Influence of density and environmental factors on decomposition kinetics of amorphous polylactide – Reactive molecular dynamics studies

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ABSTRACT

In this work, we investigate the influence of the surrounding environment and the initial density on the decomposition kinetics of polylactide (PLA). The decomposition of the amorphous PLA was investigated by means of reactive molecular dynamics simulations. A computational model simulates the decomposition of PLA polymer inside the bulk, due to the assumed lack of removal of reaction products from the polymer matrix. We tracked the temperature dependency of the water and carbon monoxide production to extract the activation energy of thermal decomposition of PLA. We found that an increased density results in decreased activation energy of decomposition by about 50%. Moreover, initiation of decomposition of the amorphous PLA is followed by a rapid decline in activation energy caused by reaction products which accelerates the hydrolysis of esters. The addition of water molecules decreases initial energy of activation as well as accelerates the decomposition process. Additionally, we have investigated the dependency of density on external loading. Comparison of pressures needed to obtain assumed densities shows that this relationship is bilinear and the slope changes around a density equal to 1.3 g/cm^3. The conducted analyses provide an insight into the thermal decomposition process of the amorphous phase of PLA, which is particularly susceptible to decomposition in amorphous and semi-crystalline PLA polymers.

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1. Introduction

Biodegradable polylactide (PLA) is an aliphatic thermoplastic polyester frequently used in biomedical engineering [1] but is also a promising material for industrial applications [2,3]. Industrial usage of PLA could significantly reduce the problem of solid waste disposal but is still limited by its properties such as low strength and durability. Degradable polymeric materials are particularly sensitive to environmental factors such as temperature or humidity and are susceptible to accelerated degradation, which considerably alters their properties [4–7]. Degradation of PLA can also be influenced by the manufacturing process [8], which can cause molecular scission or a partial disappearance of the crystal structure [9]. Thermal decomposition of PLA is caused by random chain scission which involves oxidative degradation, hydrolysis,

cis-elimination and transesterification [10,11]. The complexity of the
decomposition process and difference in material stability inside the bulk and at the surface, encouraged us to investigate this phenomenon with the use of molecular dynamics methods as described in the following sections.

PLA occurs in three forms: semi-crystalline PLLA (L-PLA), PDLA (D-PLA) and PDLLA (an amorphous mixture of PLLA and PDLA) [12]. Amorphous regions are more susceptible to hydrolysis and decomposition than crystals due to the higher mobility of polymer chains and easy water absorption. Hydrolysis of ester bonds, which occurs at the beginning of decomposition, leads to chain scission through de-esterification and formation of degradation by-products, such as oligomers and finally lactic acid which is transformed through the tricarboxylic acid cycle to water and carbon dioxide [13]. Reaction by-products formed in the course of decomposition, can further accelerate this process. Acceleration of hydrolysis occurs especially inside the bulk due to the difficulty of removing degradation by-products. The rate of degradation and decomposition of polymers also depends on mechanical

loading. External loading accelerates chemical processes, which affects the performance of polymers. Influence of mechanical loading on polymer aging can be predicted by means of chemomechanical models [14]. Chemomechanical models require a number of material parameters, including parameters of reaction kinetics as well as constitutive models describing the stress–strain relationship for different loading and strain rates. Selected parameters, such as stress–strain curves, can be estimated from experiments or molecular dynamics (MD) simulations [15,16] that take into consideration the molecular structure of the material as well as its chemical reactivity [17,18]. The reactive nature of phenomena like degradation, pyrolysis, desulfurization or combustion may be considered with the MD method by applying a special class of reactive force field [19–22]. One well-known reactive potential is ReaxFF, developed by van Duin et al. [23]. Although ReaxFF was initially parameterized only for hydrocarbons, it is now used for a broad range of materials including metals, ceramics, nitroamines, high-energetic materials and carbon nanotubes. ReaxFF was also successfully applied to stability studies of organic compounds, i.e. epoxy resin [24], cellulose [25], PMMA [26] or PDMS [27] polymers. However, there is no reported research concerning the use of ReaxFF for decomposition studies of biodegradable materials such as PLA, PGLA, PCL or PHB.

