



Enzymatic Self-Degradable PLA-Based Electrets

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Abstract

In recent years, the demand for sustainable and degradable materials and electronic devices has increased significantly. Among a range of biodegradable polymers, poly(lactic acid) (PLA) is a good alternative to conventional petrol-based polymers because of its attractive mechanical properties and its easy processability. Recently, PLA has also been described as a promising dielectric material with piezoelectric and electret properties. We expect that PLA—after further optimization—will play an important role as a material for environmentally friendly sensors in the future, where first applications such as air filters and pressure sensors have already been proposed. However, degradation under normal ambient conditions is very slow, and an accelerated and controllable degradation process is highly desirable for any type of PLA-based sensors. Enzymatic hydrolysis with embedded enzymes has been proposed as an approach to accelerate and control degradation. In this work, we investigate the properties of PLA in terms of dielectric and mechanical properties with a focus on its ability to store charges after the enzyme proteinase K (*Trit. album*) has been incorporated. Results reveal that proteinase K has a positive effect on the charge stability of solvent-cast PLA electrets after complete evaporation of the solvent. Furthermore, we observed a concentration-dependent acceleration of mass loss in a Tris-HCl buffer. A fast degradation within only one day occurred at a concentration of 6 wt% proteinase K.

Keywords Polylactic acid · Proteinase · Enzymatic degradation · Electret · Hydrolysis · Charge storage

Introduction

Electrets are dielectric materials that exhibit quasi-permanent electric charge or dipole polarization, where “quasi-permanent” means that the characteristic time constant for

charge decay is longer than the time period over which studies are performed with the electret [1]. There exist both inorganic and organic electret materials, where latter, usually polymers, have been utilized in many applications in the last decades, such as microphones, air filters, sensors, and

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energy harvesters [2]. The main advantage of this class of materials is its ease of processing and fabrication, although this is often accompanied by lower temperature stability than found in inorganic electret materials. Polytetrafluoroethylene (PTFE) and its derivative fluorinated ethylene propylene (FEP) have particularly good electret properties. Both are non-polar polymers with a high charge storage stability and a low conductivity. However, these fluorocarbon-based polymers are not ecologically friendly in either fabrication or disposal.

Due to growing environmental awareness and the increasing amount of electronic waste, the demand for environmentally friendly, biodegradable materials is increasing. In this context, poly(lactic acid) (PLA) is one of the best known biopolymers, mainly used for compostable packaging. It is fabricated from corn and degrades depending on the environmental conditions [3]. PLA has recently been described as a promising dielectric material with piezoelectric [4] and electret properties [5–7]. However, the charge stability of PLA is still poor compared to the fluorine-based electret materials. The charge storage characteristics of electrets are influenced by various factors, including electrical conductivity, charge transport properties, and polar relaxation frequencies [8]. At room temperature (RT), PLA exhibits good insulation properties, with low conductivity ranging from 10^{-16} – 10^{-17} S/m. However, compared to PTFE with a conductivity $< 10^{-18}$ S/m [9], the higher conductivity of PLA may contribute to its lower charge stability. Furthermore, above a temperature of 60 °C, the insulation properties of PLA deteriorate and the conductivity rises to approximately 10^{-12} S/m at 150 °C [10, 11]. Research has been presented with the aim of improving the charge stability of PLA by incorporating inorganic micro- and nanoparticles, such as barium titanate [7], magnesium oxide [6], silicon dioxide [5] or montmorillonite [12] as filler materials. Depending on the particles, improvement in charge stability was clearly achieved. This can be explained by the fact that embedding filler materials creates structural defects in the polymer matrix, which are claimed to act as traps for charge carriers [12, 13].

Against this background, PLA can be expected to play an important role as an electret material for environmentally friendly sensors in the future. First applications, such as PLA-based air filters, high-sensitive sensors and ultrasonic transducers, have already been proposed [14–16]. Independent of the application, a controllable and adjustable degradation time of PLA-based devices is highly desirable. In general, the biodegradation of PLA proceeds in two stages: In an aqueous environment, macromolecular chains are first cleaved into monomers and oligomers due to hydrolysis of ester bonds. In a second step, microorganisms mineralize these so-formed lower-weight molecules, which are

harmless for humans and the environment [17]. The hydrolysis step depends strongly on environmental conditions like pH value and temperature [18–20] and can be accelerated within certain limits through co-polymerization [21], blending [22], or the addition of filler materials [23, 24].

A new and biocompatible approach to accelerate and control the degradation of polymers (not only suitable for PLA but also for some petrol-based polymers) is enzymatic hydrolysis or enzymatic degradation. Enzymes are highly specialized proteins that act as biological catalysts and can accelerate the hydrolysis process by lowering the reaction activation energy [25]. Several studies deal with the enzymatic degradation of PLA by adding enzymes like proteinase [26, 27], esterase (lipase) [28, 29], and cutinase [30] to the aqueous environment. However, the lack of suitable enzymes in the natural environment is a limitation here. Therefore, a promising approach is the integration of enzymes in the polymer matrix [27, 31, 32]. Huang et al. [27] investigated the degradation of embedded proteinase K in solvent-cast PLLA samples. In general, proteinase (also called protease or peptidase) is an enzyme that breaks proteins into smaller polypeptides or single amino acids [33]. Proteinase K has the ability to degrade PLA as its monomer structure is similar to the amino acid alanine [34]. These promising results pioneer the way for investigation of PLA as a novel electret material for sensors that decompose in a controlled manner. However, studies of the impact of proteinase K on the electret properties of PLA are lacking. Therefore, we investigate the effect of embedded proteinase K on the dielectrical and mechanical properties of PLA-based electrets in this work.

