphous region); (**b**) THz spectra for the different crystalline forms of PLA indicating a characteristic spectral response at 2.01 THz (Reprinted (adapted) with permission from Ref. [124]. Copyright 2022, American Chemical Society; (**c**) Absorption peaks for PLA in the frequency band 1−15 THz [125].

Polylactic acid is a common filament material for consumer 3D printers, enabling better component development in mechanical engineering fields, including for component needs in building THz systems. The absorption coefficient and the refractive index are important in this context. Typically, for optimal performance of 3D printed THz optical components, a material with a higher refractive index and lower absorption due to light refraction at more extreme angles at the same material thickness is desirable. Research has shown that PLA composites containing Cu, Fe and W particles can be effective for THz optical components up to the maximum allowable frequencies of 0.54 THz, 0.48 THz, 0.46 THz and 0.52 THz, respectively [126].

4.2. Polyhydroxyalkanoate (PHA) and Poly-3-Hydroxybutyrate (PHB)

PHA is a natural thermoplastic polyester polymer that can fully degrade in soil and marine environments. It is used for various applications, such as food packaging materials [127] or medical applications [128]. As it is difficult to produce end products consisting only of 100% of PHA, improvements in its processability and mechanical properties [129] are being sought to make it easier and cheaper to produce PHA industrially for wider commercial use. Chemical modifications [130], copolymerisation [131] and composites obtained by mixing with nanoparticles or other additives [132] can be used to modify the thermal and mechanical properties of PHA. On the one hand, the production of composites with renewable and biodegradable materials improves the properties of the materials while maintaining their degradability in the environment.

A THz time-domain spectrometer was used to determine the THz spectra of poly(3-hydroxyalkanotes) (PHA) [133]. A difference was observed in the THz spectra, indicating a distinction between crystalline and amorphous PHA. The THz spectra of PHA, exactly of the crystalline and amorphous polyhydroxybutyrate (PHB), were also measured in the temperature range from 10 K to 465 K using a liquid helium cryostat and a heating cell [134]. The THz spectra at different temperatures reveal frequency shifts and broadening of absorption peaks with temperature, indicating a large anharmonicity of the vibrational potential at lower frequencies below 10 THz. Hoshina et al. assigned the peak at 2.92 THz to the vibration of helical structure along the fibre axis, and the peak at 2.49 THz is attributed to vibration due to the hydrogen bonding between helix structures [135]. THz spectral peaks are visible in Figure 5, obtained by the THz spectrometer. One study has also shown that the energy of THz photons, which corresponds to the vibrational energy of the hydrogen bonds in polymers, can effectively excite intermolecular motion [136]. Thus, some vibrational modes are associated with intermolecular hydrogen bonds in the THz range. Since the energy of THz photons is relatively low compared to the energy of covalent bonds, a conformational change occurs without damaging the chemical structure. THz-TDS spectroscopy was also used to determine the glass transition temperature of bio-degradable PPH (Polyester-5,7), which is a relatively new polymer [137].

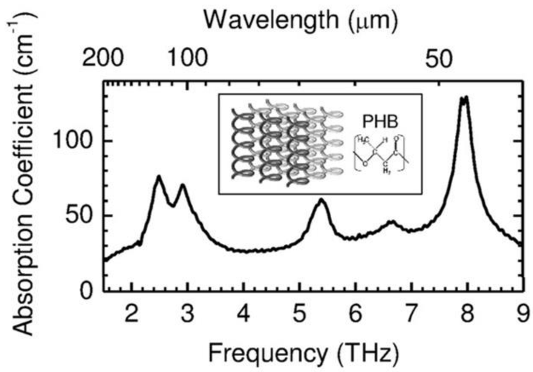


Figure 5. THz absorption spectra of crystalline PHB in the frequency range between 1.5−9 THz [136].

4.3. Polyamide 11 or Nylon 11

Polyamide 11 or nylon 11 is a bio-based polymer, mainly produced from bio-renewable sources such as castor oil. It belongs to the nylon family and is produced by the polymerisation of 11-aminoundecanoic acid. Its high chemical and mechanical stability also makes it a very attractive production material for use in the manufacture of longer-life products from an environmental point of view [138]. It is mainly used in the manufacture of construction products such as natural gas pipes, water pipes, electrical cable sheathing and as a fabric in the textile industry. It is also used in the aerospace, automotive and everyday consumer products industries (footwear, racquet strings, toothbrush bristles) [52]. Although polyamide 11 is not biodegradable, it can be recycled together with its composites.

Ishii et al. measured THz spectra of various crystal conformations of nylon, including nylon-11, with a Fourier-transform infrared spectroscopy (FTIR) [139]. Differences in spectral features below 10 THz in response to the crystalline conformations of the nylons were observed between the different types of nylon. The peak at 3 THz occurs in all types of nylon, independently of the crystalline form. Nylon-11 has some unique absorption peaks in the frequency range between 10 and 18 THz, which could be characteristic of this crystalline conformation of nylon. Different nylon filaments with specific mechanical characteristics were developed to overcome the issues caused by nylon-6 (water absorption, high print temperatures, for 3D printing of THz system components. Their optical characteristics were verified within the THz frequency range. All nylon filaments show similar THz spectra, where the absorption increases with frequency in the THz region [140].

4.4. Bio-Based Polyhydroxyurethane (BPHU)

Bio-based poly(hydroxyurethanes) (BPHUs) are new biopolymers to produce environmentally and health-friendly polyurethane (PU) materials, which are commonly used to reduce emissions that harm people and animals in the food chain and cause cancer. The plastics and rubber industry have started to focus its development and production on innovative green PU materials due to the increasing adoption of circular economy models. This contributes to reducing the hazardous waste stream and increasing the use of sustainable raw materials.

Most recent studies on BPHUs focus mainly on understanding the synthesis of these polymers and their properties. The synthesis of bio-based PHUs uses biological precursors as a substitute for petrochemical starting monomers such as isocyanates and diols, which usually cause environmental problems. The main starting molecules/materials used to synthesise PUs and BPHUs are shown in Figure 6.

