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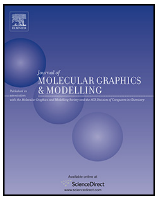

Influence of density and environmental factors on decomposition kinetics of amorphous polylactide – Reactive molecular dynamics studies

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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.

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

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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 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 g/cm^3 and 1.47 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