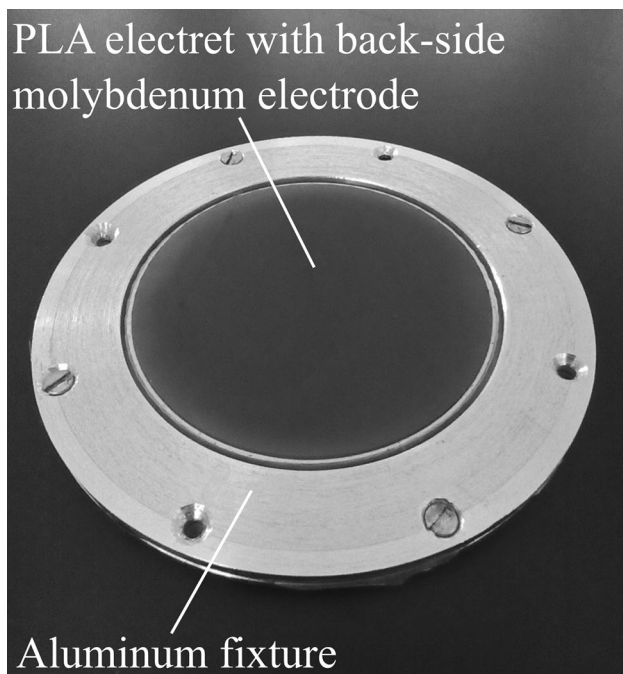
Experimental

Sample Preparation

The fabrication process of the PLA-based electrets with embedded proteinase K is based on a spin coating process of polymer-enzyme-solvent-suspensions. Different weight proportions of proteinase K were used to investigate the impact of the proteinase K on the electret properties. For fabrication, proteinase K (Carl Roth, Karlsruhe, Germany), isolated from the fungus *Tritirachium album* with a specific activity of 30 U/mg, was added to trichloromethane (TCM) (Carl Roth GmbH & Co. KG, Karlsruhe, Germany) and was magnetically stirred for 24 h followed by ultrasonification for 30 min to get a homogeneous suspension. After that, PLA pellets (Ingeo 4043D, Natureworks LLC, Minneapolis, USA) were dissolved in the enzyme-TCM-suspension. Table 1 shows the quantities of PLA, proteinase K, and TCM used for the suspensions. The weight percentages

Table 1 Amount of proteinase K, PLA, and TCM used for the preparation of the suspensions

Proteinase K in mg (in wt%)	PLA in mg	TCM in ml
0 (0)	1000	5.00
10 (1)	990	4.95
20 (2)	980	4.90
40 (4)	960	4.80
60 (6)	940	4.70

**Fig. 1** Fabricated PLA electret in an aluminum fixture with a molybdenum electrode

refer to the total mass of the composite (PLA + proteinase K). The ratio of PLA and TCM is the same for all suspensions and is 200 mg/ml.

The suspensions were spin coated with a spin speed between 1,000 and 1,150 rpm and an acceleration of 500 rpm/s² for 30 s on a borosilicate-glass wafer (Schott AG, Mainz, Germany). The reason for the varying spin speed is that the viscosity of the suspensions increases with increasing proteinase K concentration. Therefore, to achieve the same layer thickness, the spin speed was increased by 25 rpm per weight%. For a homogeneous thickness, it is also important to start spinning directly after application of the suspension because of the fast evaporation of the solvent. Cooling of the suspension prior to spin coating can improve the spin coating results as well. After drying at RT for 24 h, the films were carefully removed from the wafer. For measurement of the electret properties, samples were clamped in an aluminum fixture and metallized on one side with molybdenum, which is biodegradable, using a DC sputtering process

(150 W, 15 min) (see Fig. 1). As a next step, the non-metallized surface was charged to -1 kV using a corona triode setup with a biased grid. The corona voltage was -9 kV and the distance between tip and sample was 5 cm.

Microscopic Characterization of Electret Foils

The particle size of the used proteinase K was investigated using a scanning electron microscope (SEM) (MAIA3, Tescan GmbH, Dortmund, Germany). In order to prevent charging of the samples, they were coated with a thin chromium layer using a DC sputtering process (150 W, 2 min).

Thermogravimetric Analysis

For investigation of the weight proportion of chloroform in the samples and the evaporation time at an elevated temperature, a thermogravimetric analysis (TGA 4000, PerkinElmer, Rodgau, Germany) was carried out. To determine the evaporation time, samples were heated to 65 °C, and the mass was measured for a period of 24 h. This temperature was chosen because it is above the boiling point of TCM (61.2 °C) and less than the denaturation temperature of the used proteinase K (75 °C). For comparison, samples were also heated to 200 °C at a rate of 10 °C/min and cooled at a rate of 5 °C/min. All measurements were carried out in a nitrogen atmosphere.

Homogeneity Measurements of Surface Potentials

To investigate the homogeneity of the surface potential of charged samples, scanning of the surface potential was done with a commercial field-compensating non-contact electrostatic probe (Model 244, Monroe Electronics Inc., Lyndonville, USA). Surface potential measurements were taken every 3 mm in the x- and y-direction over an area of 66 mm x 66 mm. The sample together with the holder was positioned in the middle of the scanned area, and its charged surface was 50 mm in diameter.