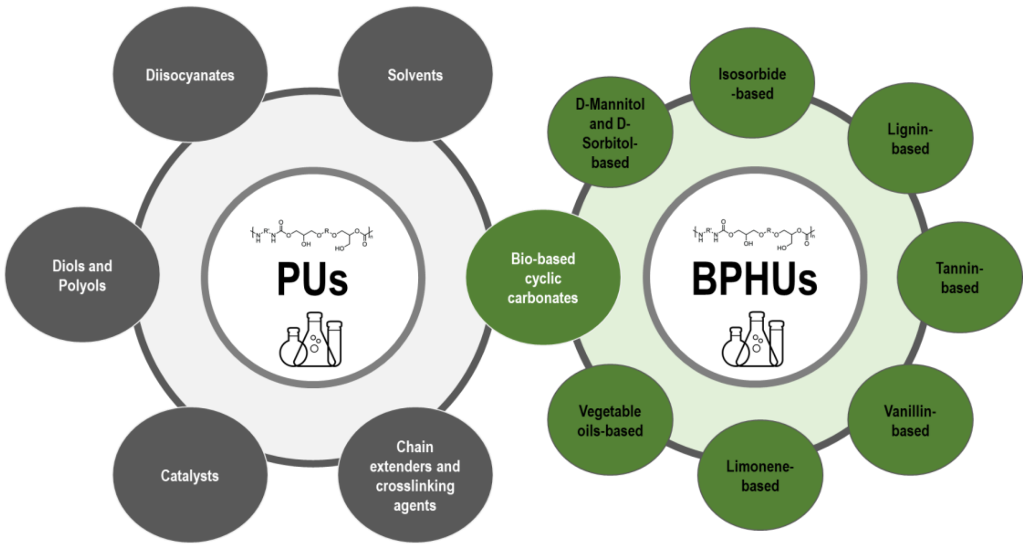
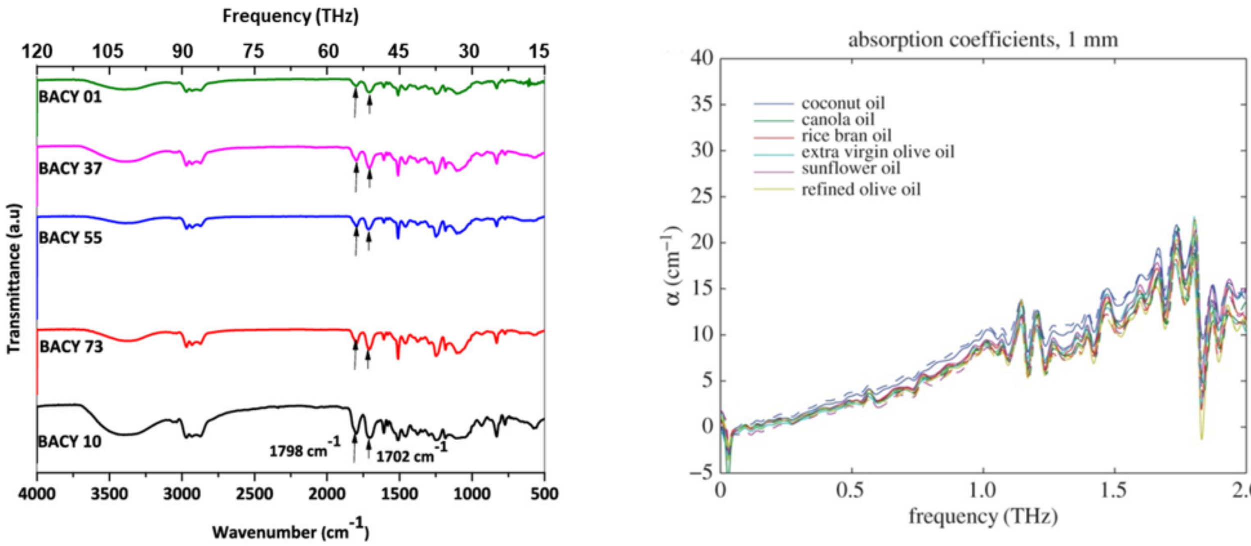


Figure 6. Precursors for polyurethanes synthesis (left) and bio-based cyclic carbonate precursors as green resources for bio-based polyhydroxy urethanes production.

It is almost impossible to find experiments on PHUs performed in the THz frequency range in the literature. There are a few FTIR experiments, but these only get as close as 500 cm^{-1}, which corresponds to 15 THz (Figure 7a). Sukumaran et al. research the H-bonded interactions between −CO and OH/NH functional groups within PHUs using temperature-dependent FTIR [141]. However, some more studies have been done on polyurethanes [142,143] and compounds that can be used as bio-based cyclic carbonates precursors for BPHU synthesis (Figure 6, right circle). The THz time-domain spectrometer was used to verify the THz properties of lignin, including refractive indices and absorption coefficients. They found that the refractive indices and absorption coefficients of the various lignins differ due to their chemical composition [144]. Newnham et al. studied the THz spectra of D-mannitol and D-sorbitol using the Attenuated Total Reflection (ATR) technique in the frequency range of 0.3 THz to 3.6 THz [145].

A lot of THz spectroscopy research has been done on vegetable oils. Jiusheng measured the THz spectra of 4 vegetable oils (sunflower seed oil, peanut oil, soybean oil, and rapeseed oil) from 0.2 THz to 1.5 THz [146]. Dinovitser et al. analysed with THz spectroscopy chemical and physical changes of edible oils when heated above the smoke point [147]. In the frequency range between 0.05 THz and 2.0 THz, no significant changes in the THz spectra of edible oils were observed (Figure 7b). However, other authors using FTIR spectrometers have shown significant unique absorption characteristics of different oils around 21 THz and 36 THz [148]. In future studies with heat-treated oils, it would be useful to investigate frequencies above 2 THz further. THz systems based on organic electro-optic crystals can exceed frequencies of 20 THz [68]. Chen et al. analysed the biomolecular structure of isomer vanillin regarding the van der Waals interaction using terahertz time-domain spectroscopy (THz-TDS) combined with quantum chemical calculations [149]. They observed four significant absorption peaks at different frequency positions between 0.5 THz and 2.0 THz (0.61 THz, 1.10 THz, 1.48 THz, and 1.89 THz).



(**a**) (**b**)

Figure 7. (**a**) FTIR spectra of some PHUs showing the presence of a −CO group of poly(hydroxyurethane) and an unreacted cyclic carbonate group [141]; (**b**) THz absorption spectra for edible oils up to 2.0 THz [147].

4.5. Cellulose-Based Biopolymers

Cellulose is one of the dominant natural biopolymers in lignocellulosic biomass, which includes agricultural residues, energy crops, wood residues and municipal paper waste. Chemically, lignocellulosic biomass consists of 35–55% cellulose, a chain structure of large molecules. Cellulose-based biopolymers are gaining much attention due to their biodegradability, high durability, strength and stiffness [150]. The weak hydrogen bonds between the molecules can lead to rapid degradation and reduce the mechanical properties, such as the strength and flexibility of cellulose-based materials. The latter can be improved at the expense of incorporating additives, such as pectin and chitosan [4] or by functionalising them into polymeric derivatives or nanomaterials with physical and chemical modifications [151,152].