Despite a large amount of scientific literature on the degradation and decomposition of PLA, there is still an open research question: How to estimate the parameters of reaction kinetics of polymers and dependency on material density, especially inside the bulk? This question is essential for the prediction of the thermal decomposition of massive polymeric parts. It results from the fact that restricted volatility of the products of chemical reactions, act autocatalytically on the process of decomposition of polymers.

The objective of this work is to investigate the influence of initial density on reaction kinetics of PLA using the reactive MD method. We have created a model which has allowed us to investigate the influence of density, water, and oxygen content on the time evolution of activation energy during decomposition of amorphous PLA.

2. Materials and methods

Simulations were performed on the amorphous D,L-PLA system. The pure amorphous PLA system consisted of 12 linear strands per unit cell at an initial density of $1.27 \, \text{g/cm}^3$. Each strand consisted of 25 monomer units, which gave an overall number of atoms equal to 2724. We also studied two other densities: $0.84 \, \text{g/cm}^3$ and $1.47 \, \text{g/cm}^3$. These densities were obtained by cubic deformation of the initial system. Additionally, we performed simulations of amorphous PLA decomposition in contact with water and oxygen. We chose the amorphous structure because large amorphous domains are more susceptible to decomposition due to the higher chain mobility and higher levels of water absorption [28] which significantly affects overall material behavior. The PLA system with water, consists of 182 water molecules, while the system with oxygen consists of 272 oxygen molecules. Initial simulation boxes were prepared and optimized using "Scigress" molecular design modeling software (www.fqs.pl). Molecular simulations of decomposition were carried out using reactive molecular dynamics code created by Prof. Adri van Duin group "ReaxFF ADF" (www.scm.com) [23,29] and ReaxFF parameters reported in [30] which are suited for reactions with water. To visualize the results, we used the "ADF Modeling Suite" (www.scm.com). To compute the parameters of the Arrhenius equation we used our in-house scripts. The procedure used in simulations of polymer decomposition involved energy minimization using non-reactive MD followed by relaxation of the PLA system. The bond order cutoff for calculation of covalent

bonds was set to 2 Å. The higher value of cutoff radius was defined in order to avoid any influence of this parameter on interpretation in terms of chemical components, especially of PLA of higher densities which were obtained by cubic deformation of the initial system. To analyze kinetics of the decomposition process we performed a series of 36 NVT-MD simulations with a time step of 0.1 fs lasting 10 ps for six temperatures: 2500 K, 2700 K, 2900 K, 3100 K, 3300 K and 3500 K. Artificially increasing the simulation temperatures above those in experimental conditions allows us to accelerate the decomposition process and is a common computational practice [24,27,31]. The selected temperature range is consistent with those used for the calculation of Arrhenius parameters as reported by the van Duin group in [27]. The choice of shortened simulation times results from the fact that energy of activation is calculated based on the slopes of the "carbon monoxide molar concentration in time" function. Consequently, to calculate activation energy, we only take an increase in the number of molecules. Because of this, we can reduce the simulation time to 10 ps, after which no further significant changes in the number of reaction products are observed. By performing reactive MD simulations at different temperatures, we were able to determine the temperature-dependent reaction rates. For this purpose, we compared the distribution of all PLA decomposition products and found that for each simulated case the most frequently occurring products were water and carbon monoxide. The increase in number of other major reaction products in time is much smaller, thus cannot be used for the calculation of activation energy. Since water was already included in half of the simulation boxes (the other half of boxes contained oxygen), we rejected its application for the purpose of reaction kinetics calculation. Therefore, for each temperature for a given density/environmental case, we plotted a function of carbon monoxide molar concentration in time. Based on the slope of each curve, we obtained six values of the reaction rate coefficient k one for each simulated temperature T. This procedure allowed us to create an Arrhenius plot (in the coordinates $\ln(k) - 1/T$) and, by applying the linear regression, to determine the coefficients for a fitted linear function ($ax + b$). Finally, by transferring the basic formula of the Arrhenius equation (Eq. (1)) into the logarithmic form (Eq. (2)), we were able to compare values of coefficient a with corresponding components in the Arrhenius equation (Eq. (3)):

$$k = Ae^{-(E_a/RT)} \tag{1}$$

where k is reaction rate coefficient; E_a is activation energy; R is gas constant; T is temperature.

$$\ln(k) = -\frac{E_a}{R} + \ln(A) \tag{2}$$

$$\frac{E_a}{R} = a \tag{3}$$

As a result, for a given density/environmental case, we were able to calculate the values of activation energy E_a.