Measurement of Thermally Stimulated Currents

Measurements of thermally stimulated current (TSC) were performed utilizing an open-circuit setup (see Fig. 2) with a probe area of 17.35 cm² and a distance from probe to the sample of 5 mm. A pico ampere-meter (Keithley 617, Tektronix, Beaverton, USA) was used to measure current. The temperature of the sample was controlled with a heating controller (Eurotherm 2404, Eurotherm Germany GmbH, Limburg, Germany). Before TSC measurements, all samples were charged to -1 kV for 3 min. Then, samples were

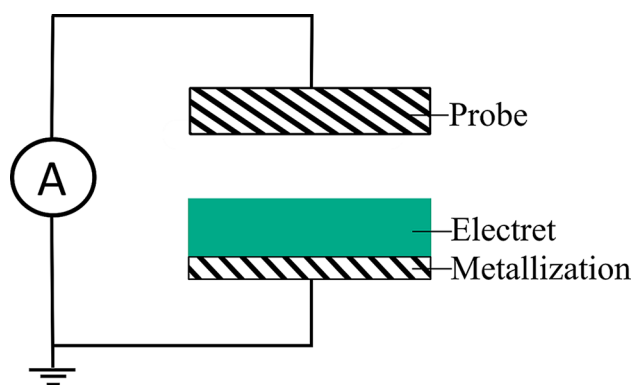


Fig. 2 Schematic of the open-circuit TSC setup [35]

heated to 120 °C at a heating rate of 4 °C/min. Current values were taken every second.

Measurement of Charge Stability

To investigate the charge stability of the electrets, the surface potential was measured using a non-contact electrostatic voltmeter (Trek 541-1, Trek Inc., New York, USA) with a vibration probe. An automatic measurement setup based on an xy linear positioning system (Conucon UG, Hamburg, Germany) was used for this purpose. Both the voltmeter and the positioning system were connected via a serial interface. The control and the readout of the measurement data were performed with a MATLAB program. Because charge stability strongly depends on temperature and humidity, measurements were performed in a chamber with a controlled humidity of $30 \pm 5\%$ and a temperature of 20 ± 1 °C.

Investigation of Mechanical Properties

To investigate how the proteinase K influences the mechanical properties of the fabricated PLA electrets, quasi-static tensile tests (EZtest EZ-L, Shimadzu Deutschland GmbH, Duisburg, Germany) were carried out. Samples were cut into stripes with a width of 2 cm and pulled apart at a constant speed of 10 mm/min or determination of the tensile strength and elongation at break. For measurement of the Young's modulus a lower pull speed of 1 mm/min was used.

Measurement of Electret Degradation

The enzymatic degradation of the PLA electrets with different proteinase K concentrations was evaluated through mass loss (%) measurements according to Eq. 1, where m_0 is the mass of the electret before degradation, and m_t is the mass of the electret after different durations of degradation, i.e.

$$\text{Mass loss (\%)} = \frac{m_0 - m_t}{m_0} \times 100 \quad (1)$$

Before performing the measurements, all samples were heated to 65 °C for 24 h, enabling evaporation of the TCM. Degradation experiments were carried out at 20 and 37 °C in different solvents (DI water and 50 mM Tris-HCl). Due to the strong dependence of the pH value on temperature, different mixing ratios of the Tris-HCl were used to adjust the pH to 8 for both temperatures. All samples were cut into equal-size pieces (4.8 cm²) with nearly the same mass (≈ 20 mg) and put into Petri dishes containing 10 ml of the medium. In case the medium evaporated, it was refilled to this level. For the mass measurement, the samples were removed and dried on a sieve with a mesh size of 1 mm.

Results & Discussion

Morphological Characterization of PLA Electret Foils

The first step in processing thin, homogeneous PLA-based electret foils was to analyze the size of the proteinase K particles using SEM; see Fig. 3 (a). It can be observed that the size of the particles varies strongly, with sizes up to 100 μm, where large particles are detrimental to the homogeneity of thin electret foils. However, the size of the particles can be successfully reduced by treatment with a magnetic stirrer and ultrasonification (see Fig. 3 (b)). Figure 3 (c) shows the cross-section of a PLA electret with the embedded proteinase K. Note that proteinase K is soluble in water but not in solvents like TCM. Therefore, small particles of the proteinase K were embedded into the polymer matrix. With the mixing ratio and rotation speed described in section "Sample Preparation", the electrets reached a thickness of 35 μm. Due to the flexible spin coating fabrication process of the electrets, the layer thickness can be easily varied by changing the mixing ratio of the suspension or by changing the spin speed. The electret properties, especially the charge stability, depend on the film thickness, with better charge stability at higher thicknesses. However, a higher film thickness has a negative effect on the mechanical behavior, especially for thermoformed piezoelectrets. Therefore, for all experiments we carried out, we used electrets with a thickness of 35 μm because it is a compromise between moderate charge stability and flexibility.

Solvent Evaporation

It is well known that solvent residues are detrimental to the charge stability of electrets [36]. Therefore, complete evaporation of TCM from the samples is a key issue that was

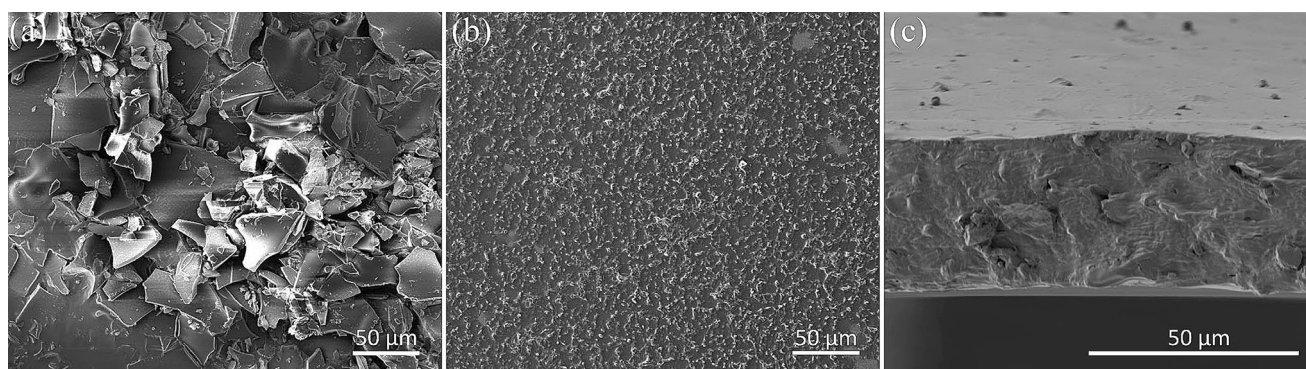


Fig. 3 SEM images of (a) proteinase K particles (as purchased), (b) proteinase K particles after magnetic stirring (24 h, 500 rpm) and ultrasonification (30 min) and (c) a cross-section of a PLA electret foil with embedded proteinase K particles (6 wt%). The foil was fabricated by