In the low-frequency band, such as the THz region, studies on the characteristics of the absorption peak of cellulose have been limited for a long time. However, with the development of THz spectroscopy, research results showing the absorption peak characteristics of cellulose have become available [153]. Yang et al. performed THz spectroscopic measurements of four cellulose samples: wood cellulose, microcrystalline cellulose, cotton cellulose nanofiber and wood cellulose nanofiber. The highest crystallinity was found in cotton cellulose nanofiber and the lowest in wood cellulose. Measurements have shown that the absorption coefficient of cellulose samples is proportional to the crystallinity [96]. Their characteristic THz absorption peaks are shown in Figure 8.

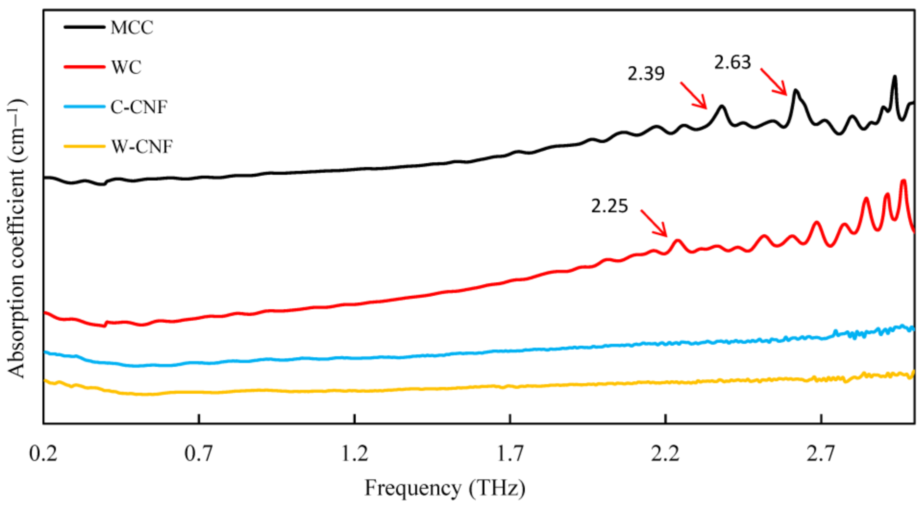


Figure 8. THz absorption spectra of different cellulose samples [96].

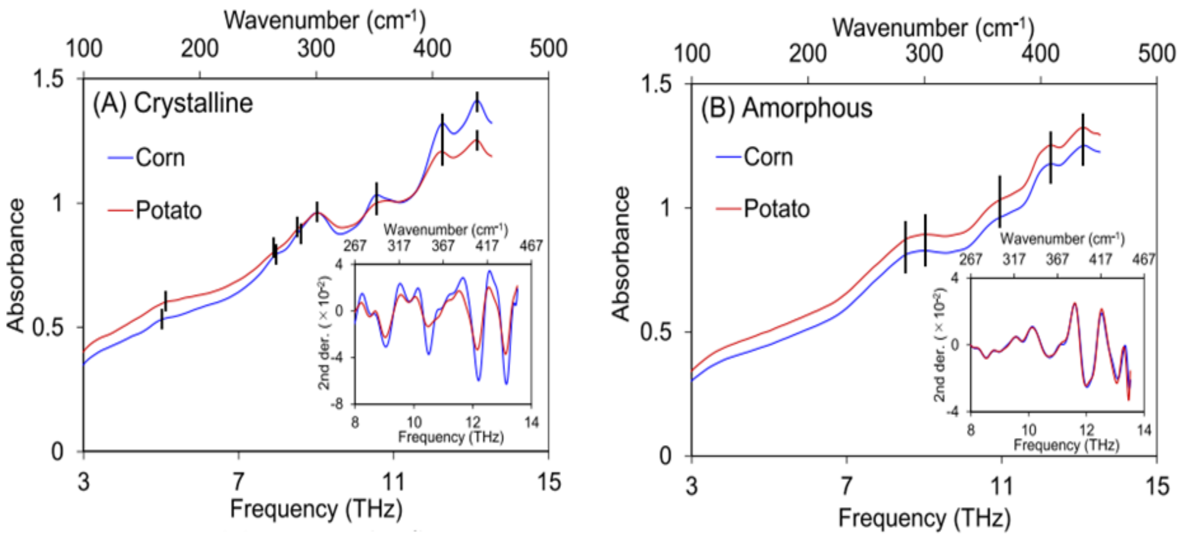
Some THz research has also been done on nanofibre cellulose-polymer composites. For example, polypropylenes have been used as polymers, where the addition of nanofibre cellulose has been observed to produce an additional absorption peak at 7 THz in the composite. In contrast, the other spectral peaks, which are considered to originate from polypropylene, have remained unchanged [154].

4.6. Starch-Based Biopolymers

Starch-based biopolymers are the next group of new materials gaining attention due to their renewability, biodegradability, high availability, low cost, and ease of production. Starch, which is made up of monomeric glucose, is found as a form of carbohydrate storage in a variety of agricultural products such as cereals, tubers, beans and fruit [155]. Starch is composed of two glucans, amylose and amylopectin. The main sources of starch are crops, with maise accounting for 80% and cassava, wheat, rice, and potatoes making up the rest [156]. The use of food crops to produce starch for the bioeconomy raises concerns about the competition between food crops for the food industry and cultivated land use [157].

Nakajima et al. measured THz spectra of native, amorphous and dried starch derived from maise and potato using an FTIR spectrometer in the frequency range from 3 THz to 15 THz [155]. Natural corn and potato starch showed seven absorption peaks in the THz range, while five peaks were observed in the amorphous state (Figure 9a,b). Drying of the starch samples affected the intensity of the THz peaks. Correlations between THz peaks and X-ray signals were also found. This proof is particularly useful in determining the crystallinity of starch, as the THz peak at 9.0 THz was correlated with the crystallinity obtained by X-ray diffraction. The THz experimental method has also been applied to real-time monitoring of the starch ageing process [158], which means that THz technology can provide an effective tool in starch-related production and processing industries, including the bioeconomy.