3. Results and discussion

3.1. Influence of water, oxygen and temperature on the decomposition of amorphous polylactide

To analyze the influence of the surrounding environment and external loading on the rate of decomposition, we created two initial PLA systems. The initial simulation box of PLA molecules with oxygen is presented in Fig. 1b, while the simulation with water is presented in Fig. 2b. Simulations of PLA decomposition with oxygen and water (Figs. 1 and 2) confirmed that a higher decomposition rate is induced by higher temperatures. The rate of water and carbon monoxide production in the NVT-MD simulations with
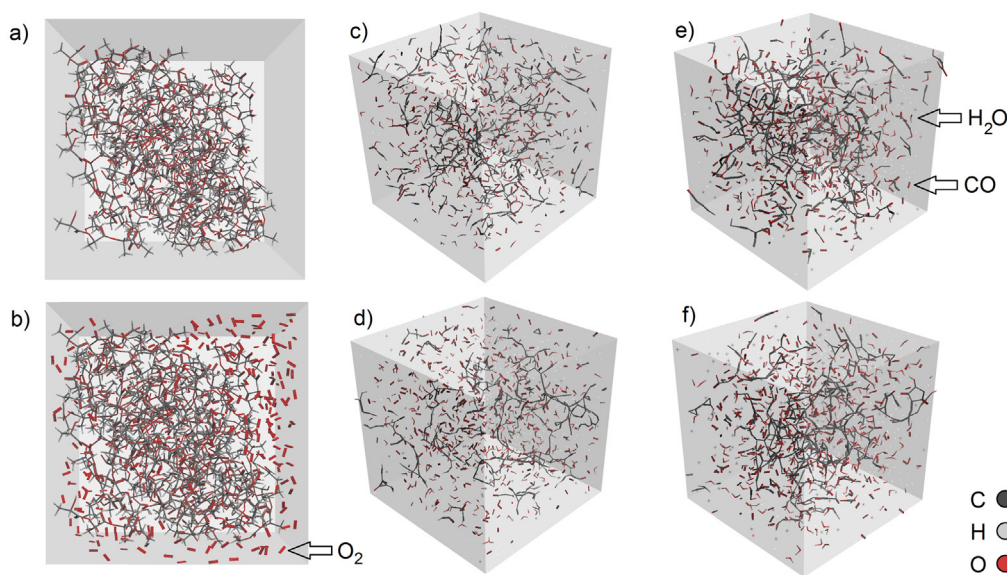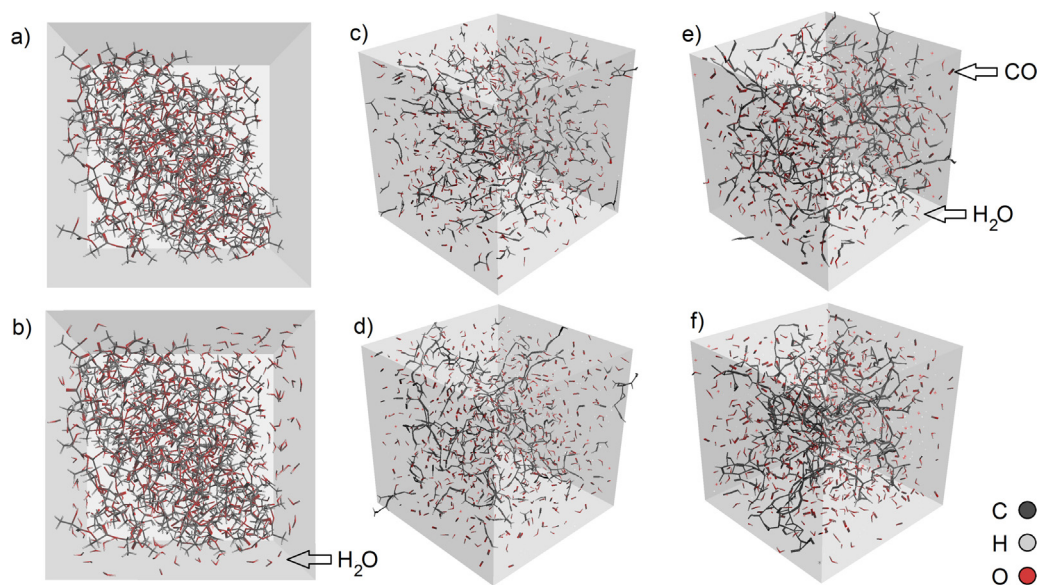
Fig. 1. Decomposition of the PLA in contact with oxygen; (a) initial configuration of PLA at the beginning of the simulation; (b) initial configuration with added oxygen molecules; (c) final configuration of the 2500 K NVT-MD simulation at a density of 0.84 g/cm³; (d) final configuration of the 3500 K NVT-MD simulation at a density of 0.84 g/cm³; (e) final configuration of the 2500 K NVT-MD simulation at a density of 1.47 g/cm³; (f) final configuration of the 3500 K NVT-MD simulation at a density of 1.47 g/cm³.