spin coating a PLA/TCM/proteinase K-suspension at a spin speed of 1,000 rpm for 30 s. After drying, the foil was carefully detached from its glass substrate

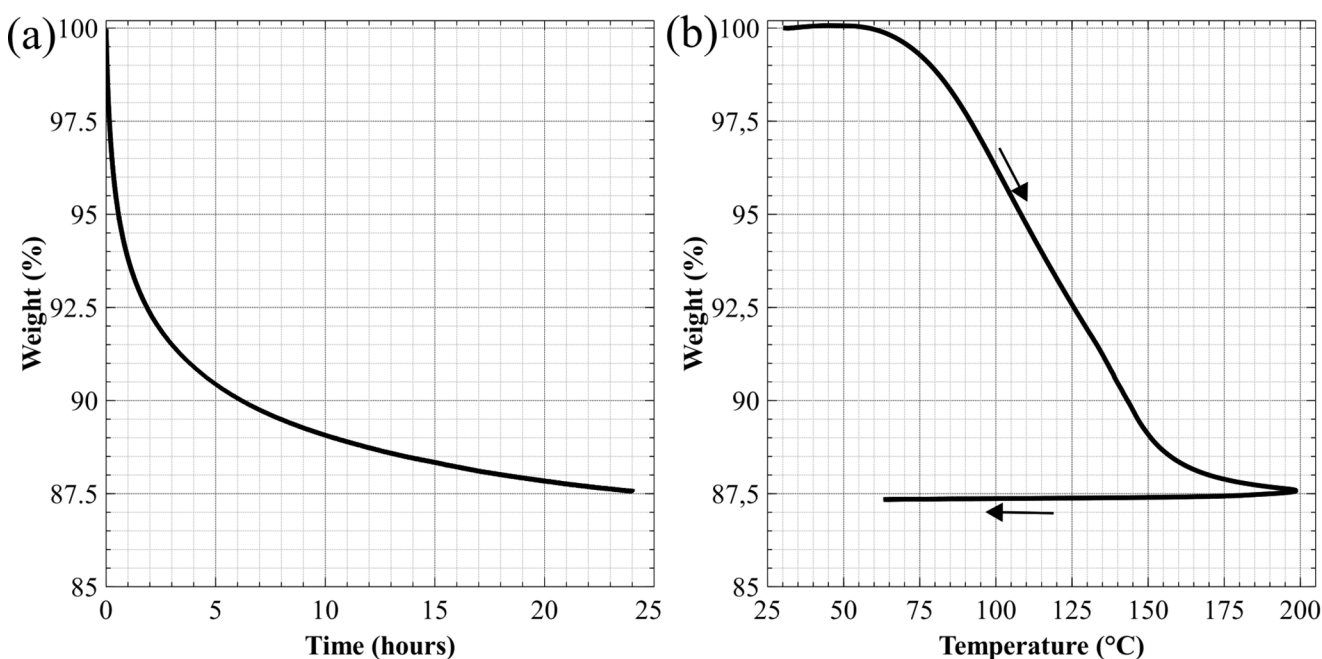


Fig. 4 Exemplary thermogravimetric analysis of PLA-based electret (a) heated at an elevated temperature of 65 °C for 24 h and (b) heated from RT to 200 °C at a heating rate of 10 °C/min and cooled to 65 °C at

a cooling rate of 5 °C/min. All measurements were done in a nitrogen atmosphere. The thickness of the samples was 35 μm

investigated here by measuring the mass loss at an elevated temperature of 65 °C; see Fig. 4 (a). A mass loss of 12.43% occurred after 24 h due to evaporation of TCM. However, it is not clear whether the evaporation is completed under these conditions. Therefore, the samples were heated to 200 °C at a heating rate of 10 °C/min and cooled to 65 °C at a cooling rate of 5 °C/min; see Fig. 4 (b). These high temperatures lead to denaturation of the proteinase K, and they are used solely to study the evaporation process. Interestingly, this temperature step also leads to almost the same mass loss of 12.65%, indicating that the treatment at 65 °C for 24 h is sufficient. Samples also can be placed in a heated vacuum chamber for faster evaporation of the TCM. Note that the

evaporation time strongly depends on the vapor pressure of the used solvent. TCM has a vapor pressure of 119.4 hPa (20 °C), which is lower than other common solvents that dissolve PLA such as dichloromethane, with a vapor pressure of 470 hPa (20 °C). If the vapor pressure of a solvent is too high, the solvent evaporates too fast in the manufacturing process, resulting in inhomogeneous layers.