The use of natural polymers as components of composite materials has become very popular in the last decade, especially in medical devices or food packaging. The use of such bio-based composites also helps to reduce the risk of pollution from traditional plastics. Two- or three-component composite systems are being developed that combine natural materials and approach the quality of purely synthetic specimens. Krystyjan et al. have thus developed a new bio-nanocomposite composed of starch/chitosan/graphene oxide by green synthesis [159]. Another such biocomposite system is gelatine-starch-glycerol-bentonite, which is a drug delivery system. It is based on a biopolymer matrix of gelatine and starch-filled with plasticising glycerol and varying levels of reinforcing bentonite clay particles. THz optical property analyses were also performed on this biopolymer, the influence of the bentonite content on the mechanical and THz optical properties of the biopolymer. The proposed biopolymer can also be used as a substrate for in-vivo measurements of the optical properties of biofluids in the THz frequency range [160].



(**a**) (**b**)

Figure 9. THz absorbance spectra of (**a**) crystalline (native) and (**b**) amorphous starches in corn and potato samples indicate absorption peaks by vertical lines in the frequency range between 3 THz and 15 THz. Insets represent the second derivative spectra in the range of 8.0−13.5 THz (Reprinted from Ref. [155], Copyright (2021), with permission from Elsevier).

4.7. Protein-Based Biopolymers

Bioplastics can be made from a variety of plant and animal proteins, such as wheat gluten, soy protein, whey protein, zein, casein, collagen and gelatine [52]. Protein-based biopolymers in the form of films are widely used for packaging materials. Compared to lipids and polysaccharides, such protein-based biopolymer films have outstanding mechanical properties and barriers to gases and flavours.

The application of THz spectroscopy and imaging of proteins is discussed in many review articles [16,161,162]. It can be divided into three measurement parts: molecular conformations, molecular interactions and quantitative detections [163]. THz spectroscopy of protein-based biopolymers provides many methods, such as the measurement and analysis of their absorption. Transmission and reflection characteristics properties in the THz frequency range can also be measured. THz investigation of molecular vibrations provides insight into collective motions, hydrogen bonding, and intermolecular interactions, which play a crucial role in determining the structure, conformation, and dynamics of proteins, peptides, and amino acids.

THz imaging techniques have also been employed to visualise and map protein-based biopolymers with the non-destructive analysis of their distribution, composition, and organisation in complex biological systems [16,39,163]. THz spectroscopy and imaging are also promising for advancing our understanding of the fundamental properties of protein-based biopolymers. Some applications of THz spectroscopy and imaging on proteins, peptides and amino acids are summarised in Figure 10. This could facilitate the development of new therapeutic strategies and contribute to the broader field of bio-engineering and biotechnology.

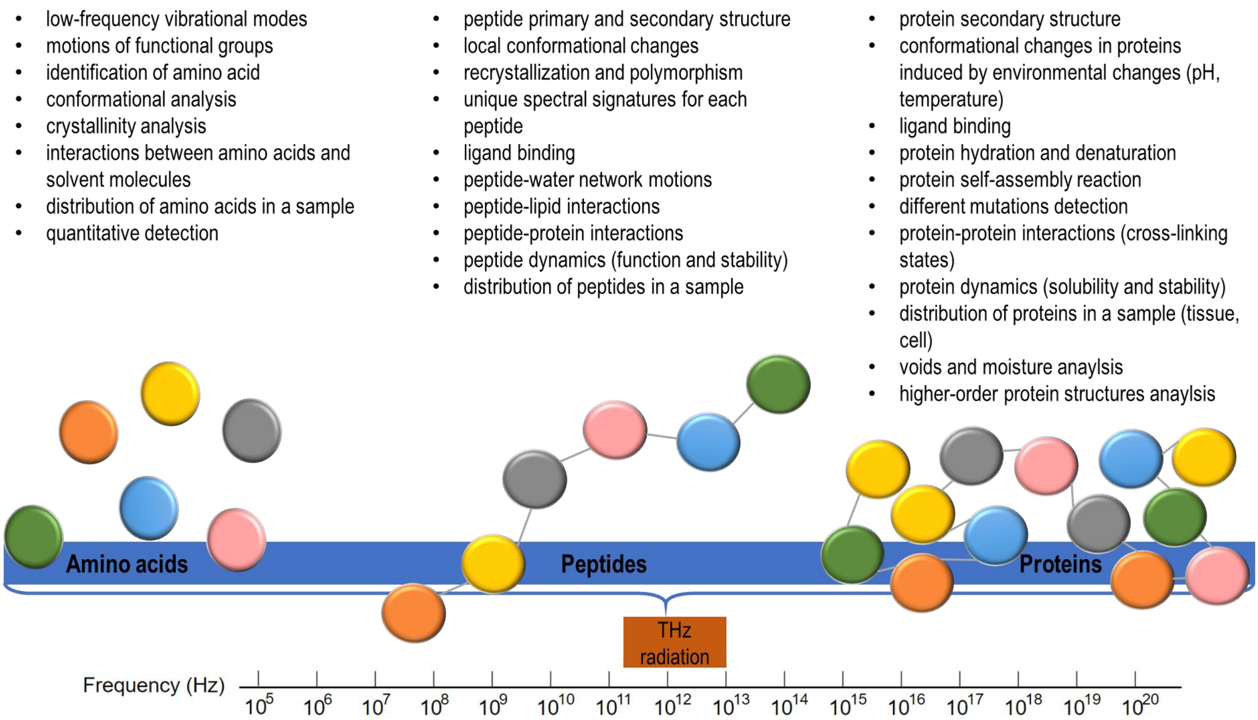


Figure 10. THz spectroscopy and imaging application for amino acids, peptides and proteins analysis.

THz spectral characteristics are closely related to amino acid crystallinity and their composition in peptides. One can clearly distinguish between the amino acids and the polypeptides in the THz frequency range. Differences in wheat and soybean varieties lead to significant differences in their protein, fat, and other constituent content. THz spectroscopy, together with chemometric methods, was demonstrated to be an appropriate tool to distinguish between different soybeans [164] and wheat varieties [165]. THz-TDS can probe the elasticities of polymer biomolecules. It was demonstrated in the case of polypeptides such as poly-L-proline, poly-L-alanine, and polyglycine [166]. THz radiation with lower peak power was used to demolish the actin filaments, which serve as biopolymer material [167]. Low-frequency THz spectroscopy was used to study two photoactive protein systems, rhodopsin and bacteriorhodopsin, considering the motions that are involved in conformational activation pathways of biomolecules [168].

THz-TDS was applied to monitor the cross-linking states of polyethylene oxide (PEO), which is a biocompatible and biodegradable polymer present in the anti-adhesion films in medicine [169]. They also noticed that THz-TDS has the potential to non-destructively analyse the voids and moisture characteristics within the biopolymer film. THz-TDS was demonstrated as a powerful complement to other spectroscopic techniques because of its unique frequency band that energetically vibrates and rotates the polymer structure. Liu observed that sample preparation in film form significantly impacts the loss behaviour of polymer materials and the effect of crosslinking can be detected on the dielectric constant across the THz frequency band [170].