water and oxygen at various temperatures is shown in Figs. 3 and 4 respectively.

The final products of thermal decomposition of PLA in high temperature are carbon dioxide and methylketene, however, carbon monoxide is also reported to evolve in the initial phase of this process [32]. At this stage, the rate of carbon monoxide production is much higher than that of carbon dioxide. Because of this, the concentration of CO molecules was selected for analysis of the influence of temperature and polymer density on the rate of decomposition.

Influence of temperature on the rate of decomposition of PLA in oxygen (Fig. 3) was much higher than PLA in water (Fig. 4). This is in

agreement with experimental observations that the vicinity of oxidizing agents accelerates the scission process of polymers [33,34]. However, it should be noted that this phenomenon occurs only at the surface of the PLA components, while hydrolysis is observed inside the bulk, and is connected to water uptake [35]. Fig. 4 shows the population of water molecules that results from water production and initial water content. High water content and temperature induces hydrolysis inside the bulk, while the surface is exposed mainly to oxidation. We performed reactive MD simulations, which will enable us to determine activation energy, described in the next section, and also to investigate the influence of density on the kinetics of decomposition.


Fig. 2. Decomposition of the PLA in contact with water; (a) initial configuration of PLA at the beginning of the simulation; (b) initial configuration with added water molecules; (c) final configuration of the 2500 K NVT-MD simulation at a density of 0.84 g/cm³; (d) final configuration of the 3500 K NVT-MD simulation at a density of 0.84 g/cm³; (e) final configuration of the 2500 K NVT-MD simulation at a density of 1.47 g/cm³; (f) final configuration of the 3500 K NVT-MD simulation at a density of 1.47 g/cm³.
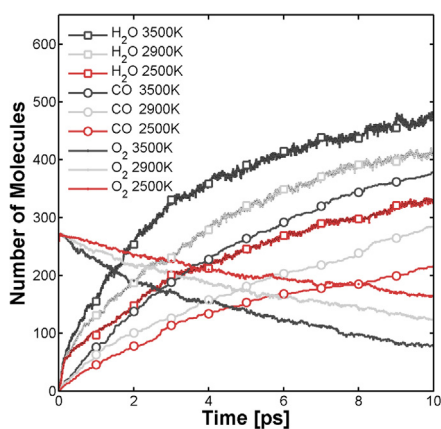
Fig. 3. Population of water, oxygen and carbon monoxide molecules observed in NVT-MD simulations of decomposition at temperatures of 2500 K, 2900 K and 3500 K. Polylactide with oxygen molecules at a density of 0.84 g/cm³.
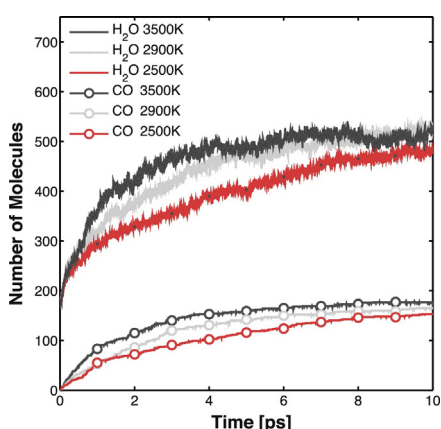
Fig. 4. Time evolution of water and carbon monoxide during decomposition of polylactide with water at a density of 1.27 g/cm³ and temperatures 2500 K, 2900 K and 3500 K.