Homogeneity of the Surface Potential

Scanning with an electrostatic voltmeter was done to test if the proteinase K particles have any impact on the homogeneity of the surface potentials. For that, non-annealed and

annealed samples (65 °C, 24 h), which were charged at RT and 65 °C were investigated. Obtained results from samples with a proteinase K content of 6 wt% are shown in Fig. 5. All samples show a high degree of homogeneity of the surface potential, especially in the central region. Therefore, the values of the surface potential measured in this region were used. The non-annealed and annealed samples charged at RT showed -1002 ± 8 V and $-1009 \text{ V} \pm 6$ V, respectively, which is in good agreement with the utilized grid voltage of -1 kV. However, the sample charged at 65 °C had a surface potential of -934 ± 32 V. We assume that the potential drop can be explained by the motion of charges from the surface into the bulk of the samples during corona charging.

Thermally Stimulated Currents

Valuable information on the charge storage stability can be gained by the TSC method. Samples without and with heat treatment (65 °C, 24 h) and samples with and without proteinase K were investigated. TSC results for PLA electrets

with a thickness of 35 μm without proteinase K are shown in Fig. 6 (a). As previously reported, two characteristic transitions in thermally stimulated surface potential decay are observed in PLA films, occurring at temperatures of about 50–55 °C and 70–75 °C and presumably associated with charge release from shallow and deep traps, respectively [37]. One can see from Fig. 6 (a) that PLA films without temperature treatment show peaks at 33 and 47 °C. These low temperatures can be explained by chloroform residues in the polymer that persist even after storage for several weeks at RT. At the same time, the annealed sample (65 °C, 24 h) with completely removed solvent shows two peaks at 56 and 79 °C, which is in good agreement with values reported in the literature. It should be noted that PLA contains a polar group C=O, and therefore, can exhibit some dipole relaxation processes at elevated temperatures. To show that this does not matter for a present analysis, we additionally demonstrate in Fig. 6 (a) the TSC spectrum for an uncharged annealed PLA sample. This sample shows almost zero current over the entire temperature range, indicating that there

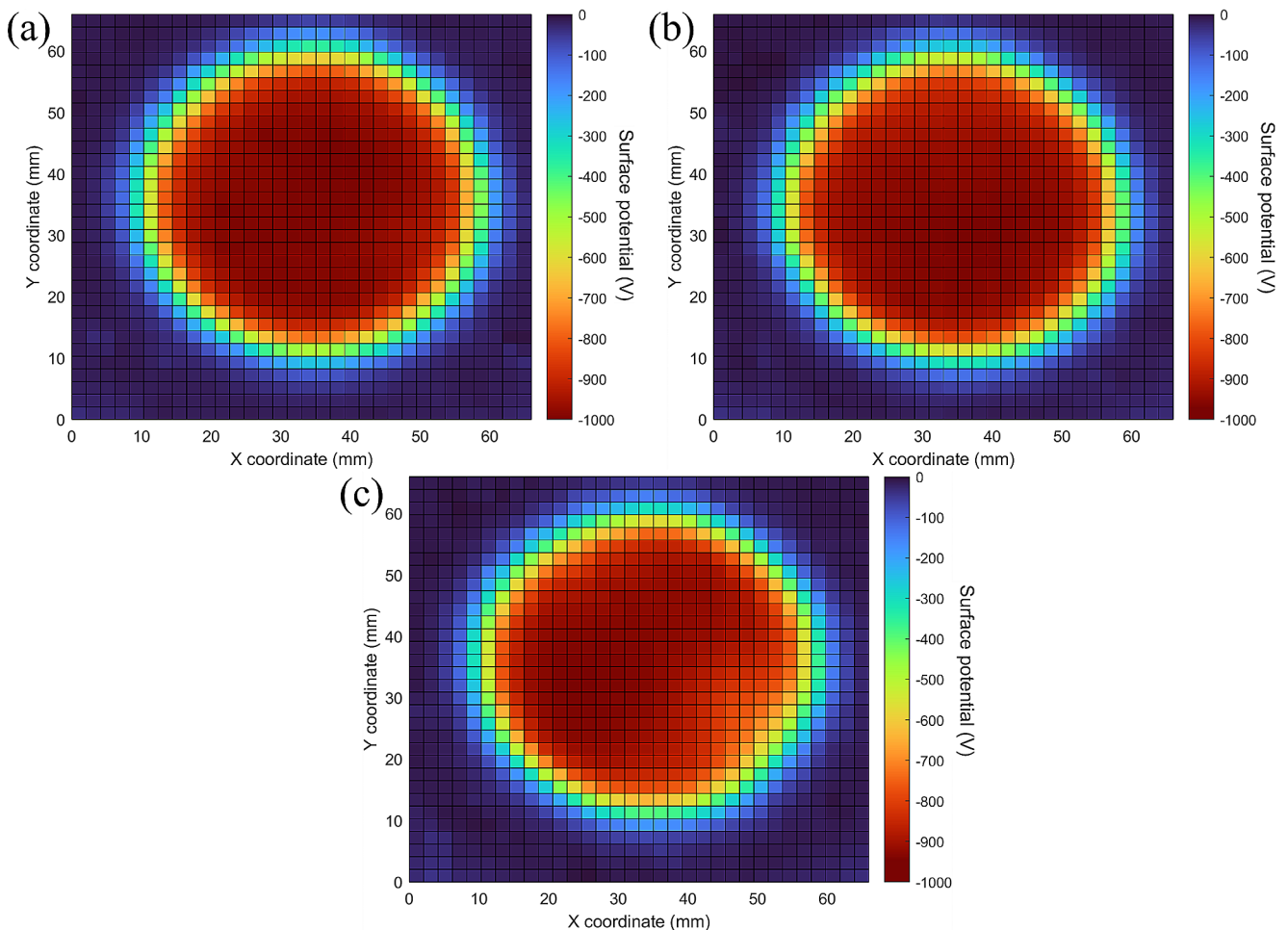
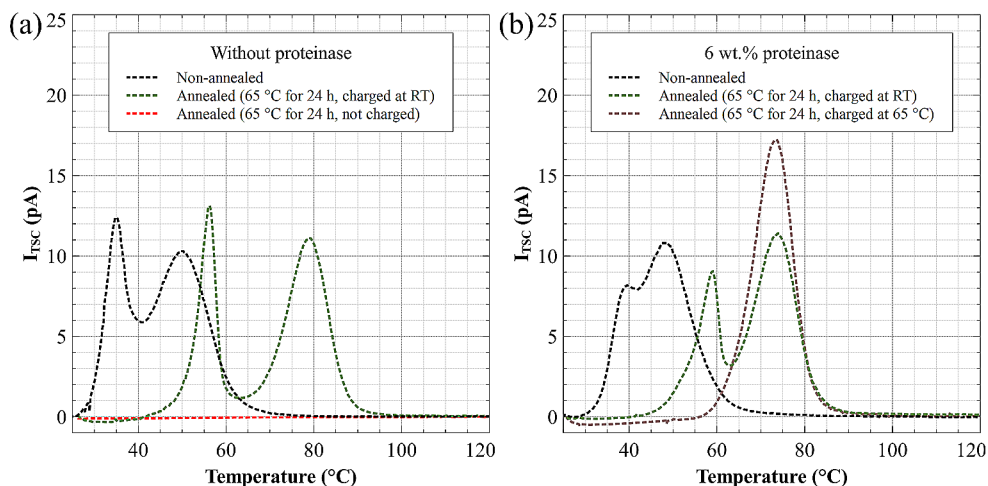