4.8. Lipid-Based Biopolymers

The use of lipids, which are derived from plants and animals and consist of fatty acids, glycerides, terpenes, fatty alcohols, and phospholipids, has recently appeared in the form of edible films and coatings. Some advantages of such products are their glossy appearance, moisture preservation and low production costs [52]. Biopolymer films made from oils and fats have additional favourable properties such as transparency, elasticity, and water resistance. They can be used for packaging fruit, vegetables and meat products, which also extends their shelf life [171]. Wax-based biofilms with improved thermal, mechanical and physical properties are also emerging [172]. Lipid-based biopolymers are, therefore, of great interest to the food industry.

THz technology was utilised for the investigation of microalgae metabolism detection, considering lipid quantification under nitrogen stress [173]. THz spectra of S. obliquus were collected and analysed to determine the composition, especially the characteristic peak at 9.3 THz was used to determine the lipid content (Figure 11). Jiang et al. also measured THz absorption spectra of fatty acids and their analogues at room temperature. Saturated fatty acids such as palmitic and stearic acids had some sharp spectral peaks, while unsaturated fatty acids such as oleic, linoleic and linolenic acids had up to two distinct spectral peaks in the frequency range between 0.3 THz and 12 THz [174]. Moreover, edible oils, whose main constituents are fatty triglycerides, have also been investigated in the THz frequency range [36,147]. THz spectra for six edible oils are shown in Figure 7b.

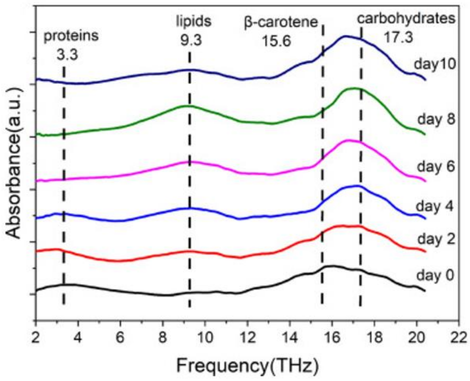


Figure 11. THz spectra in the range of 2–20 THz of components (protein, lipids, carbohydrate and carotenoids) in microalgae S. obliquus during metabolism [173].

THz-TDS experimental measurements were carried out on wax samples, explicitly thermal analysis and optical properties of paraffin wax, beeswax and liquid paraffin wax were characterised [175]. The spectral characteristics of natural waxes can be used to analyse the adulteration of natural waxes, and it is also possible to monitor the crystallisation process of paraffin wax, as the refractive index of paraffin wax changes with temperature.

Table 1. Summary of studies on biopolymers and related substances in the THz frequency range.

Biopolymer	Investigated Absorption Band	THz Technique	Study	Spectral Peak (THz)	Reference
PLA	1.0–8.5 THz	FTIR	crystallinity	1.8, 4.0, 4.7, and 7.1 THz for the 80 °C sample	[122]
	1–2.5 THz	THz-TDS, FTIR	crystallinity, conformational transition	2.01	[124]
	1–15 THz	FTIR	chirality	2.0, 4.1, 4.8, 7.2, 9.0, 10.4, 11.9, 12.3	[125]
	1–2.5 THz	THz-TDS	relative content, crystallisation behaviour	2.01 (shifted to 1.82 due to different crystallisation procedure)	[123]

Table 1. *Cont.*

Biopolymer	Investigated Absorption Band	THz Technique	Study	Spectral Peak (THz)	Reference
	0.2–2 THz	THz-TDS	the absorption coefficient, refractive index	NA	[126]
PHB	0.3–3.5 THz	THz-TDS	higher order conformation	2.49, 2.92	[135]
	0.3–4.0 THz (THz-TDS) 1–20 THz (FTIR)	THz-TDS, FTIR	crystalline and amorphous compound	1.5 (weak), 2.49, 2.92	[134]
	1.5–9 THz	THz-free electron laser (FEL)	polymer morphological change	2.5, 2.9, 5.4, 6.6 (weak), 8.0	[136]
PPH	NA	THz-TDS	glass transition temperature	Temperature-dependent refractive index at 1 THz	[137]
Nylon-11	0.2–20 THz	FTIR	crystal conformations	3, 6.5 (weak), 12, 13, 15, 16.5, 17.5	[139]
BPHU	15–120 THz	FTIR	H-bonded interactions	53.9, 51.0	[141]
Precursor for BPHU	03–2 THz	THz-TDS	refractive indices and absorption coefficients of various lignins	NA	[144]
	0.3–3.6 THz	THz-ATR	D-mannitol and D-sorbitol	NA	[145]
	0.2–1.5 THz	THz-TDS	absorption spectra and refractive indices of vegetable oils (sunflower seed oil, peanut oil, soybean oil, and rapeseed oil)	1.1, 1.5 (hydrogen -bond bending)	[146]
	0.05–2 THz	THz-TDS	chemical and physical changes of edible oils when heated above the smoke point	lots of uncertainty	[147]
	0.4–2 THz	THz-TDS	biomolecular structure of isomer vanillin	0.61, 1.10, 1.48, and 1.89	[149]
Cellulose	01–4.0 THz	THz-TDS	crystallographic analysis	2.11, 2.38, around 3.0	[153]
	0.2–3.0 THz 19.5–120 THz (FTIR)	THz-TDS FTIR	crystallinity of wood cellulose, microcrystalline cellulose, cotton cellulose nanofiber and wood cellulose nanofiber	2.25 (wood cellulose) 2.39, 2.63 (microcrystalline cellulose)	[96]
	1–10 THz	THz-FTIR	nanofibre cellulose-polymer composites (CNF)	7 THz (for CNF-PP composite, when CNF was added) 3.1, 5.1, 7.5, 9.6 for polypropylene (PP)	[154]