Density of PLA polymers depends on the manufacturing process but can also be altered by severe mechanical loading. The influence of density on the population of water and carbon monoxide molecules observed in NVT-MD simulations at a temperature of 3500 K is shown in Fig. 5. Different densities were obtained by cubic
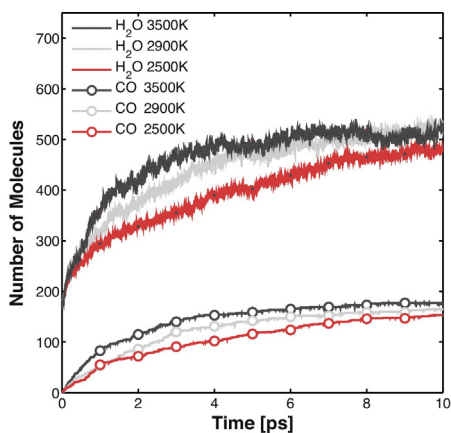
compression or expansion of the original simulation box. Results from NVT-MD simulations showed that an increase in density results in higher rates of decomposition. Compression applied to the specimen led to changes in bond length and angles. Moreover, mechanical load also caused motions of lateral groups and reduced the distance between reacting molecules. Consequently, deformed polymer chains are more susceptible to decomposition due to their higher energy state. This observation is in agreement with experimental results that external loading affects reactivity of polymeric materials [14]. On the basis of the production rate of carbon monoxide as a function of temperature, we determined the energy of activation for PLA decomposition. The influence of density and surrounding water and oxygen molecules at different temperatures on activation energy is described in the next section.

3.2. Influence of water, oxygen, temperature and density on the evolution of activation energy during decomposition of amorphous polylactide

Decomposition of polymers is an example of a radical reaction which occurs when the energy sufficient to overcome the reaction barrier is delivered to the corresponding radicals. A minimum amount of energy that must be acquired to initiate reaction is defined in the Arrhenius equation as activation energy. To extract values of activation energy for the amorphous PLA, we tracked the temperature dependency of carbon monoxide production during decomposition. Additionally, we investigated the influence of increased densities on the rate of PLA decomposition. We observed that decomposition rate rises considerably with density, leading to the formation of more carbon monoxide and water molecules. Time evolution of the activation energy at different densities is presented in Fig. 6.

The values of activation energy during decomposition of polylactide with water at densities of 0.84 g/cm³, 1.27 g/cm³ and 1.47 g/cm³ are equal to 16.03 kJ/mol, 10.92 kJ/mol, 8.86 kJ/mol respectively. Higher density, obtained by cubic deformation of the simulation box, results in decrease of initial activation energy by about 50%. External pressure, applied to the simulation box, has provided enough energy to decrease activation energy, but to activate the decomposition process, it is still necessary to provide energy to the system in the form of elevated temperature or, e.g. radiation. The relationship between density and applied external loading will be discussed in subsequent paragraphs.
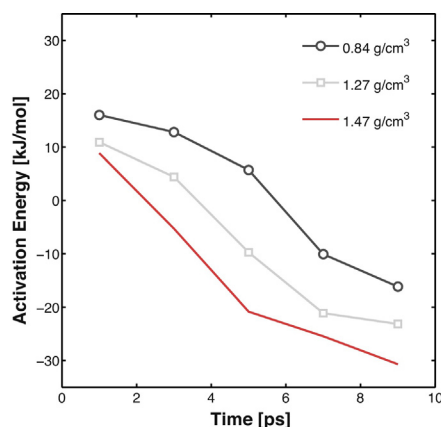

Fig. 5. Time evolution of water and carbon monoxide during decomposition of polylactide with water at a temperature of 3500 K and density of 0.84 g/cm³, 1.27 g/cm³ and 1.47 g/cm³.