Fig. 5 Surface potential scanning of an (a) untreated sample, (b) heat-treated samples (65 °C, 24 h) and (c) heat-treated samples (65 °C, 24 h) that were charged at 65 °C. For measurement samples with 6

wt% proteinase K were used. All samples were charged to -1 kV for 3 min. The thickness of the samples was 35 μm

Fig. 6 TSC measurements of PLA electrets (a) without and (b) with 6 wt% proteinase K. The heating rate was 4 °C/min. All samples were charged to -1 kV for 3 min. The thickness of the samples was 35 μm



is no contribution of internal dipoles to the open-circuit TSC current. In comparison, the TSC spectra of samples with proteinase K (6 wt%) are shown in Fig. 6 (b). As in the case of samples without proteinase K, both TSC peaks shifted towards a higher temperature after heat treatment, namely to 59 and 74 $^{\circ}\text{C}$, respectively. Considering that two TSC peaks in the annealed samples with and without proteinase K occurred at similar temperatures, one can expect similar charge stability in both films. To improve the charge stability, we also charged the samples at a temperature of 65 $^{\circ}\text{C}$ because it has been reported that poling polymer films at elevated temperatures leads to charge stabilization in PLA [38, 39] and FEP films [40] and piezoelectrets based on them [41–43]. It can be assumed that shallow traps release charges during charging, while the deeper traps fill gradually until the sample is fully poled. Accordingly, the TSC spectrum shows only one high-temperature peak corresponding to the release of charges from deep traps. In general, the above results indicate that the embedded proteinase has no negative effect on charge storage. In order to confirm these outcomes, the isothermal decay of surface potential was additionally measured over 14 days.

Charge Stability

The surface potential of the PLA electrets with and without embedded proteinase K was measured after negative corona charging to -1 kV in order to evaluate the effect of proteinase K on the charge stability. Note that all measurements were carried out under controlled conditions with a humidity of $30 \pm 5\%$ and a temperature of 21 ± 1 $^{\circ}\text{C}$. Deviation from these conditions can result in differences of the measured potential. Measurements were performed on samples, which were charged at RT and at 65 $^{\circ}\text{C}$ after temperature treatment at 65 $^{\circ}\text{C}$ for 24 h. The charge decay of samples, which were charged at RT is shown in Fig. 7 (a). It is shown that charge decay depends on the weight proportion of the

proteinase K. Samples with a concentration of 6 wt% of proteinase K show the lowest decay of the surface potential with a value of -746 V after 14 days. Our hypothesis is, as mentioned in the introduction, that the proteinase K acts as filler material, and structural defects occur in the polymer matrix that may act as charge carrier traps. No additional increase in charge stability was observed at higher concentrations of 8 and 10 wt%. Therefore, the results for these concentrations are omitted in Fig. 7. Our interpretation is that agglomerates will form due to higher concentration of proteinase K, whereby the interface between particles and PLA does not increase further. In addition, the cost of proteinase K is high, making higher concentrations unattractive for most industrial applications. The surface potential decay for samples that were charged at 65 $^{\circ}\text{C}$ is shown in Fig. 7(b). The temperature treatment leads to additional charge stabilization. This is true for both pure PLA and for samples with proteinase. However, the improvement is only in the range of 5–10% compared to samples charged at RT. It must also be taken into account that the starting potential was lower, as shown in Sect. 3.3. Therefore, the surface potential decay is only 19.5% after 14 days for the sample with 6 wt% proteinase K. It should be noted that the charge stability of non-annealed samples was also measured. Due to the hardly controllable evaporation of the TCM and the poor charge stability, these results are not shown.