Table 1. *Cont.*

Biopolymer	Investigated Absorption Band	THz Technique	Study	Spectral Peak (THz)	Reference
Starch	3–15 THz	FTIR	crystallinity of native, amorphous, and dried starch	Corn starch: main peaks (9.0, 10.5, 12.2, 13.2) and shoulder peaks (4.9, 7.9, 8.6) Potato starch: 5.1, 7.8, 8.5, 9.0, 10.5, 12.2, 13.1	[155]
	0.25–4.5 THz	THz-TDS	starch ageing process	lots of uncertainty	[158]
Soybeans	0.1–1.5 THz	THz-TDS	soybean varieties discrimination by PLS analysis	optical parameters are very similar	[163]
Wheat	0.2–2.5 THz	THz-TDS	wheat varietal discrimination by PLS analysis	optical parameters are very similar	[165]
Rhodopsin and bacteri-orhodopsin	0–1.5 THz	THz-TDS	conformational activation pathways of biomolecules	NA	[168]
Polyethylene oxide (PEO)	0.1–4 THz	THz-TDS	cross-linking states	NA	[169]
Fatty acids and their analogues	0.3–12 THz	FTIR	THz absorbance	Oleic, linoleic, linolenic acids: 2.3, 5.0, 7.4, 9.8, 11.3 Triolein: 2.3, 9.8 Diolein: 2.0, 9.8 Monoolein: 9.26, 9.8, 11.3	[174]
Natural wax	0.2–2.5 THz	THz-TDS	thermal analysis and optical properties of paraffin wax, beeswax, and liquid paraffin wax	Paraffin: 2.2 (intermolecular interaction between parallel molecules) Beeswax: 1.6 and 2.25 (C=C double bond stretching)	[175]
Microalgae Scenedesmus obliquus	2–20 THz	THz-FTIR	lipid content and composition	7.4 and 9.8 (oleic acid, linoleic acid, and linolenic acid) 9.3 (C=O and –COO– vibration for lipids)	[173]

5. THz Spectroscopy and Imaging in Combination with Machine Learning and Other Artificial Intelligence Tools for Bioplastics Analysis and Production

Different data processing approaches are used to analyse THz spectra and images. THz-TDS has been used with chemometric methods, from simple linear regression to more complex machine learning approaches for quantification performance or quality control. In most cases, THz analysis means detection, identification, classification and quantification [176,177]. In materials characterisation, first data extraction from measured THz signals and spectra should be performed, ensuring additional THz data processing and interpretation. The exact procedures for dielectric constants extraction and thickness determination from THz signal and THz spectra in transmission and reflection spectroscopy are described by many authors [177–182]. From the THz measurement, we can calculate the complex refractive index of the sample. Here, the extinction coefficient is related to the absorption coefficient. In the simplest interpretation, when we have two THz pulses propagating through the air and through the sample, respectively, their amplitude and phase can be expressed in the form of transmittance T [183]:

$$T = \frac{E_s(v)}{E_O(v)} = A\ \exp(-i\varphi) \approx \frac{4n}{(1+n)^2} \exp\left[\frac{i2\pi\nu(\tilde{n}-1)d}{c}\right] \tag{1}$$

where E_O and E_S are the incident and transmitted THz amplitude, respectively; φ is the phase difference between the sample and reference waveforms; $\widetilde{n} = n + i\kappa$ is the complex refractive index of the sample; d is the sample thickness; ν is the frequency, and c is the speed of light in the vacuum. From there, we can obtain the extinction coefficient κ and refractive index n as well as the power absorption coefficient α [183]:

$$\kappa = \frac{c}{2\pi dv} \ln\left(\frac{4n}{A(1+n)^2}\right) \tag{2}$$

$$n = \frac{c\varphi}{2\pi dv} + 1 \tag{3}$$

$$\alpha = \frac{4\pi v\kappa}{c} = \frac{2}{d} \ln\left[\frac{4n}{A(1+n)^2}\right] \tag{4}$$

5.1. Conventional Chemometric Methods in THz Spectra and Imaging Analysis

THz spectroscopy takes advantage of chemometrics, which is also used in other fields of spectroscopy. Using chemometric methods such as Principal Component Analysis (PCA), Partial Least Squares (PLS) regression and Multi-Linear Regression (MLR), we can analyse larger data, i.e., the THz spectra of different bioplastic polymers, to obtain information on the molecular composition and properties of the samples. The results can be used to identify differences and similarities between different bioplastics or to monitor changes in the structure of bioplastics over time during the manufacturing processes themselves. The most widely applied chemometrics methods are:

- Principal Component Analysis (PCA): This is a feature extraction method that allows the linear combination of several independent variables according to the principle of maximum variance and replaces the original variable with a small number of synthetic variables [184]. This method is used to reduce the dimensionality of the spectral data by identifying the most significant features or components. It helps to identify the key differences between samples and to classify them based on their THz response.
- Partial Least Squares Regression (PLS): This method is used to establish a correlation between the spectral data and a set of reference values, such as the concentration of a particular compound in a sample. It helps to quantify the amount of a specific compound in a sample based on its THz response. It is used for quantitative analysis. It uses the absorbance values within a given frequency range, extracts the spectrum features, and then establishes the correlation between the instrumental measurements and the values of the interest property [185]. A detailed description of PLS as a basic tool of chemometrics is presented in [186].
- Multi-Linear Regression (MLR): This method is efficient where there is no correlation between variables and is convenient to calibrate THz data [177]. It can be used in THz spectroscopy to establish a correlation between the spectral data and a set of reference values, such as the concentration of a particular compound in a sample. MLR involves fitting a linear equation to the spectral data and the reference values, where the coefficients of the equation represent the contribution of each spectral feature to the reference value. It is particularly useful when the spectral data contains a limited number of features and the relationship between the spectral data and the reference values is linear. For example, MLR can be used to determine the concentration of a particular chemical in a polymer sample based on its THz response.

PCA is usually used for identification, recognition, and sorting without the need for quantitative results. For quantitative analysis, especially when the THz spectrum contains many spectral features correlated to the varying parameter, it is necessary to use multivariate analysis. MLR is used where there is no correlation between variables. In the case of the existence of a correlation, the PLS method is used. When the relationship between THz response and analyte concentration is non-linear, more advanced machine learning algorithms, such as artificial neural networks (ANN), should be used [187]. This allows optimisation of the production, processing and monitoring of (bio)plastics throughout their life cycle.

Software solutions, e.g., Gaussian, have already been used for numerical simulations for modelling THz spectra by density functional theory (DFT) to determine to which mechanisms and parts of the molecular structure the spectral features that are visible from the THz spectra of a compound or mixture of substances can be attributed. Thus, researchers can better understand the origin of the absorption lines of organic molecules for single crystals, microcrystalline and powder [177].

5.2. Machine Learning and Deep Learning Techniques for THz Signal Processing, Spectral Data and Image Analysis

THz technology can also be very useful in combination with artificial intelligence (AI) [188,189] and machine learning (ML) [190–192]. AI and ML can predict some mechanical, thermal, and other properties of bioplastics and biopolymers based on their chemical composition and structure. This is particularly useful in the case of bioplastics, which are built from the complex molecular structures of biopolymers.