Fig. 6. Time evolution of the activation energy during decomposition of polylactide with water at a density of 0.84 g/cm³, 1.27 g/cm³ and 1.47 g/cm³.
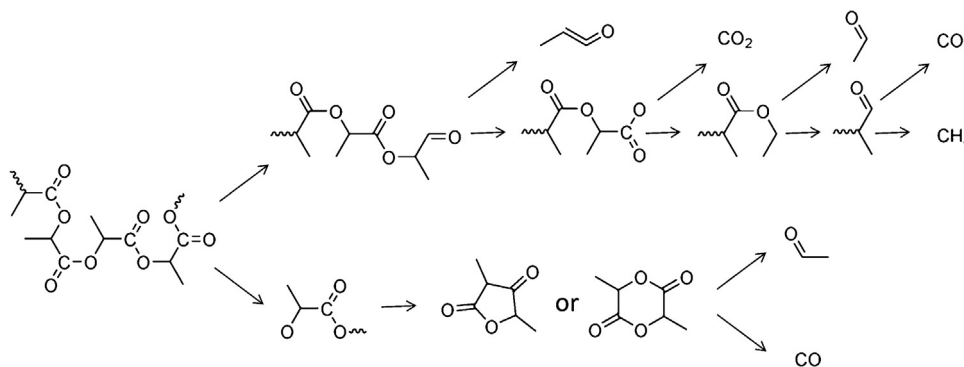
Fig. 7. Mechanisms of decomposition of polylactide.

During the decomposition process, a various processes occur. Hydrolytic reactions, recombination, β-elimination, radical degradation and transesterification all take place simultaneously, releasing gas products such as acetaldehyde, ketene, carbon monoxide and carbon dioxide (Fig. 7) [10,11]. Acetaldehyde and CO have been formed by homolytic reactions. Since the reaction products formed during the beginning of the process facilitate further decomposition, it is justifiable to observe a decrease in the activation energy of the polymer decomposition as compared to the very beginning of the process, where the non-autocatalyzed reaction occurs. The lower values of the activation energy most likely represent average values between the activation energies of non-autocatalyzed and autocatalyzed reactions. Similar effects of decrease in activation energy were described by Vyazovkin and Sbirrazzuoli [36] during a cure reaction of epoxy polymers. The drop in values of activation energy below zero as time progresses is due to the formation of volatile products and an intermediate complexes containing carboxylic end-groups. An increasing number of compounds containing carboxylic end-groups, which are not able to permeate to the outer shell, leads to autocatalytic barrier-less reaction. Such processes at the beginning cause a decrease in the molecular weight without variation of the specimen weight.

The influence of polymer density on activation energy of PLA decomposition with water, presented in Fig. 8 is linear in the corresponding time ranges. An increase in density results in a decrease of activation energy. Initial activation energy needed to trigger the decomposition process of PLA with water is between 16.03 kJ/mol and 8.44 kJ/mol at the studied densities. Values of activation energy

for PLA obtained by means of DSC methods are reported to be between 135 kJ/mol and 227 kJ/mol [9,32,37]. We have obtained lower values, which can be related to the chosen type of simulation. Our simulated system corresponds to the situation inside the bulk, without the possibility to evaporate the reaction products, while experimental values mainly describe processes at the surface. This discrepancy could be also due to the fact that our model consisted of low molar mass amorphous PLA chains, while experimental results described the reactions of high molar mass PLA. Moreover, the reaction rate of PLA of similar molar masses may vary depending on the synthesis of the polymer [38]. Additionally, results can also be affected by timescale, the main restriction of the MD method. Nevertheless, in all simulations we defined the same temporal and spatial scale, thus analysis of the influence of temperature and densities on decomposition kinetics was not affected by simulation parameters. Fig. 8 presents equations describing the relationships between density and energy of activation at 1–3, 3–5 and 5–7 ps of the NVT-MD simulation of decomposition of polylactide with water. A fit of linear functions describing decreasing trends of activation energy with density shows additionally, that initial activation energy needed to trigger the decomposition process depends less on density than on values of energy needed to maintain the reaction.