To correlate the above TSC results in Fig. 6 with the isothermal decay shown in Fig. 7, one has to consider that the two TSC peaks of the annealed samples with and without proteinase occur at similar temperatures, which corresponds to comparable activation energies. However, the height of the low-temperature peaks is markedly different. The peak height in the sample with proteinase is significantly lower, implying that for this sample a smaller fraction of charges is captured by shallow traps. Obviously, the charge release from shallow traps determines the rapid decay of the surface potential, while deep traps allow for long-term stability

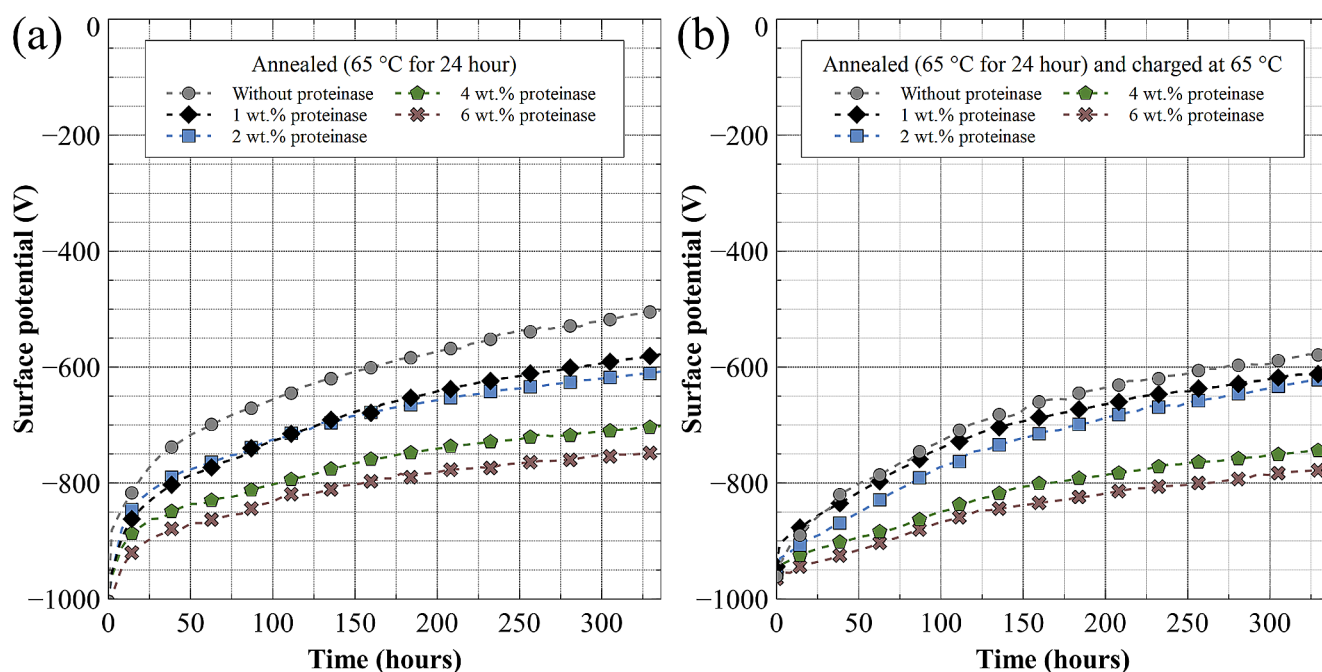


Fig. 7 Surface potential measurements of tempered (65 °C, 24 h) PLA electrets with embedded proteinase K (a) charged at RT and (b) and charged at 65 °C. Measurements were carried out in a chamber with a controlled humidity of $30 \pm 5\%$. The thickness of the samples was 35 μm

Table 2 Measured mechanical properties of PLA electrets ($n=6$)

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
Without proteinase	63.23 ± 1.86	4.92 ± 0.35	2375 ± 123
1 wt% proteinase	58.31 ± 2.21	4.36 ± 0.50	2425 ± 158
2 wt% proteinase	56.38 ± 2.67	3.81 ± 0.42	2520 ± 181
4 wt% proteinase	53.01 ± 2.70	3.51 ± 0.51	2582 ± 176
6 wt% proteinase	51.38 ± 2.91	3.19 ± 0.39	2650 ± 124

[35]. Therefore, the sample with proteinase has a better overall temporal stability of the surface voltage.

Mechanical Properties

Tensile tests were carried out on fabricated PLA electrets with different concentrations of proteinase K. Table 2 shows an overview of measured mechanical properties ($n=6$). All samples had a width of 20 mm and a thickness of 35 μm . Measurements reveal that the sample without proteinase K shows the highest tensile strength, at 63.23 ± 1.86 MPa. The tensile strength decreases with increasing concentrations of proteinase K. Here, the lowest tensile strength of 51.38 ± 2.91 MPa was achieved with a proteinase K concentration of 6 wt%. The elongation at break also decreases with increasing proteinase K concentration. Maximum elongation at break of $4.92 \pm 0.35\%$ was reached in samples without proteinase K, and the lowest elongation at break, $3.19 \pm 0.39\%$, was measured in samples with 6 wt% proteinase K. This can be explained by the fact that the proteinase

K particles induce defects in the polymer matrix, which can cause cracks in the polymer matrix that propagate and ultimately lead to breakage of the sample. Furthermore, the Young's modulus of the samples rises with increasing proteinase K concentrations. This phenomenon can also be attributed to the proteinase K particles, which restrict the movement of the polymer chains, consequently reducing their ability to deform. As a result, the material exhibits increased stiffness. This observed increase in Young's modulus aligns with previous research findings in the literature, specifically studies on the impact of adding fillers to PLA [44–47].

Enzymatic Degradation

The enzymatic degradation of the PLA electret foils was evaluated in DI water and Tris-HCl (pH=8) at 20 °C (RT) and at 37 °C (human body temperature) for samples with proteinase K concentrations ranging from 0 to 6 wt%. The mass loss measurements of PLA electrets in DI water are shown in Fig. 8 (a). Independent of temperature, the mass loss of the samples is low (<15%), which can be explained by the fact that no activator for the enzymic reaction is present in DI water. The small mass loss is related to the disintegration of proteinase K particles at the interface between PLA and solvent, while samples without proteinase K particles show only a negligible mass loss. Even if the mass loss in water is low, it should be noted that alternative methods have been explored to expedite hydrolysis in water. These

methods encompass degradation at elevated temperatures [48, 49], surface treatment to enhance PLA's hydrophilicity [50, 51], blending [52], and copolymerization [53]. However, especially blending and copolymerization will probably have a decisive influence on the electret properties. Therefore, this needs to be investigated in further studies.