In THz spectroscopic measurements, the maximum detection of the THz signal at the detector is essential, which is usually limited by several factors, such as atmospheric attenuation due to the atmospheric moisture content. This results in a loss of information in the detected signal, changes in slope, baseline shifts and redundancy in the data. All this affects the conversion of the signal into a spectrum and the quality of identifying the spectral features needed for reliable classification. The correct selection of signal pre-processing techniques for THz spectroscopy systems can significantly improve the quality and quantity of pre-processed data, its accuracy, signal-to-noise ratio and the resolution of the THz sensing and imaging system.

THz spectroscopy often produces unconvincing THz spectra which show false spectral characteristics due to, e.g., scattering effects on the particles or due to the characteristics of the THz systems themselves. Some of these effects on spectral results can be measured and predicted when measuring and interpreting a compound's spectral characteristics from THz spectral data. Spectral feature extraction is particularly important in material classification. Successful THz identification and classification measurements require the development of reliable and efficient identification algorithms. Complementary machine learning techniques that classify materials based on their spectral absorption coefficients in the THz range can play an important role. Helal et al. have reviewed and summarised different techniques that can potentially be used for THz signal processing [193]. They focused on the following classification techniques:

- Support Vector Machine (SVM): SVM algorithm is based on a statistical learning method and is a supervised learning algorithm that can be used for classification or regression analysis [194]. SVM is used in many areas where there is a need for fewer learning samples, shorter learning times and faster identification. In the THz data analysis, SVM can be used to classify different samples and to identify the main content's proportion of mixtures based on their THz spectra [194,195].
- K-Nearest Neighbour (KNN): KNN is a simple and effective supervised learning algorithm that can be used for classification. The algorithm stores all possible instances of a class and works by classifying new instances based on distance functions (a similarity measure). A class is classified according to the most votes of its neighbours, with an instance being assigned the most popular class among its K nearest

neighbours, as measured by a distance function [196]. In other words, it works by finding the k-nearest neighbours of a given sample in the training set and assigning the sample to the class that is most common among its neighbours. In THz data analysis, KNN can be used to classify different samples based on their THz spectra. The method is especially valuable in medicine and pharmacy. The proposed ML algorithm has been applied to detect and classify abnormalities in human breast tissue using a THz imaging system that classifies breast cancer as benign or malignant based on pattern recognition [197]. Together with the SVM algorithm, it was used for rapid recognition of pharmaceutical bi-heterocyclic compounds [198].

- Partial Least Square-Discriminant Analysis (PLS-DA): PLS-DA is a supervised learning algorithm that can be used as a multivariate classification technique based upon the classical partial least squares regression method. It works by finding the relationship between the measured spectral features and the target variables containing the class label, i.e., linear combination of variables that explains the maximum amount of variance between the classes [195]. In THz data analysis, PLS-DA can be used to classify different samples based on their THz spectra. This method was used to establish a multivariate model to estimate the authentication and identification of biological samples, e.g., identification of edible oils or the quality estimation of bio-products, e.g., honey [199,200].

All of these methods can be used to analyse THz data by training the algorithm on a set of priori known samples with known classes and then applying the algorithm to new, unknown samples to predict their class. Another ML algorithm for the analysis and classification of THz spectra is also a linear discriminant analysis (LDA) [201], which is a decision-making statistical method for optimal characteristic feature search and selection without omitting other complementary features [202]. This supervised learning dimensionality reduction algorithm finds a linear combination of features that best separates the classes in a dataset. In comparison to PCA, LDA uses categories as the main factor to make the sample after projection as divisible as possible [203]. It is usually used for classification, dimension reduction, and data visualization to produce robust, decent, and interpretable classification results. For example, LDA can be used to classify different types of materials based on their THz spectra, even the geographical origin of biological samples, or to distinguish between healthy and diseased tissue based on their THz signatures and images [203–205]. By reducing the dimensionality of the THz data, LDA can also help visualize the differences between different classes of data and identify the most important features for classification.

Machine learning algorithms are often used to extract shallow spectral features. In contrast, deep learning algorithms can extract deeper spectral features even in the multi-component absorption spectrum of gases and liquids due to the different convolution and pooling layers [206,207]. By analysing THz spectroscopic data, AI and ML algorithms can help researchers to understand better the molecular structure of these materials, which can form the basis for developing new biopolymers or improving the properties of existing ones. If a library of data is compiled on this basis, it can help researchers and manufacturers to select the most suitable biopolymer for the preparation of a bioplastic or composite for the required application.

Machine learning algorithms are widely used for classifying THz imaging data. THz imaging still has one major drawback, which is the ratio between image quality and imaging speed. In fast THz imaging mode, there is usually a lot of noise in the recorded THz image. Various conventional algorithms have been used to improve THz images, such as adaptive filtering, which filters out high-frequency noise while preserving edge sharpness, and the deconvolution method, which improves the resolution of THz images and removes noise by accurately modelling the point spread function [208]. Recently, deep learning has also achieved impressive results in the field of THz imaging. Deep learning has been applied to segmentation and classification tasks in THz images [209,210] and to low-resolution problem-solving with superresolution techniques based on deep learning [211,212]. In fast THz imaging, deep learning can significantly increase the signal-to-noise ratio. An optical ML algorithm based on the spatial transmission modulation of a THz beam was applied to improve the recognition speed in the recognition of objects with only a single measurement [213]. As well as ML, THz tomographic imaging is also an emerging technology in the non-destructive testing of materials, including polymers. Both techniques have been used to detect anomalies in plastics during inline process monitoring [214]. This type of monitoring allows direct intervention during the production process and, consequently, a reduction of product waste, which is linked to the circular economy. Experimental results have shown that the use of THz radiation in combination with a classification algorithm has great potential for monitoring production processes in a polymer line. THz technology can thus be integrated into an industrial plastics sorting system that also includes other relevant complementary sensors, e.g., various in-line scanning cameras. Nüßler et al. are developing an innovative THz-based system, especially for the recycling of black plastics, where a combination of optical sensors with a THz line array in the lower THz frequency range seems to be a promising approach [215].