The density of PLA polymers depends mainly on the manufacturing process, but can also be altered by severe mechanical loading. In our simulations, different densities were obtained by cubic deformation of the simulation box. In order to investigate the dependence of density on external loading, we compiled the density-pressure plot shown in Fig. 9. Comparison of pressures
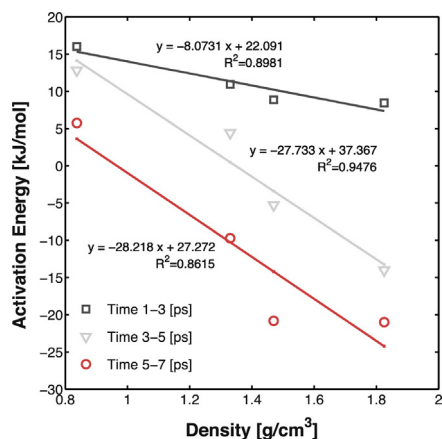

Fig. 8. Activation energy as a function of polymer density at 1–3, 3–5 and 5–7 ps of the NVT-MD simulation of decomposition of polylactide with water.
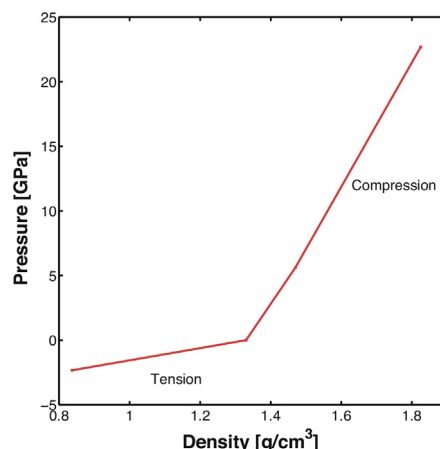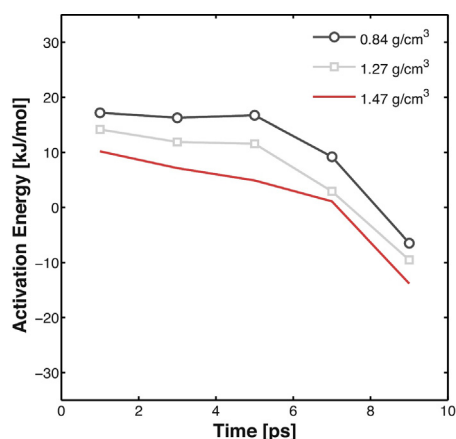

Fig. 9. Influence of the external loading on polylactide density.

Fig. 10. Time evolution of the activation energy during decomposition of polylactide with oxygen at a density of 0.84 g/cm^3, 1.27 g/cm^3 and 1.47 g/cm^3.

Fig. 11. Time evolution of the activation energy during decomposition of polylactide with oxygen and water at a density of 1.27 g/cm^3 and 1.47 g/cm^3.

needed to obtain the assumed densities shows that this relationship is bilinear. In order to investigate the dependence of density on pressure in confined compression, we performed an additional NVT-MD simulation up to a pressure of 25.4 GPa. The relationship between density and pressure in confined compression is roughly linear. The curvature of the pressure–density plot close to a density equal to 1.3 g/cm^3 is related to change of the loading from tension to compression.
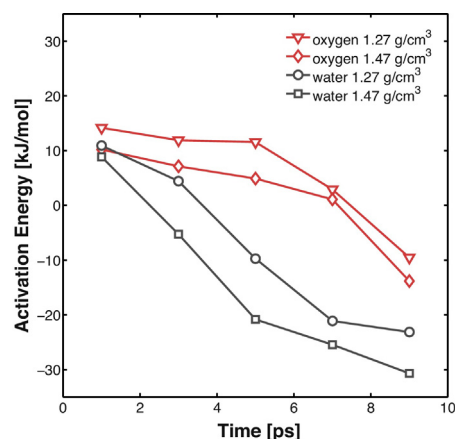
In order to investigate the decomposition of PLA in oxygen we performed a series of reactive MD simulations at different densities. The initial values of activation energy during decomposition of polylactide with oxygen at densities of 0.84 g/cm^3, 1.27 g/cm^3 and 1.47 g/cm^3 are equal to 17.19 kJ/mol, 14.17 kJ/mol, 10.19 kJ/mol respectively. Fig. 10 shows the influence of density on the evolution of activation energy during the decomposition process of PLA system with oxygen. As in the case of decomposition with water, an increase in the density of the system with oxygen results in decreased activation energy, which leads to a barrier-less reaction. However, the values of activation energy are higher than during decomposition of PLA with water (Table 1). Comparison of activation energy evolution during decomposition of PLA with water and oxygen (Fig. 11) shows that presence of water molecules accelerates the drop in value of activation energy much higher than the presence of oxygen. This relationship is observed for all investigated densities.