In Tris-HCl, the mass loss of PLA electret foils is much higher, and a positive correlation with the concentration can be observed, while samples without proteinase K particles show no mass loss; see Fig. 8 (b). In addition, the temperature of the solvent clearly accelerates the degradation process. Accordingly, the fastest degradation in our experiment occurred at 37 °C at samples with 6 wt% proteinase K. Note that the degradation may be accelerated further, as the temperature optimum for the enzyme used is 65 °C. However, these high temperatures are rarely found in the environment.

Our results show that the enzyme proteinase K does not lose its function after contact with TCM for 24 h and temperature treatment at max. 65 °C for 24 h. It should be noted that the measured mass loss is a superposition of the hydrolysis of the PLA, the disintegration of the proteinase K, and the detachment of the molybdenum layer.

Conclusion

The degradation of the electret PLA is slow under normal environmental conditions, which is a limitation for its use as a biodegradable material for environmentally friendly sensors. Enzymatic hydrolysis with embedded enzymes has been proposed as an approach to accelerate and control the degradation of polymers. In this work, the enzyme proteinase K is employed to accelerate the degradation of solvent-cast PLA electrets. We addressed the question of

how electret and mechanical properties are influenced by the embedded enzyme.

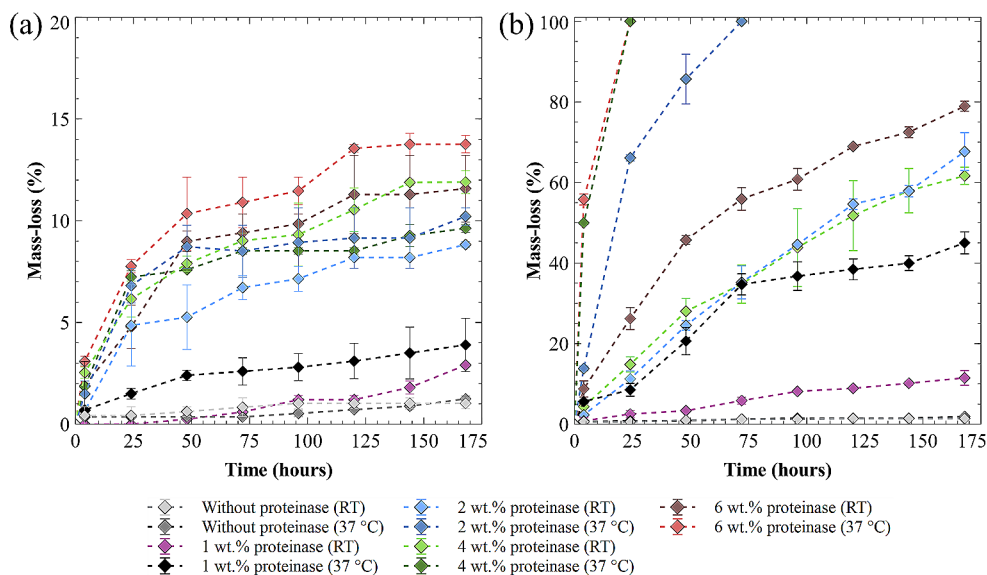
The dielectric properties of the PLA electrets are investigated, focusing on the ability to store charges after the proteinase K enzyme is incorporated. An important observation is that the solvent TCM has a negative impact on the electret properties, namely TSC peaks and charge stability. Therefore, complete evaporation of the solvent at a temperature less than the denaturation temperature of the proteinase and above the boiling point of TCM is essential before charging the samples. Further, results show that proteinase K has a positive effect on the charge stability of solvent-cast PLA electrets after complete evaporation of the solvent. Measurements of the surface potentials show that with the embedded proteinase (6 wt%), values up to -780 V can be reached after 14 days for samples that were annealed at 65 °C for 24 h and charged at 65 °C.

Investigation of the mechanical properties show that the tensile strength, elongation at break and Young's modulus decrease with increasing proteinase K concentration. Compared to pure PLA, the PLA with 6 wt% proteinase shows a reduction of 25.2% in tensile strength, 28.2% in elongation at break and 20.7% in Young's modulus.

We also observed a concentration-dependent acceleration of mass loss in Tris-HCl buffer. The fastest full degradation of a 35 μm thick foil was observed within only one day at a concentration of 6 wt% proteinase K. However, this result is limited to Tris-HCl buffer solution. In DI water, the degradation process is slower due to the absence of an enzymatic activator in the DI water.

Overall, PLA is a promising new sustainable electret material that degrades in Tris-HCl in a controlled manner after the incorporation of proteinase K. Advantageously, the enzyme improves the charge stability in a dose-dependent

Fig. 8 Investigation of the enzymatic degradation by means of mass loss measurements of PLA electrets ($n=4$) with proteinase K (0–6 wt%) at 20 and 37 °C (a) in DI water and (b) in 50 mM Tris-HCl (pH=8). The thickness of the samples was 35 μm



manner but deteriorates the mechanical properties of the polymer. Future work will focus on activators that accelerate the degradation of PLA in water. Furthermore, the focus will be on the fabrication of piezoelectrets as well as pressure sensors made of the PLA electrets with embedded proteinase K.

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Declarations

Competing Interests The authors declare no competing interests.

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