5.3. AI-Based THz Analysis of Bioplastics

When THz technology is used in combination with other sensors, AI and ML algorithms can be used to ensure quality control during the bioplastics manufacturing process itself. By analysing data from different sensors and systems, AI and ML algorithms can detect imperfections and defects in real-time, allowing for rapid adaptations to the production process. This also impacts the reduction of waste during the production process, which contributes to the realisation of circular economy models. A convolutional neural network (CNN) based on THz signal processing was used to quantitatively discriminate overlapping signals from micro-defects in glass fibre-reinforced polymer composites. The simulated THz signals versus defect thickness were used to train a CNN deep learning model, from which a probabilistic classification map of the size and depth of micro-defects (size and thickness of defects) within the composites was derived [216]. This approach for micro-defect analysis can also be applied to bio-based composite materials. Sarjaš et al. used THz spectroscopy and convolutional neural networks (CNNs) to automatically classify inorganic pigments of plastic materials. They proposed a method to preprocess 1D THz data into 2D data, which is efficiently processed using convolutional neural networks [217]. Recycling bioplastics is sometimes made more difficult by the presence of additives such as pigments, which are present in almost every finished plastic product [218]. Thus, the proposed method can also be used for the detection of pigments in bioplastics, where it is particularly important that the compostability of the material is not affected by the added pigments and dyes. Most of the organic and inorganic pigments commonly used today are not biodegradable and remain in the environment in the form of microparticles long after the bioplastic is gone. The content limits of such substances within bioplastics are defined by national and EU standards. AI and ML are widely used in the optimisation of polymer and biopolymer synthesis. By analysing the big data obtained during experiments, which may include THz spectra, AI and ML algorithms can determine the most promising reaction conditions and optimise the process to produce high-quality biopolymers with the desired properties. THz spectroscopy and machine learning analysis were used to evaluate the hydration properties of biological materials that can be used in bio-medical fields [219]. THz-TDS was used with feed-forward neural networks to analyse the animal origin of gelatine, which is a non-toxic natural biomacromolecule, often used as an ingredient for biopolymer composites [220].

As mentioned above, THz materials research can contribute to material life cycle analysis by monitoring the characteristics of specific properties over time or through different life cycle phases, including raw material extraction, processing, use and disposal. Using AI algorithms, we can incorporate more data into the analysis itself, including from other sensors, and study the environmental impacts on the material itself at different life cycle stages or the material's impact on the environment. By combining THz measurements and AI, we can gain insights into reducing the environmental impact of bioplastics and biopolymers (Figure 12).

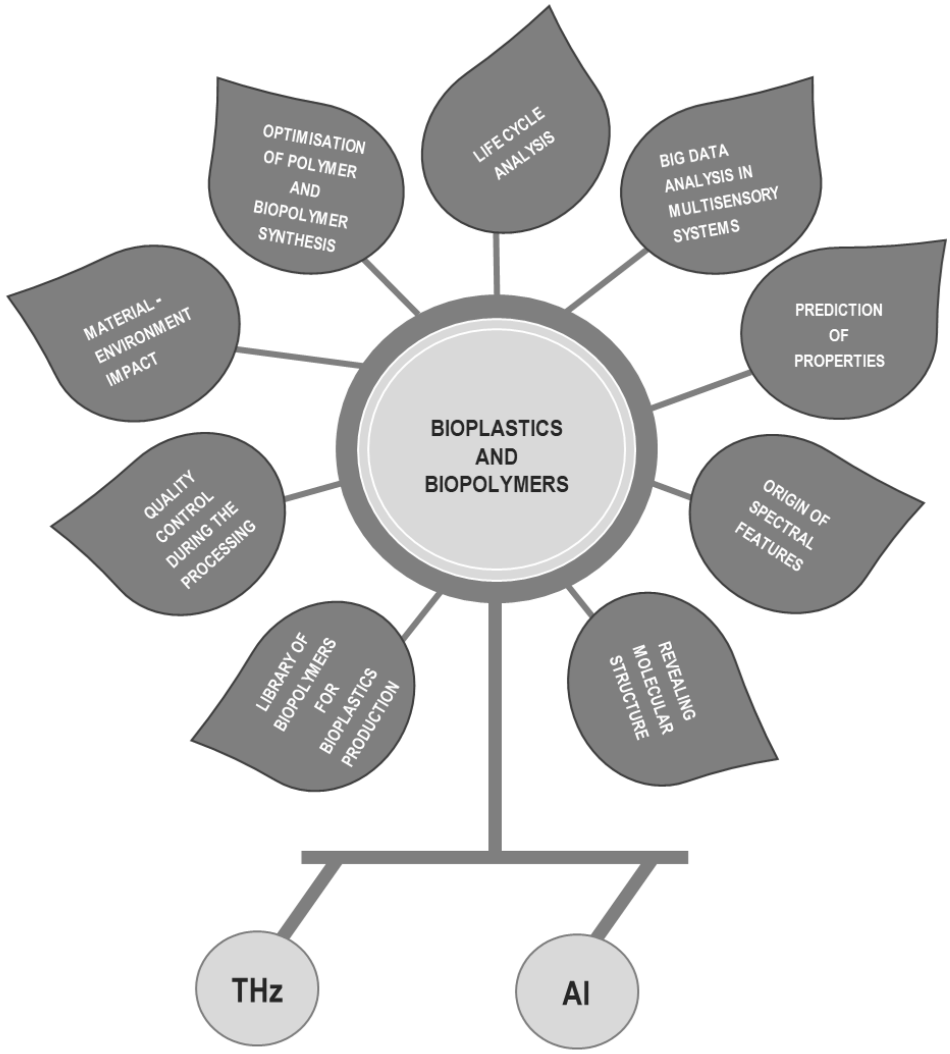


Figure 12. Potential contributions of using a combination of THz technologies, artificial intelligence and machine learning to the circular economy in bioplastics and biopolymer research and production.

6. Conclusions

Plastics based on petroleum-derived polymers still dominate many applications, but they are slowly being replaced by alternative materials that have a positive impact on the environment and human health throughout their life cycle. To reduce consumption and dependence on fossil fuel-based materials, biopolymers are increasingly being explored and introduced as examples of environmentally friendly plastics. Their use has been increasing over the years, mainly due to the improvement of their physical and mechanical properties using various additives. To investigate these properties, various methods are used for the quantitative and qualitative analysis of bioplastics or their degradation by-products. One such method is THz spectroscopy, which has already shown great potential in the field of analysis of polymers as well as plastic and rubber materials. The favourable research results can also be transferred to the field of characterisation of biopolymers and bioplastics, as we have shown in this review. We have discussed different biopolymers and demonstrated attempts to use THz spectroscopy for their analysis in the further development and production of bioplastics.

Furthermore, the combination of THz spectroscopy and imaging with AI and ML algorithms can help researchers and manufacturers to understand better and optimise bioplastics and biopolymers, leading to more sustainable and efficient materials produced with the precise properties needed for different applications and end-user requirements. In the future, we can expect an intensive deployment of ML, DL and other AI tools in THz imaging and spectroscopy systems to improve the quality of recorded data and data analysis. The findings of this review underline that THz technology can bring technological circularity in important areas of biotechnology and related plastic and rubber industry as well as the agricultural sector.

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