Oxidation, which is the main degradation mechanism of PLA at temperatures above 100 °C [39], has comparable energy of activation to that of the hydrolysis process. The low initial values of calculated activation energy result from short simulation times and assumed amorphous PLA structure. The rapid drop in activation energy is due to the closed simulation system (which reflects polymer inside the bulk), without the possibility to evaporate the reaction products, which accelerate the decomposition process.

In spite of the temporal and spatial limitations of reactive MD methods and the assumed simulation system, qualitative comparison allowed us to investigate the influence of density and presence of water or oxygen on the kinetics of PLA decomposition. It shows that reactive MD methods can be used to analyze scenarios which are difficult to observe by means of experimental methods. Applicability of the results presented in this article is limited to qualitative analysis of the decomposition process of PLA with water and oxygen. Further work, which is required to develop a general chemomechanical model, is proposed below.

4. Conclusion

In the presented work we have investigated the influence of polymer density and surrounding environment on the thermal decomposition of amorphous polylactide inside the bulk by means of reactive molecular dynamics simulations. Our computational experiments revealed noteworthy observations:

- Presence of water molecules decreases initial activation energy of thermal decomposition of the amorphous polylactide inside the bulk and accelerates the drop in value of activation energy in the course of decomposition.
- Initiation of the thermal decomposition of the amorphous phase of polylactide inside the bulk is followed by a rapid drop in energy of activation. This sudden decrease in activation energy is caused by an increasing number of compounds containing carboxylic end-groups, which are not able to evaporate from the thick polymeric parts. This results in barrier-less autocatalytic reaction
- Elevated density or severe mechanical loading decreases activation energy and accelerates thermal decomposition of amorphous polylactides inside the bulk.

Studies on the influence of external load on material density showed that the pressure–density chart is bilinear, with curvature of the plot around a density equal to 1.3 g/cm^3, which results from change of loading from tension to compression. Analysis of the results leads to other open research questions: What is the influence of external loading and different environments on the stability of crystalline polylactides? Reactive molecular dynamics methods allow us to investigate the influence of new additives on the stability of polylactides in degradative environments. This will enable better control of degradation of components made from

Table 1
The initial values of activation energy during decomposition of polylactide with oxygen and water at densities of 0.84 g/cm^3, 1.27 g/cm^3 and 1.47 g/cm^3.

Activation energy during decomposition	Density (g/cm^3)		
	0.84	1.27	1.47
With oxygen (kJ/mol)	17.19	14.17	10.19
With water (kJ/mol)	16.03	10.92	8.86

polylactides, which is a key issue in many areas of engineering. The results presented in this manuscript, lead to the conclusion that thicker components made of polylactide-based plastics are more vulnerable to thermal decomposition inside the bulk due to the catalytic action of reaction by-products. However, one should remember that during decomposition in real-life conditions, other phenomena are no less important. Aside from reaction kinetics, the rate of decomposition also depends on permeability, which is dependent on external loading and the degree of crystallinity, etc. Further research is necessary to fully understand the decomposition of thick components made of polylactides under external loading, including analyses of semi-crystalline structures and the diffusion process. Such results are interesting not only to engineers working on the issue of recycling and combustion of plastic materials, but also for researchers working on the stability of biological implants.

Acknowledgements

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